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Effect of Structural Relaxation on the Electronic Structure of Graphene on Hexagonal Boron Nitride

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We performed calculations of electronic, optical, and transport properties of graphene on hexagonal boron nitride with realistic moiré patterns. The latter are produced by structural relaxation using a fully atomistic model. This relaxation turns out to be crucially important for electronic properties. We describe experimentally observed features such as additional Dirac points and the “Hofstadter butterfly” structure of energy levels in a magnetic field. We find that the electronic structure is sensitive to many-body renormalization of the local energy gap.

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The physical properties of van der Waals heterostructures can change drastically in comparison with the ones of the constituent two-dimensional materials [1]. Recent experiments of graphene on hexagonal boron nitride (hBN) show that hBN can act like an effective periodic potential for graphene, leading to secondary Dirac points [2,3]. The graphene-hBN heterostructures are of fundamental interest as an example of a quantum mechanical system with tunable incommensurate potentials. Such incommensurate potentials are important for quasicrystals [4], but they are not tunable, whereas in the graphene-hBN systems it is possible to change the potential by changing the mutual orientation of graphene and hBN layers. It was long ago predicted that a system under the influence of both a crystal potential and a magnetic field, with a magnetic period incommensurate with that of the crystal, would exhibit a recursive spectrum now called Hofstadter’s butterfly [5], which was observed in experiments with misaligned graphene on hBN in 2013 [6–8].

Although hBN has a structure similar to that of graphene, the lattice mismatch of 1.8% will cause moiré patterns, meaning that there is no uniform stacking in the sample. An extra difficulty is posed by the recently observed transition at very small angles from an incommensurate state, with little deformation of graphene, to a commensurate state, where regions of stretched graphene are separated by narrow regions of compressed graphene [9]. The computational challenge lies in the fact that at such angles these superlattices have unit cells consisting of tens of thousands of atoms, making it impossible to study them using methods such as density functional theory (DFT). A classical atomistic approach instead is able to describe the experimentally observed structures [10], and the tight-binding propagation method (TBPM) described in Ref. [11] can be used to study the electronic properties of systems with hundreds of millions of atoms, circumventing this problem. In this

research, we apply TBPM to graphene-hBN heterostructures with various rotation angles, based on structures determined by atomistic simulations of realistic moiré patterns.

Various approaches have been developed to describe graphene on top of hBN with an effective tight-binding (TB) Hamiltonian [12–14]. While these methods give reasonable results, they lack the flexibility needed to apply them to other systems. We present an approach consisting of three parts: namely, (i) structural relaxation of graphene on top of hBN with an empirical potential, (ii) modification of the TB parameters due to this relaxation, and (iii) calculation of electronic properties with these modified TB parameters. There are multiple advantages to this approach. First, the construction of the TB model is solely based on the three-dimensional coordinates of the carbon atoms; thus, one could use this same method for graphene on top of other substrates or graphene under mechanical strain. Second, it is easy to incorporate extra disorder such as carbon vacancies, adatoms, ripples, etc.

The first step is the relaxation of graphene on hBN. We follow the approach of Ref. [10], where it was shown that moiré patterns can be used as a probe of interplanar interactions for graphene on hBN. We construct supercells of rotated graphene on hBN with misorientation angles θ and corresponding moiré patterns with period λ [15]. The graphene atoms interact through the reactive empirical bond order potential REBO [16], as implemented in the molecular dynamics code LAMMPS [17]. The hBN substrate is kept rigid, mimicking a bulk substrate. As no empirical potential for the interactions between graphene and hBN is available, we use the registry-dependent Kolmogorov-Crespi potential [18] developed for graphite. We neglect the correction for bending introduced to describe carbon nanotubes. We set the ratio of C-B/C-N interactions to 30% with the C-N interaction twice as strong as the original C-C interaction [19], as this leads to better agreement with

