Band gaps in incommensurable graphene on hexagonal boron nitride

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Introduction. The constant velocity of the charge carriers in graphene that results from the linear dispersion of the energy bands about the Dirac point gives rise to many of its intriguing properties [1–3] but also poses a serious limitation to its application in high-performance electronic devices [4, 5]. For logic applications, transistors with on-off ratios of order $10^6$ are needed, requiring band gaps of $\sim 0.4$ eV [5]. Different approaches have been adopted to open a gap, the most promising of which is to use the interaction of graphene with a substrate to modify the linear dispersion of the bands.

The current front runners to open a band gap using a sublattice-symmetry breaking interaction are SiC [6] and $h$-BN substrates [7, 8]. Because of its flatness, similarity to graphene, and the development of practical methods for preparing single layers of graphene on hexagonal boron nitride substrates [8] there has been an explosion in the number of studies of this system. $h$-BN is a very suitable insulating substrate for making graphene-based devices [9] because it has dielectric characteristics similar to those of SiO$_2$, but contains fewer charged impurities and is atomically flat [10, 11]. These properties result in a higher charge carrier mobility for graphene on $h$-BN compared to graphene on SiO$_2$ [8], and in electron-hole puddles [12] that are larger in size and less deep [13, 14].

In this paper we will show that the recently observed gap of order 30 meV [15] results from a large many-body enhanced quasiparticle gap being cancelled by the incommensurability of graphene and $h$-BN that is only partially restored by a lateral variation of the height of graphene above the $h$-BN substrate. The large size of the underlying band gap and the mechanism of its cancellation suggest ways of recovering the large bare bandgap.

Graphene on top of $h$-BN experiences a perturbing potential comprising two components. Firstly, the 1.8% lattice mismatch between the two honeycomb lattices and orientational misalignment give rise to a slowly varying component that has been observed as moiré patterns in scanning tunneling microscopy images [13, 14]. Because of the chiral nature of the states close to the Dirac point [16], this component does not open a gap [17–20]; the superlattice Dirac points predicted by these effective Hamiltonian studies have recently been observed in scanning tunneling spectroscopy experiments [21].

Secondly, the heteropolar $h$-BN substrate also gives rise to a sublattice symmetry-breaking potential that opens a gap at the Dirac point when graphene and $h$-BN are commensurable [7]. The initial failure [8, 13, 14] to observe the band gap of order 50 meV predicted by these first principles calculations was attributed to the lattice mismatch [13, 22]. On the basis of binding energies calculated from first principles, it was argued that the energy gained by graphene bonding commensurably to $h$-BN was insufficient to offset the energy cost of achieving this by stretching graphene (or compressing $h$-BN). Tight-binding (TB) analyses led Xue [13] and Sachs [22] to argue that the symmetry-breaking interaction between graphene and $h$-BN would average out in the incommensurable case to a much smaller (but not vanishing [23]) band gap.

Recent temperature-dependent transport studies indicating the occurrence of a metal to insulator transition at the charge neutrality point at low temperatures, suggest that the situation may be more complex [15, 24, 25]. The low temperature insulating state has been interpreted to be induced by disorder (Anderson transition) [24] or to result from substrate-induced valley symmetry breaking [15, 25]. It has also been suggested that even small symmetry-breaking-induced band gaps may be greatly enhanced by many body interactions [26].

Because the gap suppression by lattice mismatch depends on details of the approximations made in deriving effective Hamiltonians for graphene [23], we use first-principles calculations to derive explicit $\pi$-orbital non-orthogonal TB Hamiltonians for graphene on $h$-BN that do not appeal to perturbation theory to fold the graphene-substrate interaction into an effective Hamiltonian. The band gap induced by a commensurable $h$-BN substrate survives the small lattice mismatch between graphene and $h$-BN but is indeed greatly reduced; it does
not survive misaligning the two lattices. Taking into account a local variation of the graphene-h-BN separation and quasiparticle energies calculated within the GW approximation of many body perturbation theory leads to a band gap of 32 meV.

**Computational details.** We use DFT at the level of the local density approximation (LDA) [27] within the framework of the plane-wave projector augmented wave (PAW) method [28], as implemented in VASP [29–31], to determine the electronic structure of a graphene sheet on top of a h-BN substrate. A plane wave basis with a cutoff energy of 400 eV is used in combination with a 36 × 36 k-point grid (in a 1 × 1 unit cell). Many-body effects are studied within the GW approximation [32] starting with LDA Kohn-Sham (KS) orbitals [33] calculated for a cell containing two h-BN layers and a graphene layer. We use the GW implementation in VASP [34], with 12 occupied and 52 empty bands and 50 points on the frequency grid. Interactions between periodic images in the z direction lead to a dependence of the GW band gap on the cell size that we remove by linearly extrapolating the calculated gaps as a function of the inverse cell size to infinite separation [35].

