1. Introduction

Graphene has attracted intense experimental and theoretical efforts since its first isolation and identification in 2004 [1]. The properties of graphene have been studied experimentally using a wide range of techniques, including electrical transport measurements (for a review, see [2]), optical spectroscopy measurements [3, 4], and local scanning probe measurements [5–7]. Local scanning probe microscopy plays a unique role among these techniques, providing simultaneous local topographic and electronic information (for example: lattice structure, band structure, and electronic scattering) at the atomic scale. Prior reviews of scanning probe microscopy results have mainly focused on graphene on SiO2 [5–7] or graphene on graphite [7] samples. Since 2010, hexagonal boron nitride (hBN) supported graphene samples have triggered a new surge in graphene research [8, 9].

This review focuses on the electronic properties of graphene on hexagonal boron nitride (hBN) heterostructures accessible with scanning tunneling microscopy (STM) and spectroscopy (STS) measurements, as well as the application of these results to transport measurements. STM and STS measurements show that hBN provides a flatter and cleaner substrate for graphene than SiO2. As such, hBN permits the observation of intrinsic properties of graphene which were previously obscured by the rough and electronically inhomogeneous SiO2 substrate. Additionally, the interaction between graphene and boron nitride provides a path for the study of new physical phenomena not present in bare graphene devices. This review focuses on recent advancements in the study of graphene on hexagonal boron nitride devices from the perspective of scanning tunneling microscopy with highlights of some important results from electrical transport measurements.

Keywords: graphene, boron nitride, scanning tunneling microscopy

(Some figures may appear in colour only in the online journal)
Graphene is a critical ingredient in these experiments, not only for increasing the sample cleanliness, but in many cases the Hofstadter quantization being one particularly nice example is itself responsible for the observed effect.

Similarly, hBN can be quite beneficial for the study of graphene-based optical devices as well. Optical measurements such as spatially resolved Raman spectroscopy can better probe the intrinsic optical response of graphene due to the reduced charge inhomogeneity [51–54]. Additionally, they may probe the effects induced by the hBN substrate itself at higher energies normally inaccessible to optical transport experiments, providing a more complete picture of the physics of these heterostructures over a wide energy range [55]. Unique optical characteristics of graphene on hBN heterostructures may also be utilized to design novel devices, such as re-writable p-n junctions [56]. The combination of local and nonlocal measurements of graphene on hBN heterostructures has resulted in rapid developments in the field, yielding studies of new and interesting physical phenomena and important developments necessary for the production of next-generation electronic devices utilizing these materials.

We introduce our review in section 1 with a brief discussion of the basic properties of graphene (section 1.1). There have already been several comprehensive reviews written about the basic structural and electronic properties of graphene [2, 57], so we restrict our attention here to the most relevant properties needed to understand the new developments seen in graphene on hBN devices. We similarly discuss the basic properties of hexagonal boron nitride in section 1.2. We cover the basic physical and experimental methods of STM in section 1.3. We then focus on experimental results in this new research field from the perspective of local scanning probe microscopy. Section 2 discusses basic scanning probe microscopy characterization of graphene on hBN devices and compares them with previous results from graphene on SiO$_2$ devices. We discuss the results of basic topography measurements in section 2.1 and of basic spectroscopy measurements in section 2.2. In section 3, we discuss the renormalized band structure of graphene on hBN devices due to the periodic electric potential from the hBN substrate. We discuss the calculation of moiré wavelengths seen in graphene on hBN devices in section 3.1. Section 3.2 develops the theory of superlattice Dirac points in graphene on hBN, and section 3.3 discusses their experimental signatures. We compare these results to those seen in graphene on metallic crystalline substrates in section 3.4. In section 4 we cover the unique electronic properties which can be seen in graphene on hBN devices due to the cleaner charge landscape. Sections 4.1–4.3 discuss long-wavelength local density of states oscillations, manipulation of atomic surface adsorbents, and effects seen in an external magnetic field. In section 5 we cover a small sample of important electrical transport measurements which are made feasible only by using an hBN substrate. Sections 5.1 and 5.2 cover recent transport results demonstrating clean integer and fractional quantum Hall effects. Sections 5.3 and 5.4 discuss results from novel device structures exhibiting features such as an insulating state at charge neutrality and the 'Hofstadter butterfly' spectrum. Finally, we conclude our review in sections 6.