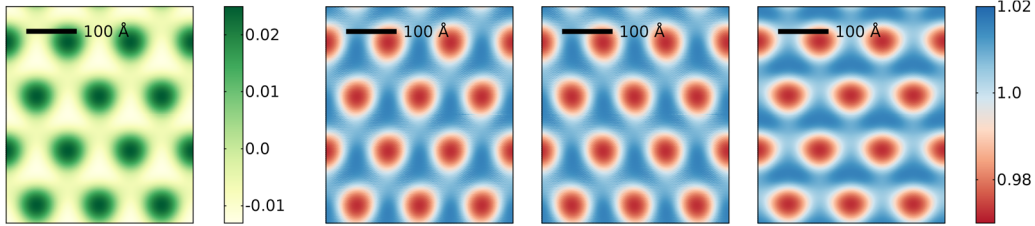


FIG. 1 (color online). The modified TB parameters for a relaxed sample of graphene on hBN with $\theta = 0^\circ$ ($\lambda = 13.8$ nm). From left to right, the on-site potential v and the hopping parameters t_1 , t_2 , and t_3 . The color bars are in units of $t = 2.7$ eV.

experimental results [9,10] and *ab initio* calculations [20,21]. We minimize the total potential energy by relaxing the graphene layer by means of FIRE [22], a damped dynamics algorithm. For aligned samples ($\theta = 0^\circ$), this relaxation leads to significant changes in bond length along the moiré pattern. The degree of deformation decreases with increasing angle [23].

After relaxation, we use the following graphene TB Hamiltonian. The main idea of our method is that the TB parameters are modified as a function of a small displacement out of equilibrium of the carbon atoms. The general TB Hamiltonian for graphene is given by

$$H = -\sum_{\langle i,j \rangle} t_{ij} c_i^\dagger c_j + \sum_i v_i c_i^\dagger c_i, \quad (1)$$

where only the nearest-neighbor hopping and on-site potential are taken into account. Including next-nearest-neighbor hoppings will result in minor changes [24]. The change in the hopping parameter t_{ij} can be written as [25]

$$t_{ij} = t \exp[-3.37(r_{ij}/a_0 - 1)], \quad (2)$$

where r_{ij} is the distance between atoms i and j , $t = 2.7$ eV is the regular hopping parameter, and $a_0 = 1.42$ Å is the equilibrium carbon-carbon distance for graphene. For the on-site potential v_i we calculate an effective area S of each carbon atom [26], which will be changed due to local deformations resulting in a modulated value for v_i :

$$v_i = g_1 \frac{\Delta S}{S_0}, \quad (3)$$

where $g_1 = 4$ eV. This value corresponds to the screened deformation potential, which gives a reasonable description of transport properties [27], and is close to density functional estimates [28]. Figure 1 shows the change of the on-site potential and of the hopping parameters for a relaxed layer of graphene on hBN with rotation angle $\theta = 0^\circ$. A clear periodic modulation with period λ is found in all parameters.

Electronic properties are calculated using the TBPM, a method based on the propagation of a random complex wave function $|\varphi\rangle$ according to the time-dependent Schrödinger equation using Chebychev polynomials

[11,29]. The correlation function $\langle \varphi | e^{-iHt} | \varphi \rangle$ is calculated at each time step. The density of states (DOS) can then be obtained by a Fourier transform of these correlation functions. To increase the accuracy of the electronic calculations, the supercells are repeated so that the total system consists of $\sim 6000 \times 6000$ carbon atoms.

The first step to validate our method is to compare the DOS of pristine graphene (unrelaxed) to that of graphene on hBN after energy minimization (relaxed), as shown in Fig. 2(a). Secondary Dirac cones appear at both the electron and hole side, as seen in experiments [2,3,6–8]. The positions depend on the reciprocal lattice vector \mathbf{G} of the moiré pattern, and are given by $E_D = \pm \hbar v_F |\mathbf{G}|/2 = \pm 2\pi \hbar v_F / (\sqrt{3}\lambda)$, where v_F is the Fermi velocity [12,30,31]. Because of the substrate the depth of the extra cones is asymmetric and highly dependent on the value of the on-site potential. The position of the extra Dirac cones will change with misorientation angle θ as λ depends on θ [15]. Figure 2(b) shows how small angular variations shift the extra cones. The effect of the relaxation decreases with increasing θ , meaning that the differences of the DOS also become negligible for large θ .

