Twisted double bilayer graphene (tDBLG) is a moiré material that has recently generated interest because of the observation of correlated phases near the magic angle. Using an atomistic tight-binding model with self-consistent Hartree interactions, we find that the flat electronic bands of tDBLG are not sensitive to doping, nor to the in-plane variations of the Hartree potential. Rather, the dominant factor is the average on-site energy difference between the layers of each bilayer. We find that, whilst in qualitative agreement with ab initio calculations, the layer-dependent on-site potential (referred to as the crystal field) from Hartree theory is significantly smaller than what is required to yield band structures with ab initio accuracy. To understand the origin of the crystal field, we analyse the ion-electron, Hartree and exchange-correlation potentials from large-scale first-principles density functional theory calculations on tDBLG, and show that the crystal field arises from subtle differences in the contributions of these terms on each layer.

I. INTRODUCTION

Twistronics \[1\] is concerned with the effects that occur when stacking low-dimensional van der Waals materials and introducing a relative twist angle between them \[3\]. The prototypical example of such a system is twisted bilayer graphene (tBLG), where a twist angle between two graphene sheets creates an emergent honeycomb pattern on a much larger length scale than the graphene honeycomb lattice \[4-9\]. The physics of tBLG is quite rich, and exhibits superconductivity in proximity to correlated insulators \[10-13\], highly tunable van Hove singularities \[14-16\], Dirac revivals \[17, 18\], strange metallic behaviour \[19-20\], and nematic order \[14, 16, 21\]. This has motivated the investigation of other graphene-based moiré materials, such as twisted double bilayer graphene (tDBLG) \[22-27\].

In transport experiments on magic-angle tDBLG, correlated insulators have been observed at a doping of two electrons per moiré unit cell in applied electric fields \[23, 25, 28, 30\]. A substantial gap at charge neutrality also emerges in the presence of a perpendicular electric field, which is a trivial band gap instead of an interaction-driven transition. There are signatures of superconductivity too, but robust superconductivity has not yet been confirmed \[23, 25, 28, 30\]. Scanning tunneling microscopy (STM) experiments have also observed correlated insulating states \[31, 32\] and nematic ordering \[33\] near the magic angle.

The electronic structure of tDBLG has been studied using atomistic tight-binding models. In Ref. \[24\], however, it was found that there is a discrepancy between the tight-binding band structure and that calculated with first-principles density functional theory (DFT), in terms of the predicted band gap at charge neutrality. To obtain better agreement, a phenomenological on-site energy of approximately \(-30\) meV on the inner layers relative to the outer layers was introduced in the model, which was referred to as the “intrinsic symmetric polarisation” (ISP) or crystal field. Moreover, Refs. \[34\] and \[35\] also found that better agreement with DFT, in terms of the gap at charge neutrality, could be obtained with an additional on-site potential. These works have suggested that in tDBLG, because the outer layers experience a different chemical environment to the inner layers, charge transfer can occur and, therefore, electron-electron interactions could be important for understanding the electronic structure of the normal state.

In the normal state of tBLG \[36-41\], it was found that there are significant effects from long-ranged electron-electron interactions (within Hartree theory), and the electronic structure acquires a strong doping dependence, where the van Hove singularities become pinned at the Fermi energy \[36-41\]. In contrast to tBLG, however, no pinning of the van Hove singularities upon doping has been observed in tDBLG, and is corroborated by continuum model calculations of the electronic structure \[31-33\]. However, there have not been any atomistic tight-binding calculations of the electron interactions in tDBLG. Moreover, if the origin of the ISP is from charge transfer, then the additional layer-dependent on-site energy should naturally emerge, e.g, from an atomistic Hartree theory, but this investigation has not yet been performed.

In this paper, we investigate the role of Hartree interactions in tDBLG within self-consistent atomistic Hartree theory. We consider how Hartree interactions are affected by the twist angle, dielectric screening, and applied electric fields. Firstly, we analyse the doping dependence of the electronic structure of tDBLG, and find that the electronic states are not sensitive to doping or the in-plane variations of the Hartree potentials. Next we perform calculations in an applied electric field to show how tDBLG screens an external electric field. We then analyse in detail our results at charge neutrality as a function of twist angle and dielectric environment. We find that, whilst the Hartree potential is in good qualitative agree-
ment with DFT, a DFT-accurate on-site potential difference requires an understanding of the origin of the crystal field. An analysis of the Kohn-Sham potential from a large-scale DFT calculation on tDBLG reveals that the origin of crystal field is the subtle differences in the electron-electron interactions and the ion-electron potential, with exchange-correlation effects enhancing the crystal field.