**Density Functional Calculations.** We start by analyzing the electronic structures of rotationally aligned, commensurable graphene/h-BN at the DFT and GW levels, before using the results to construct a TB Hamiltonian for rotated, incommensurable structures. We focus for convenience on the three high symmetry configurations: (a) with one carbon over B, the other over N; (b) with one carbon over N, the other centered above a h-BN hexagon; (c) with one carbon over B, the other centered above a h-BN hexagon [7]. Panels (a)-(c) of Fig. 1 show the LDA energy bands for graphene on h-BN for the (a), (b) and (c) configurations at their RPA equilibrium separations of \( d_{eq} = 3.55, 3.50 \) and 3.35 Å [22], respectively, with LDA gaps \( \Delta \varepsilon \equiv \varepsilon_3(K) - \varepsilon_2(K) \) of 30-40 meV opened at the K point by the symmetry-breaking interaction with the substrate [7]. The Dirac point is situated asymmetrically in the h-BN band gap about a third of the way from the top of the valence band. Apart from the formation of the small gap, the dispersion of the \( \pi \) bands is largely unchanged by the interaction with the h-BN substrate within about 1 eV of the Dirac point.

If we expand the energy scale about the Dirac point, we see that the centers of the gaps, \( (\varepsilon_2(K) + \varepsilon_3(K))/2 \), do not coincide for the different configurations (lower panels); the interaction between graphene and h-BN gives rise to an interface potential step \( \Delta V \). The source of this potential step is a configuration-dependent interface dipole layer that can be visualized in terms of the electronic displacement \( \Delta n(r) \) obtained by subtracting the electron densities of the isolated constituent materials, \( n_{Gr} \) and \( n_{BN} \), from that of the entire system \( n_{Gr,BN} \) [36]. The potential step is related to the dipole layer, illustrated in Fig. 1 for the (a), (b) and (c) configurations, by \( \Delta V = -e^2/(4\pi \varepsilon_0) \int z\Delta n(r) \, dx \, dy \, dz \) where \( A \) is the area of the surface unit cell and the integration is over all space.

The potential step depends sensitively on how the graphene and h-BN lattices are positioned. Starting from the (c) configuration, and displacing graphene laterally by \((x, y)\) yields the potential landscape \( \Delta V(x, y) \) shown in Fig. 1(d). For each value of \((x, y)\), the graphene sheet is a distance \( d_{eq}(x, y) \), the RPA equilibrium separation, from the h-BN substrate. \( \Delta V \) reaches appreciable values ranging from 20 to 90 meV, where the minimum and maximum values are found for the high symmetry configurations (b) and (c), respectively. The full \( d \)-dependence of \( \Delta V \) is shown for the three configurations in Fig. 1(e).

**GW correction** We perform \( G_0 W_0 \) calculations for the three symmetric configurations in order to find the
many body corrections to the LDA band gaps. Fig. 2 shows the quasiparticle gaps as a function of the inverse cell size 1/a in the direction perpendicular to the graphene sheet [37] for the three symmetric configurations and for values of the height of graphene above the h-BN substrate that span the full range of RPA equilibrium separations. We are interested in the band gap for an isolated layer of graphene on h-BN that we determine by extrapolation to a → ∞. The gap is seen to increase dramatically, from 43, 28, and 30 meV (horizontal lines) in the LDA to 278, 178 and 193 meV, for the (a), (b) and (c) configurations at the RPA equilibrium separations (thick lines), respectively.

**Band gap in graphene on h-BN** Before we use the results of the full ab-initio calculations for the commensurable systems to construct a TB Hamiltonian for the incommensurable case, it is useful to estimate the size of the band gaps we expect to find. We can make use of the weakness of the interaction between the graphene and h-BN and the large separation in energy between the Dirac point eigenvalues and the h-BN valence and conduction band edges to construct an effective Hamiltonian for the graphene layer by Löwdin downfolding. The substrate can then be replaced by three effective potentials [23]: one that locally shifts the Dirac point; another that opens a local gap; and a third that has the form of a pseudo magnetic field. By applying first order degenerate perturbation theory to the downfolded Hamiltonian, we estimate the gap of the incommensurable system to be

\[ \Delta \varepsilon = \frac{1}{3} \left( \Delta \varepsilon_{(b)} + \Delta \varepsilon_{(c)} - \Delta \varepsilon_{(a)} \right) \]  

(1)

in terms of the gaps of the commensurable systems.

This estimate should be valid in the limit that the mismatch is very small and all possible configurations are sampled equally. Using Eq. (1) and assuming that the structure is locally at its RPA equilibrium separation, we expect the band gap of aligned, commensurable graphene on h-BN to be 31 meV at the G_0W_0 level, as compared to 5 meV at the LDA level. Assuming the graphene sheet is flat results in much smaller G_0W_0 gaps of 10, 5 and 4 meV for separations of 3.35, 3.45, 3.55 Å, respectively. This indicates that it is important to take the modulation of the equilibrium separation into account. We will find that the gaps estimated using Eq. (1) are very close to the results obtained by full numerical diagonalization of the TB Hamiltonian.