The real-space distribution of eigenstates can be compared with the LDOS images obtained from STM measurements. In general, it is hard to obtain the eigenstates corresponding to a TB Hamiltonian of a system with millions of atoms. We obtain the so-called quasieigenstates

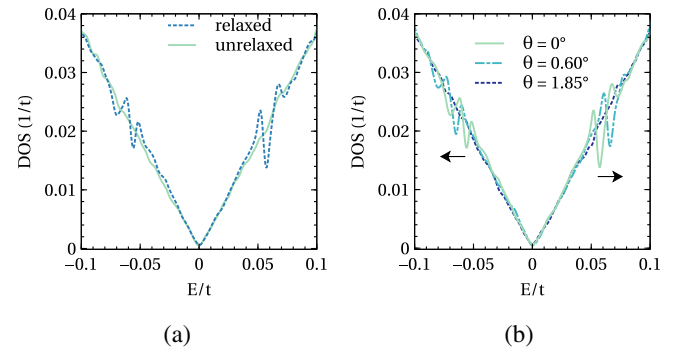


FIG. 2 (color online). (a) Numerical results for the DOS of unrelaxed and relaxed graphene. (b) DOS for different angles θ . The extra cones move outward, indicated by the arrows, and disappear for large angles. The corresponding moiré lengths λ are 13.8, 11.9, and 6.7 nm, respectively.

[11], which are close to the real eigenstates, by using the TBPM. Figure 3 shows the amplitude of some of these quasieigenstates close to the additional Dirac cones. The hBN substrate breaks the sublattice symmetry, and therefore we plot the quasieigenstates separately. Some localization is found for the quasieigenstates. We see that for energies close to the Fermi energy the difference between amplitudes is negligible. For energies closer to the additional Dirac cones, a clear moiré pattern can be distinguished.

The appearance of additional Dirac cones in the DOS and the signatures of localization in the quasieigenstates indicate that the electronic structure is strongly influenced by relaxation. The transport measurements of dc conductivity of graphene on hBN in recent experiments [6–8] show clearly asymmetric drops of the conductivity at the secondary Dirac points on the hole and electron sides. The decreasing of the conductivity on the hole side is more significant, with a value even lower than the minimum conductivity at the Dirac point in Ref. [7]. We calculate the dc conductivity by using the Kubo formalism [32] within the TBPM [11] as

$$\sigma = \lim_{\tau \rightarrow \infty} \frac{\rho(E)}{\Omega} \int_0^\tau dt \text{Re}[e^{-iEt} \langle \varphi | J e^{iHt} J | E \rangle], \quad (4)$$

where $\rho(E)$ is the density of states, Ω is the sample area, and $|E\rangle$ is the *normalized* quasieigenstate [11]. The results

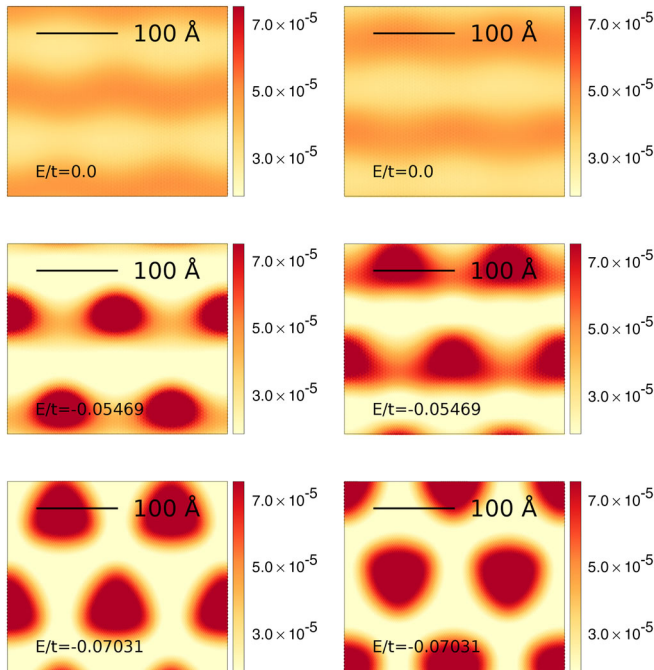


FIG. 3 (color online). Amplitude of the quasieigenstates for different energies for $\theta = 0^\circ$. The left-hand panels show sublattice A and the right-hand panels show sublattice B. For energies closer to the extra Dirac cones, a clear moiré pattern can be distinguished. Only a small part, roughly one thousandth, of the system is shown.