II. METHODS

We study commensurate moiré unit cells of tDBLG consisting of twisted AB stacked bilayers. The bilayers are initially stacked directly on top of each other, similar to the structure of graphite, and the top bilayer is rotated anticlockwise about an axis normal to the bilayers that passes through a carbon atom in each bilayer. The moiré lattice vectors are \( \mathbf{R}_1 = n \mathbf{a}_1 + m \mathbf{a}_2 \) and \( \mathbf{R}_2 = -(n+m) \mathbf{a}_2 \), where \( n \) and \( m \) are integers that specify the moiré unit cell in terms of the graphene lattice vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \).

We relaxed these tDBLG structures using classical force fields as implemented in the LAMMPS software package [42]. The AIREBO-Morse potential [43] was used for intralayer interactions; while the Kolmogorov-Crespi potential [44] was used for interlayer interactions. More details of the relaxations can be found in Ref. [45].

The electronic structure of tDBLG was investigated with an atomistic Hartree model. The model outlined here is very closely related to that discussed in Ref. [39]. For completeness, we provide all details here. The atomistic Hamiltonian that we solve is given by

\[
\hat{H} = \sum_i \varepsilon_i \hat{c}_i^\dagger \hat{c}_i + \sum_{i,j} [t(\mathbf{r}_i - \mathbf{r}_j) \hat{c}_i^\dagger \hat{c}_j + \text{H.c.}],
\]

where \( \hat{c}_i^\dagger \) and \( \hat{c}_i \) are, respectively, the electron creation and annihilation operators associated with the \( p_z \)-orbital on atom \( i \), and \( \varepsilon_i \) is its on-site energy.

The hopping parameters \( t(\mathbf{r}_i - \mathbf{r}_j) \) between atoms \( i \) and \( j \) (located at \( \mathbf{r}_{ij} \)) are determined using the Slater-Koster rules [40,47]

\[
t(\mathbf{r}) = \gamma_1 e^{q_s (1-|\mathbf{r}|/d)} \cos^2 \varphi - \gamma_0 e^{q_s (1-|\mathbf{r}|/a)} \sin^2 \varphi,
\]

where \( \gamma_1 = 0.48 \text{ eV} \) and \( \gamma_0 = 2.81 \text{ eV} \) [24] correspond, respectively, to \( \sigma \)- and \( \pi \)-hopping between \( p_z \)-orbitals, with associated decay parameters \( q_s = 7.43 \) and \( q_a = 3.14 \) [4,7]. Also, \( a = 1.397 \text{ Å} \) is the pristine carbon-carbon bond length, \( d = 3.35 \text{ Å} \) is the pristine interlayer separation parameter, and \( \varphi \) is the angle between the \( z \)-axis and the vector connecting atoms \( i \) and \( j \), and captures the angle-dependence of hoppings. Hoppings between carbon atoms that are separated by more than 10 Å are neglected [48]. The Slater-Koster tight-binding parameters are based on a best fit to DFT low-energy band structures of graphene and bilayer graphene [6,7,47], with a slightly larger \( \pi \)-hopping parameter as introduced in Ref. [24] as a result of fitting to the low-energy DFT bandstructure of large twist angle tDBLG.