**Tight Binding Hamiltonian.** The diagonal blocks of the TB Hamiltonian and overlap matrices

\[ H = \begin{pmatrix} H_{Gr} & H_{int} \\ H_{int}^\dagger & H_{BN} \end{pmatrix} \]

are first determined separately for monolayers of graphene and h-BN. Because isolated monolayers have reflection symmetry, the p_z blocks of the corresponding matrices are decoupled from the \( \{s, p_x, p_y\} \) blocks. By introducing an overlap matrix, \( H \) and \( O \) can be chosen to have short range and the ab-initio (LDA and GW) bands can be fit essentially exactly. When we consider the interaction between graphene and h-BN, we include the interface potential step \( \Delta V \) as an additional diagonal term.

We determine \( \Delta V \) for incommensurable structures by interpolation and approximate incommensurable lattices by periodic superstructures. For example, the factor 1.018 between the h-BN and the graphene lattice parameters can be represented by the rational approximant 56/55, which leads to a supercell of 56 × 56 × 2 carbon atoms and 55 × 55 each of boron and nitrogen atoms. As the lattice mismatch is small, we assume that the graphene sheet locally follows the RPA equilibrium separation \( d_{eq}(x,y) \) as a function of position \( (x,y) \) within this supercell, as shown in Fig. 3(a). The potential step \( \Delta V(x,y) \) can then be obtained from Fig. 1(d).

To define \( \Delta V \) when the graphene lattice is rotated through an angle \( \phi \) with respect to the h-BN substrate, we make use of the fact that \( \Delta V(x,y) \) has threefold rotation symmetry and interpolate for intermediate angles. This approximation was checked for commensurable lattices where explicit DFT calculations can be performed for specific rotation angles for which the unit cell sizes are manageable.

**TB: Commensurable lattices.** The remaining parameters of the TB Hamiltonian are obtained from fits to...
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either the LDA or the GW band structures of commensurable graphene|h-BN structures. The band structures calculated with the TB Hamiltonian are compared to the LDA results in Fig. 1(a)-(c) (dashed lines). The TB Hamiltonian clearly yields a satisfactory fit for the three configurations shown. It also accurately captures the shift of the Dirac cone as a function of an \( xy \) translation of the graphene sheet over the h-BN substrate. Figure 3(b) shows the position of the Dirac point (the center of the gap) with respect to the center of the h-BN band gap

\[
\varepsilon_D(x, y) = \frac{[\varepsilon_3(K) + \varepsilon_2(K)] - [\varepsilon_4(K) + \varepsilon_1(K)]}{2}
\]  

for the height profile shown in Fig. 3 (a); it fits the LDA results exactly. Comparison of the LDA energy bands for a structure with graphene rotated through 21.78° with respect to h-BN (resulting in a \( \sqrt{7} \times \sqrt{7} \) unit cell with 14 carbon, 7 boron and 7 nitrogen atoms) again shows very good agreement. Because the rotated system was not used in fitting the TB Hamiltonian, the good description of the bands close to the Dirac points is an important measure of its predictive capability.

**TB: Incommensurable lattices.** It has been argued that the bonding between graphene and a h-BN substrate is so weak and those honeycomb structures so stiff that the small 1.8% lattice mismatch will persist in graphene|h-BN structures [22]. For perfect alignment, i.e., \( \phi = 0 \), this implies that even if we start at a position where the local bonding corresponds to the lowest energy (the (c) bonding configuration), the lattice mismatch will result in dephasing of the two lattices. However, the mismatch is sufficiently small that locally the hopping is indistinguishable from a commensurable system displaced by some amount \( (x, y) \), with an equilibrium distance \( d_{eq}(x, y) \), so the Hamiltonian for the incommensurable system can be assembled with the parameterization described above. Choosing the vacuum potential as the common potential zero leads to diagonal elements of the TB Hamiltonian that depend on the local interface potential \( \Delta V(x, y) \). The h-BN conduction and valence band edges then undulate in real space, a prediction that could be confirmed by experiment.

When \( \phi = 0 \) and assuming that the graphene sheet follows the height profile of Fig. 3(a), we calculate a (GW) band gap of 32 meV. This is consistent with reports of the charge neutrality point resistance increasing with decreasing temperature [24, 25] and of gaps between 16 and 28 meV that were extracted from temperature dependent resistivity measurements [15]. The height variation in the structure turns out to be important; using a flat graphene sheet at separations of 3.35 Å, 3.45 Å, 3.55 Å, results in gaps of 10, 6, and 5 meV, respectively. This suggests that it may be possible to realize larger gaps in graphene by suitably modulating the graphene-h-BN spacing. For rotation angles \( \phi > 0^\circ \), the gap rapidly becomes smaller. Calculations for a \( \phi = 6^\circ \), \( \delta = 2.0% \) incommensurable structure result in a vanishing gap. Further studies on even larger supercells corresponding to smaller angles have to be done to determine the critical angle at which a band gap is opened.

**Conclusions.** Many-body calculations for commensurable graphene on h-BN show that quasiparticle band gaps are much larger than previously thought. Incommensurability results in a near complete cancellation of these gaps but a detailed analysis suggests that it may be possible to realize gaps much larger than the recently observed 30 meV by suitably modulating the separation of graphene from the substrate. This might be achieved by structuring the substrate, by exciting phonons with wavelengths that frustrate the cancellation of the gap-opening interactions, or by applying modest pressure.

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