shown in Fig. 4 do not have a minimum on the hole side, such as in experiments. It could be obtained by using a much stronger interaction strength in the empirical potential used for the relaxation [33] than the strength that is suggested by *ab initio* total energy calculations [20]. However, there is an interaction that we have not yet considered, namely, the local gap opening induced by the substrate [20]. It is known that the many-body effects can increase the gap dramatically [34], and more accurate *GW* calculation gives a several times larger gap [21] in comparison with DFT [20]. To take into account the sublattice asymmetry due to the many-body effect, we add a local gap term according to the potential difference between one site and its three neighbors as

$$v'_i = v_i + \Delta v_i = v_i + \frac{g_2}{2} \left[v_i - \frac{1}{3} \sum_{\delta=1,2,3} v_{i+\delta} \right], \quad (5)$$

The strength of the local gap, which is controlled by the parameter g_2 in Eq. (5), is given by the average of the potential difference between sublattices A and B, $\Delta U = \langle |\Delta v_i| \rangle$. Numerical calculations of the DOS in Fig. 4 show that the depth of the additional minima at energy E_D can be tuned by the local gap ΔU . For increasing ΔU , the minimum on the hole side of the DOS becomes deeper, while the one on the electron side first disappears for small ΔU and then reappears for large ΔU . Although it is very difficult to estimate ΔU accurately since there is no quantitatively accurate theory of many-body effects in graphene, we can use the one obtained by Bokdam *et al.* [21], a *GW* band gap of 32 meV for incommensurable graphene on hBN with $\theta = 0^\circ$, as a reference value. For $\Delta U = 32$ meV, we see clearly a decrease (increase) of DOS and dc conductivity at the extra Dirac point on the hole (electron) side. The transport calculation with $\Delta U = 32$ meV reproduces well the experimental observations in Refs. [6,8]. On the other hand, in Ref. [7], the value of dc conductivity at the extra Dirac point on the hole side is smaller than the minimum conductivity at the Dirac point. We find that the vanishing of σ at certain carrier density is only possible by

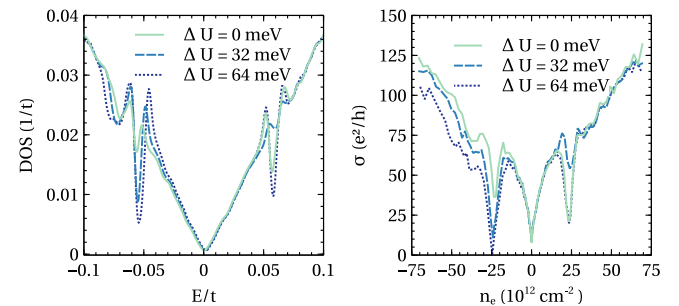


FIG. 4 (color online). Density of states (left) and dc conductivity σ (right) as a function of the carrier density n_e for $\theta = 0^\circ$ and for varying ΔU .

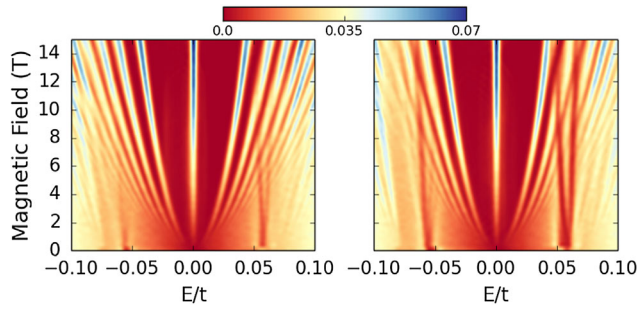


FIG. 5 (color online). The density of states for varying magnetic field with (left) $\Delta U = 32$ meV and (right) $\Delta U = 64$ meV. The DOS is calculated in steps of 0.25 T. Strong extra peaks at both electron and hole side are observed, which for higher magnetic fields split into two.

considering stronger many-body effects with a larger ΔU . For example, σ drops to zero by doubling ΔU as 64 meV. Our numerical results suggest that the experimentally observed insulating state at the extra Dirac point on the hole side [6–8] is a signature of strong local gap induced by many-body effects.