We decompose the on-site energy \( \varepsilon_i \) in Eq. (1) into two contributions, \( \varepsilon_i = \varepsilon_i^{(a)} + \varepsilon_i^{el} \). The first term, \( \varepsilon_i^{(a)} \), is a constant layer-dependent contribution, where \( a \) denotes the layer, and represents the effect of applied electric fields or intrinsic electric fields (e.g., the ISP described in Sec. [1]). This term also includes a contribution (approximately \(-0.8 \text{ eV} \) in our model) that shifts the Fermi energy to zero and whose value depends on the other on-site energies and the doping level. The second term, \( \varepsilon_i^{el} \), is the contribution to the on-site energy from electron interactions and is determined self-consistently according to

\[
\varepsilon_i^{el} = \int d\mathbf{r} \phi_i^2(\mathbf{r} - \mathbf{r}_i) V_H(\mathbf{r}),
\]

where \( \phi_i(\mathbf{r}) \) is the \( p_z \)-orbital of the carbon atoms, and the Hartree potential \( V_H(\mathbf{r}) \) is determined from the electron density \( n(\mathbf{r}) \) and the screened electron-electron interaction \( W(\mathbf{r}) \) as

\[
V_H(\mathbf{r}) = \int d\mathbf{r}' W(\mathbf{r} - \mathbf{r}') [n(\mathbf{r}') - n_0(\mathbf{r}')],
\]

where \( n_0(\mathbf{r}) \) is a reference electron density that subtrahct the Hartree interactions already accounted for in the tight-binding parameters that were fitted to reproduce DFT band structures [7]. The electron density is determined through

\[
n(\mathbf{r}) = \sum_{n_k} f_{nk} |\psi_{nk}(\mathbf{r})|^2,
\]

where

\[
\psi_{nk}(\mathbf{r}) = \frac{1}{\sqrt{N_k}} \sum_{\mathbf{R}_{ij}} c_{nk} e^{i\mathbf{k} \cdot \mathbf{R}} \phi_i(\mathbf{r} - \mathbf{r}_j - \mathbf{R}).
\]

is the Bloch eigenstate of the atomistic tight-binding model, with subscripts \( n \) and \( \mathbf{k} \) denoting the band index and the crystal momentum, respectively. Also, \( N_k \) is the number of \( k \)-points in the summation of the electron density, and \( f_{nk} = 2\Theta(\varepsilon_F - \varepsilon_{nk}) \) is the spin-degenerate occupancy of state \( \psi_{nk} \) with eigenvalue \( \varepsilon_{nk} \) (where \( \varepsilon_F \) is the Fermi energy). Inserting the Bloch states in Eq. (7) gives

\[
n(\mathbf{r}) = \sum_j n_j \chi_j(\mathbf{r}),
\]

where \( \chi_j(\mathbf{r}) = \sum_{\mathbf{R}} \phi_i^2(\mathbf{r} - \mathbf{r}_j - \mathbf{R}) \) (with \( \mathbf{R} \) denoting the moiré lattice vectors) and the total number of electrons on the \( j \)-th \( p_z \)-orbital in the unit cell being determined by

\[
n_j = \sum_{nk} f_{nk} |c_{nk}|^2 / N_k.
\]

The reference density is taken to be that of a uniform system, \( n_0(\mathbf{r}) = \bar{n} \sum_j \chi_j(\mathbf{r}) \), where \( \bar{n} \) is the average of
\( n_j \) over all atoms in the unit cell, which is related to the filling per moiré unit cell \( \nu \) through \( \bar{n} = 1 + \nu/N \), where \( N \) is the total number of atoms in a moiré unit cell [35].

In transport experiments, there is often a metallic gate above and below the tDBLG, with a hexagonal boron nitride (hBN) substrate separating the gates from tDBLG. These metallic gates add or remove electrons from tDBLG and can also create electric fields across the system. These gates also screen the electron interactions in tDBLG, and taking this effect into account has been shown to be important in tBLG [19, 51]. Therefore, we utilise a double metallic gate screened interaction

\[
W(\mathbf{r}) = \frac{e^2}{4\pi\epsilon_0\epsilon_{bg}} \sum_{m=-\infty}^{\infty} \frac{(-1)^m}{\sqrt{|R|^2 + (2m\xi)^2}},
\]

(8)

where \( \xi \) is the thickness of the hBN dielectric substrate, which provides a background dielectric constant \( \epsilon_{bg} \) and separates tDBLG from the metallic gate on each side [49, 52, 53]. We set \( \xi = 10 \) nm for all calculations, but vary the value of \( \epsilon_{bg} \).

In our atomistic model, we neglect contributions to the electron density from overlapping \( p_z \)-orbitals that do not belong to the same carbon atom, which is equivalent to treating \( \phi^2(\mathbf{r}) \) as a delta-function. Therefore, we calculate the Hartree on-site energies using

\[
\epsilon^\text{el}_{i} = \sum_{j\mathbf{R}} (n_j - \bar{n}) W_{\mathbf{R}ij},
\]

(9)

where \( W_{\mathbf{R}ij} = W(\mathbf{R} + \tau_j - \tau_i) \). If \( \mathbf{R} = 0 \) and \( i = j \), we set \( W_{0,\bar{n}} = U/\epsilon_{bg} \) with \( U = 17 \) eV [54].

To obtain a self-consistent solution of the equations, we use a 6 \( \times \) 6 or 12 \( \times \) 12 k-point grid to sample the first Brillouin zone to converge the density in Eq. (4) and we sum over a 21 \( \times \) 21 supercell of moiré unit cells to converge the on-site energies of Eq. (9). Linear mixing of the electron density is performed with a mixing parameter of 0.1 or less (i.e., the addition of 10 percent of the new potential to 90 percent of the potential from the previous iteration). Typically, the Hartree potential converges to an accuracy of better than 0.1 meV per atom within 100 iterations. For doping levels where tDBLG is metallic, smaller mixing values and a larger number of iterations are sometimes needed to reach this convergence threshold.

DFT band structures are computed using ONETEP, a linear-scaling DFT code [54, 50]. We use the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [57]. For the electron-ion interaction we employ the projector-augmented-wave (PAW) formalism [58, 59] (where PAW pseudopotentials are generated from ultra-soft pseudopotentials [60]). The kinetic energy cutoff is set to 500 eV. A minimal basis consisting of four non-orthogonal generalized Wannier functions (NGWFs) per carbon atom is employed and the ensemble-DFT approach [61, 62] is adopted for the minimisation of the ground state energy.

III. RESULTS AND DISCUSSION

A. Doping dependence

In tDBLG, a set of four bands emerge in the low energy electronic structure, which become extremely flat close to the magic angle of \( \sim 1.3^\circ \). These bands are not entangled with the other bands close to this magic angle as a consequence of the atomic relaxations. The dispersion inherits the quadratic band dispersion of the parent AB bilayers, but there is a band gap at the K and K’ points. In Fig. 1 we show the Hartree theory band structure of tDBLG for a twist angle of \( \theta = 1.89^\circ \) and for different integer doping levels per moiré unit cell, \(-3 \leq \nu \leq 3\), where \( \nu \) represents the number of electrons (\( \nu > 0 \)) or holes (\( \nu < 0 \)) added. We have used an effective dielectric constant \( \epsilon_{bg}=4 \), which corresponds to experiments in which tDBLG is encapsulated in hBN [63]. In stark contrast with tBLG [39, 40], it can be seen that the dispersion does not significantly change upon doping (all doping levels have been aligned such that the zero energy occurs at the mid-point between the upper and lower bands at K-point). The bands distort by up to only a few meV relative to the charge neutral case (black lines), which is insignificant compared to the bandwidth of these flat bands.

In tDBLG there are several reasons why the bands do not distort significantly upon doping. Firstly, the strength of the Hartree potential and how it varies with doping is relatively small. In Fig. 2 we show the locally-
averaged Hartree potential along the diagonal of the moiré unit cell on an outer (left panels) and inner (right panels) graphene layer. We find that the in-plane variation reaches values of ±25 meV on the inner layers, but only of the order of ±10 meV on the outer layers. These variations are significantly smaller than the bandwidth of the flat bands. In contrast, the Hartree potential of tBLG and twisted trilayer graphene (tTLG) reaches values of ±100 meV.

Upon electron doping tDBLG (ν > 0, top panels of Fig. 2), a positive peak in the Hartree potential emerges in the AA regions (located 2/3 of the way along the diagonal of the moiré unit cell), and when electrons are removed (ν < 0, bottom panels of Fig. 2) this becomes a negative trough. This is due to the flat bands having significant localisation in the AA regions of the inner layers, similar to tBLG \cite{39,41} and tTLG \cite{64}. However, in contrast to tBLG and tTLG, we do not find a clean separation of electronic states in real and reciprocal space \cite{65}. At the Γ-point, the states are peaked on the AB/BA regions of the inner layers, and the states at the K-point are mainly localised on the AA regions.