In the presence of a perpendicular magnetic field, the quantization of the energy eigenstates leads to discrete Landau levels. The modulation induced by the moiré patterns splits the flat Landau bands of pristine graphene into minibands, the so called “Hofstadter butterfly spectrum,” which has been conformed in several recent experiments [6–8]. In order to verify the splitting of the Landau levels in our TB model, we show the contour plot of DOS as a function of magnetic field strengths in Fig. 5. For both $\Delta U = 32$ and $\Delta U = 64$ meV, there is a clear splitting of the Landau levels with increasing magnetic field, and the splitting becomes clearer when the stronger local gap term is included.

Another quantity of great experimental and practical interest is the optical conductivity, which we calculate by using Kubo formalism at finite frequency within the TBPM [11,35]:

$$\sigma(\omega) = \lim_{\epsilon \rightarrow 0^+} \frac{e^{-\beta\omega} - 1}{\omega\Omega} \int_0^\infty e^{-\epsilon t} \sin \omega t \times 2\text{Im}\langle \varphi | f(\mathcal{H}) J(t) [1 - f(\mathcal{H})] J | \varphi \rangle dt, \quad (6)$$

where $\beta = 1/k_B T$ is the inverse temperature and $f(\mathcal{H}) = 1/[e^{\beta(\mathcal{H}-\mu)} + 1]$ is the Fermi-Dirac distribution operator. The periodic modulation of the TB Hamiltonian due to the moiré pattern leads to the emergence of minibands around the extra Dirac cones. We expect that there should be signatures of the optical excitations between the valence and conduction minibands [36]. Figure 6 shows the optical spectrum σ of graphene on hBN with three different orientation angles θ . For high energies the enhanced peak around $\omega = 2t$, resulting from the optical transition between Van Hove singularities at $E = \pm t$, is similar to

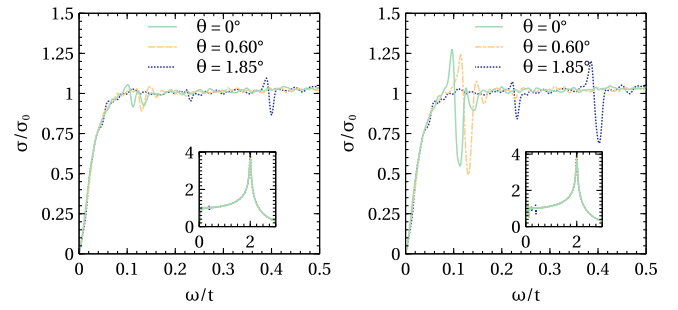


FIG. 6 (color online). Optical conductivity σ for various angles θ with (left) $\Delta U = 32$ meV and (right) $\Delta U = 64$ meV. $\sigma_0 = \pi e^2/2h$ is the universal optical conductivity of graphene. Insets: The optical conductivity for larger scales.

pristine graphene. Furthermore, there are additional peaks at photon energy about $\omega = 2|E_D|$ (around 0.1–0.2 t , depending on the angle θ), corresponding to the optical transitions between the peak states around the extra Dirac points on the hole and electron sides. The amplitudes of these peaks increase significantly with a larger local gap term. It is known that the optical conductivity of graphene for visible light has a universal value; our results with moiré patterns indicate that the optical conductivity becomes tunable by changing the relative orientations between graphene and its hBN substrate.

To conclude, we have shown that merely taking into account the periodic modulation in graphene caused by a substrate is enough to describe new features in the electronic and optical properties of graphene. The many-body enhancement of the local energy gap is crucially important to reproduce the experimentally observed insulating state at the extra Dirac point on the hole side. We also show that the optical conductivity of graphene is tunable by varying the relative orientations between graphene and its hBN substrate. The presented approach for the construction of the TB model is not limited to graphene-BN heterostructures, but can be used for graphene with other substrates, such as Ru and Cu, and can be extended to include various types of disorder.

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