The localisation of the states at the M-point, however, is not well-separated between these two regions. Therefore, the in-plane variations of the Hartree potential are not capable of causing significant band deformations in tDBLG \cite{66}. In tBLG and tTLG, on the other hand, there is a clean separation of states in real and reciprocal space: states at the edge of the hexagonal Brillouin zone are localised on the AA regions of the moiré unit cell in real space, whereas states at the middle of the Brillouin zone are localised on the AB/BA regions of the moiré unit cell. This separation couples with the spatial variations in the Hartree potential to give rise to significant deformations of the electronic band structure and is the main origin of the qualitative difference observed with tDBLG.

As we do not observe significant distortions in the bands with doping in tDBLG, this means that we do not expect to observe pinning of the van Hove singularities in tunneling experiments. In fact, recent tunneling experiments have shown that there is, in fact, no pinning of the van Hove singularities in tDBLG \cite{41,33}. The bands were not completely rigid, however, and continuous dis-
tortions to the electronic structure were observed with doping. But in the STM experiments doping is accompanied by a concomitant increase in the perpendicular electric field (because of the single-gated devices). In Ref. it was shown that these distortions are well-described by including the effect of a perpendicular electric field.

B. Electric fields

In Fig. 3 we show the Hartree (black) and tight-binding (red) band structures of 1.89° tDBLG at charge neutrality with \( \epsilon_{bg} = 4 \) for two different electric field strengths. Upon applying a perpendicular electric field, the gap between the valence and conduction bands increases dramatically with the strength of the field. Moreover, the valley degeneracy of both the valence and conduction bands is lifted in the electric field, apart from at the \( \Gamma \) and \( M \) points. This splitting of the conduction and valence bands increases substantially with the field, with the valence bands undergoing more significant distortions than the conduction bands.

In the tight-binding approximation (without any additional intrinsic symmetric polarisation fields) the band distortions are significantly more pronounced than in Hartree theory. The electric field causes the system to polarise such that in one of the bilayers there is an enrichment of electrons and in the other bilayer there is a depletion of electrons, with the outer layers exhibiting larger enrichment/depletion than the inner layers. When Hartree interactions are included the Hartree potential opposes the external electric field to reduce its effect.

The extent by which the Hartree potential screens the electric field can be determined by computing an effective dielectric constant for each layer

\[
\epsilon^{(\alpha)} = \frac{V^{(\alpha)}_{\text{ext}}}{V^{(\alpha)}_{\text{ext}} + V^{(\alpha)}_{\text{H}}},
\]

where \( V^{(\alpha)}_{\text{ext}} = \langle E z_i^{(\alpha)} \rangle \) is the average potential due to the electric field in layer \( \alpha \), with \( E \) denoting the electric field strength, \( z_i^{(\alpha)} \) the \( z \)-coordinate of atom \( i \) in layer \( \alpha \), and \( \langle \cdots \rangle \) an average over \( i \) in layer \( \alpha \), and \( V^{(\alpha)}_{\text{H}} = \langle V^{(\alpha)}_{\text{H}} \rangle \) is the averaged Hartree potential in each layer \( \alpha \).

For the electric field of 10 meVÅ\(^{-1}\), we found that the average of the dielectric constant in each layer has a value of 2.60, but an electric field of 30 meVÅ\(^{-1}\) only gives a value of 1.94. This reflects the fact that the electrons do not screen larger electric fields as effectively. Note that these values were obtained with \( \epsilon_{bg} = 4 \). For free-standing tDBLG, the effective dielectric constant would be slightly larger. It has been found from DFT calculations of different numbers of layers of stacked (untwisted) graphene, that the effective perpendicular dielectric constant is approximately 3 [67, 68]. Therefore, these values of dielectric constant for tDBLG are qualitatively consistent with that found in DFT calculations in layers of stacked (untwisted) graphene.

C. Charge neutrality and the crystal field

In Fig. 3 we show the band structures of free-standing \( (\epsilon_{bg} = 1) \) 2.45° tDBLG, comparing a number of different models. Both panels include the band structure obtained from DFT at charge neutrality as a reference (purple). The left panel also shows the tight-binding band structure (red). We find, as others also have [24], that the tight-binding band structure matches reasonably well with that of DFT. There is, however, a slight discrepancy in the band width of the flat bands and the gap between the conduction and valence bands at the \( K \) and \( K' \) points. The difference in the band width is simply a consequence of the chosen decay parameters in the Slater-Koster rules of our tight-binding model, and this does not affect the gap between the bands significantly. As shown in Ref. [24], the tight-binding band gap can be corrected by including an empirical on-site and layer-dependent intrinsic symmetric polarisation (ISP) potential to the tight-binding model, as seen in the TB+ISP band structure (black) in the left panel of Fig. 3. The value of \(-30 \) meV on the inner layers relative to the outer layers that we have used for the ISP potential is that used in Ref. [24], which was determined by fitting the gap in the band structure at the \( K \)-point to that of DFT over a range of twist angles. It can be seen that the ISP does not change the band width significantly and gives rise to better quantitative agreement with DFT.

To explore the origin of the ISP, in the right panel of Fig. 3 we compare the Hartree band structure (red) to DFT (purple). Compared to the TB bandstructure in the left panel, we find that including long-range electron interactions has a very small effect on the dispersion at charge neutrality, and the most prominent difference is a slight reduction of the gap between the valence and conduction bands at the \( K \) and \( K' \) points, where the valence and conduction bands now touch. Interestingly, overall, the Hartree band structure appears to be in worse agreement with DFT than the TB results, even without the ISP.

To understand the observed band distortions, we plot the locally-averaged Hartree potential in Fig. 3. The Hartree potential has significant variations within the inner layers, whereas it remains approximately constant in the outer layers. Overall, the Hartree potential is more negative on the inner layers than the outer layers; hence, there are more electrons localised on the outer layers than the inner layers. Adapting the definition of Ref. [24] for the crystal field, we define \( \delta \) to be the difference between the layer-averaged on-site Hartree potential in the outer and inner layers of tDBLG. We refer to this quantity as the Hartree crystal field (HCF) and it is given by

\[
\delta = \langle \varepsilon^{el}_{\text{out}} \rangle - \langle \varepsilon^{el}_{\text{in}} \rangle,
\]

where \( \langle \varepsilon^{el}_{\text{out}} \rangle \) and \( \langle \varepsilon^{el}_{\text{in}} \rangle \) are the on-site energies averaged
FIG. 3: Band structure along the high symmetry path of $\theta = 1.89^\circ$ tDBLG with $\epsilon_{bg} = 4$ and $\nu = 0$ in an electric field of 10 meVÅ$^{-1}$ (left) and 30 meVÅ$^{-1}$ (right). The results of both the tight-binding approximation (red) and self-consistent Hartree theory (black) calculations are shown.

FIG. 4: Band structure along the high-symmetry path of a $\theta = 2.45^\circ$ tDBLG with $\epsilon_{bg} = 1$ and $\nu = 0$. (Left) comparison of DFT with the tight-binding (TB) model (with no layer-dependent potential) and a tight-binding model in which a layer-dependent on-site potential of $-30$ meV on the inner layers relative to the outer layers is included, which is referred to as the tight-binding plus intrinsic symmetric potential model (TB+ISP). (Right) comparison of DFT with self-consistent Hartree theory and with a tight-binding model in which a layer-dependent on-site potential is included that is determined by the average of the Hartree potential in that layer, the interlayer potential difference resulting from which is 8 meV. This is referred to as the tight-binding plus Hartree crystal field model (TB+HCF).

over atoms in the outer and inner layer of a bilayer, respectively. The two bilayers in tDBLG are equivalent by symmetry. In the right panel of Fig. 4, we show the band structure from a tight-binding calculation in which $\delta$ (taken as 8 meV for $\epsilon_{bg} = 1$) is added to the outer layers as a layer-dependent on-site energy (referred to as TB+HCF, black lines). Comparing to the self-consistent Hartree approach shown in the same panel (red lines), it can be seen that the band structures almost lie on top of one another except at the K-point where there is a shifting of about 5 meV. Therefore, the in-plane variations of the Hartree potential do not appear to alter the band structure in any way, as explained in the Sec. III A and it is the average difference between the Hartree potential on the inner and outer layers which determines the (small) band distortions.

Upon including the ISP or Hartree potential, we observe two effects: the $\Gamma$-point energies shifts down and a gap opens/closes at the K-point. The former can be understood from the fact that the states at the $\Gamma$-point are mainly localised on the inner layers. The latter can be understood from an analysis of the localisation of the states at the conduction and valence sides of the K-point. In the TB model, the conduction states are mainly localised on the inner layers and the valence states are mainly localised on the outer layers. The addition of the ISP or
FIG. 5: Locally-averaged Hartree potential along the diagonal of the moiré unit cell for \( \theta = 2.45^\circ \) with \( \epsilon_{bg} = 1 \) at \( \nu = 0 \). The outer layers are denoted by open circles and the inner layers by filled circles. The variable \(|s|\) is the distance from the BA site of a moiré unit cell along the long diagonal of the unit cell, given by the vector \( \mathbf{R}_1 + \mathbf{R}_2 \). The vertical solid lines correspond to BA stacking of the inner layers, dotted-dashed lines to the AB stacking, and dotted lines for AA stacking. The value plotted on each atom is the average of the Hartree potential on that atom with the average of the Hartree potentials on the three nearest neighbour atoms.

HCF reduces the energy of the conduction states and increases the energy of the valence states. These states cross in energy with an avoided crossing.

The left panel of Fig. 6 shows that, for a given \( \epsilon_{bg} \), \( \delta \) remains approximately constant for the twist angles studied here. \( \delta \) should be directly proportional to the surface charge density of the layers within a bilayer, assuming an idealised parallel plate capacitor model. Therefore, we can understand the twist angle dependence of \( \delta \) by analysing the number of transferred electrons between the layers of the AB stacked bilayers per moiré unit area. If the number of transferred electrons between the layers of the bilayer remains constant with twist angle, one would expect that \( \delta \) decreases inversely with the area of the moiré unit cell, and hence as \( \theta^{-2} \), as the area of the moiré unit cell scales quadratically with the twist angle. As shown in Fig. 6, we don’t observe a \( \theta^{-2} \) decrease in \( \delta \). Therefore, the layer polarisation of the bilayers must increase with decreasing twist angle too. The total number of polarized charges in a layer is calculated from

\[
\Delta n^{(\alpha)} = \sum_{j \in \alpha} (n_j - n_0),
\]

where \( j \) runs through all the atoms in one of the layers \( \alpha \). By symmetry \( \Delta n \) is equal and opposite in the outer and inner layer of the bilayers \([\Delta n^{(1)} = -\Delta n^{(2)} = -\Delta n^{(3)} = \Delta n^{(4)}]\). In the right panel of Fig. 6 we show how the number of transferred electrons increases with the moiré unit cell area, which explains the approximately constant value of \( \delta \) over the studied twist angles.

The screened Hartree interaction depends on the dielectric screening due to the environment. The dependence of \( \delta \) and \( \Delta n \) on \( \epsilon_{bg} \) is also reported in Fig. 3. For a given twist angle, we find that \( \delta \) reduces as the dielectric constant increases. In experiments, tDBLG is typically encapsulated by thick layers of hBN. Such encapsulation approximately translates to a screened interaction with a dielectric constant of approximately 4 [63]. We find that increasing the dielectric constant from \( \epsilon_{bg} = 1 \) to \( \epsilon_{bg} = 4 \) decreases the magnitude of \( \delta \) by a factor of two (Fig. 6 left panel). A simple \( 1/\epsilon_{bg} \) argument would overestimate this by a factor of two. From the right panel of Fig. 6, however, we find that the layer polarisation \( \Delta n \) is itself dependent on \( \epsilon_{bg} \), as the larger dielectric constant permits more charges to be transferred. The failure of the simple \( 1/\epsilon_{bg} \) argument was also shown to be the case for tBLG, where it was argued that tBLG itself already has a large dielectric constant, so increasing the environmental screening by a small amount does not have a large overall effect [39, 69].

In Refs. 24, 34 and 35 it was shown that to obtain DFT accurate low-energy band structures at charge neutrality of free-standing tDBLG, the atomistic tight-binding model which uses the Slater-Koster rules requires a layer-dependent on-site energy. Empirically, it was found that the on-site energy of the inner layers had to be approximately 30 meV lower than that of the outer layers. This is equivalent to the electrons sitting in an electric field which points from inner layers of tDBLG towards the outer layers, which causes the electrons to prefer to reside on the inner layers. In Ref. 24 this was interpreted as an intrinsic symmetric polarisation (ISP). In Refs. 34 and 35 also suggested an accumulation of electrons on the inner layers.

Interestingly, we find that the bands predicted by TB+HCF model distort in a very similar manner to those caused by the on-site potential from Refs. 24, 34 and 35. As can be seen from the left panel of Fig. 6, the value of \( \delta \) we obtain from our layer-dependent average of the Hartree potential is approximately one-third of the value found by Ref. 24 for free-standing tDBLG (\( \epsilon_{bg} = 1 \)). Therefore, it does not appear that the Hartree potential alone can fully explain the crystal field.

D. Origin of crystal field

To further investigate the origin of the ISP we perform large-scale first-principles DFT calculations on tDBLG and analyse the Kohn-Sham potential. The Kohn-Sham potential in a DFT calculation has three main contributions: (1) the ion-electron (ion-el) potential, which is often approximated with a pseudo potential; (2) the Hartree contribution from electron-electron (el-el) interactions; and (3) the exchange and correlation contribution.

We find that the ion-el potential is substantially more negative on the inner layers than the outer layers. The inner layers are on average closer to more carbon nu-
FIG. 6: (Left) The average Hartree potential difference between the outer and inner layers, $\delta$, for several dielectric constants as a function of twist angle $\theta$. We refer to this quantity as the Hartree crystal field (HCF). (Right) The total excess number of electrons $\Delta n^{(1/4)}$ on one of the outer layers (which we refer to as layers 1 and 4) within the moiré unit cell at various dielectric constants $\epsilon_{bg}$ as a function of moiré unit cell area $A$.

FIG. 7: (Left) Sum of Hartree potential and ion-electron potential (referred to as the electrostatic potential) from DFT as a function of $z$ (a coordinate perpendicular to the plane of the tDBLG system) in 2.45° tDBLG. (Right) Sum of the electrostatic potential and the local exchange-correlation potential as a function of $z$ in 2.45° tDBLG. In both plots, the potentials are first averaged over the $x$ and $y$ coordinates, and the resulting function of $z$ is smoothed by taking its convolution with a rectangular function of width 3.20 Å. The dotted vertical lines correspond to the $z$-averaged atomic positions of each layer. The horizontal lines indicate where the potential crosses the $z$-averaged atomic positions of each layer.

In Fig. 7 (left panel), we show the sum of the ion-el and Hartree potential as a function of $z$, where the potential has been averaged over the $x$ and $y$ directions, and the resulting function of $z$ has been smoothed by taking its convolution with a rectangular function of width 3.20 Å. We find that the sum of these potentials is approximately $-30$ meV more negative on the inner layers than the outer layers, which therefore, produces a more negative potential on the inner layers than the outer layers. Conversely, the Hartree potential is significantly more positive on the inner layers in comparison to the outer layers because the electrons are on average closer to more electrons on the inner layers.

In Fig. 7 (right panel) we show the sum of the electrostatic potential and the local part of the exchange-correlation potential, where again the potential have been smoothed according to the procedure described earlier. When the exchange-correlation potential is included, the precise value of for the difference in potential energy of the inner layers relative to the outer layers has a slight dependence on the width of the smoothing function used, but when the width is of the order of the interlayer spac-
We investigated Hartree interactions in tDBLG as a function of twist angle near the first magic angle, doping level, dielectric screening and applied electric field. We found that the band structure is largely insensitive to the in-plane variations of the Hartree potential. The inner and outer layers of tDBLG were shown to have different average on-site Hartree potentials. Since the doping level does not significantly change the averaged layer-dependent on-site potentials, there is little effect of doping level on the electronic structure of tDBLG. The layer-dependent on-site potentials found from Hartree theory are approximately one third of that required to correct the tight-binding model to match the band gap at the K-point found in DFT calculations. To understand the origin of the discrepancy between Hartree theory and DFT, we decompose the DFT Kohn-Sham potential into tight-binding band structures to DFT band structures.

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