1.1. Fundamental graphene properties

1.1.1. Structure and electronic properties. Graphene is formed by a hexagonal lattice of carbon atoms (figure 1). It is a Bravais lattice with a two atom basis, conventionally labeled as A and B (figure 1). The band structure of graphene can be calculated using tight binding theory (see e.g. [58]), as shown in figure 2. The conduction and valence bands touch at 6 points (the so-called Dirac points) at the corners of the first Brillouin zone. The dispersion relation near these points is approximately linear [58], so the low energy electronic states can be described by a Dirac-like equation:

\[ H\Psi = \hbar v_F \begin{pmatrix} 0 & \pm k_x - i k_y \\ \pm k_x + i k_y & 0 \end{pmatrix} \Psi = E\Psi, \]

where $\Psi$ is the wavefunction of an electronic state, $\hbar$ is the reduced Planck constant, $v_F$ is the Fermi velocity, and $k_x$ and $k_y$ are the wave vectors measured from the Dirac
point. The eigenvalue and eigenfunction solutions to this equation are

$$E_{\pm} = \pm \hbar v_F k, \quad \psi = \frac{1}{\sqrt{2}} \left( \begin{array}{c} 1 \\ \pm e^{i \phi} \end{array} \right) e^{i k \cdot r},$$

where $k = \sqrt{k_x^2 + k_y^2}$, $\phi = \arctan(k_y/k_x)$, and + (−) sign corresponds to the conduction (valence) band. The eigenfunctions are two component vectors and can be characterized by a pseudospin variable, since they formally resemble the real spin vectors of an electron. The pseudospin originates from the two atoms in the basis of the graphene lattice. The components of the eigenfunctions represent the relative weight of the wavefunctions of the A- and B-sublattice atoms. For example, $(1, 0)^T$ means the total wavefunction only consists of wavefunctions from A-sublattice atoms. Due to the symmetry between the A- and B-sublattice atoms in graphene, they contribute equal weight to the total wavefunction in equation (2), only differing by a phase factor. The pseudospin has a deep influence on the electronic properties of graphene, which we will discuss in detail in section 4.1.

### 1.2. Behavior in a magnetic field.

In a perpendicular magnetic field, the continuum of electronic states in the graphene band structure breaks up into a series of discrete Landau levels (LLs) [57, 58]. Without considering the zero modes at the Dirac point, the integer quantum Hall effect conductance plateaus would lie at $N N_e = \pm 2 e^2/h$, where $N$ is an integer, $e$ is the electric charge, $h$ is Planck’s constant, and the factor of four represents the two-fold degeneracy in both the spin and valley quantum numbers. However, at the Dirac point there is a zero mode shared by the electron and hole bands. Accounting for these two extra states gives the correct expression for the Hall conductivity as $\sigma_{xy} = \pm (N + 1/2) e^2/h$. Using the linear dispersion relation of graphene $E = \hbar v_F k$, one may calculate the LL energies as $E_{n} = \text{sgn}(N) \sqrt{2 e \hbar v_F^2 N B}$, where $B$ is the magnetic field. Therefore, the LL energies follow an unusual square root dependence with magnetic field, as opposed to the usual linear relation in materials with standard $E \propto k^2$ dispersion.

### 1.3. Behavior in a periodic electric potential.

The chirality of charge carriers in graphene results in the peculiar Klein tunneling behavior [59–61], which prevents electrostatic confinement of charge carriers. Therefore, the possibility of confinement with periodic electric potentials has been explored, both with 1D and 2D potentials [62–74].

For periodic 1D potentials, the group velocity perpendicular to the potential can be strongly reduced, and at certain energies goes to zero [62, 63, 68]. At these energies, two new Dirac points are created in the graphene band structure (one in the valence band and one in the conduction band, at the same energy relative to the original Dirac point). These new Dirac points coexist with other states in k-space at the same energy, and therefore the density of states does not go to zero at these new Dirac points for the case of a 1D potential (thus, the original Dirac point remains the only energy with a vanishing DOS).

This also holds for rectangular 2D potentials, as the superlattice Brillouin zone is a rectangle and the chirality of charge carriers in graphene prevents a gap from opening at the new Dirac point energies [62, 68]. However, for triangular (or hexagonal) 2D periodic potentials new Dirac points can develop unobstructed by other states in k-space [63, 69–74]. The energy at which these new Dirac points develop grows as the superlattice period becomes smaller.

An hBN substrate creates a hexagonal superlattice potential for graphene. Its effect can be modeled as a linear combination of the bare graphene Hamiltonian (equation (1)) and a periodic potential term [75]. It is given by

$$\tilde{H} = \hbar v_F k \cdot \sigma + V \sum_{\alpha} \cos(G_{\alpha} \cdot x) I,$$

where $k = (k_x, k_y)$, $\sigma$ is a vector of Pauli matrices, $I$ is the identity matrix, and $V$ is the coupling energy. The $G_{\alpha}$ are the reciprocal superlattice vectors corresponding to the periodic potential. We will discuss the specific features of a hexagonal periodic potential created by an hBN substrate in section 3.2.

### 1.2. Fundamental hexagonal boron nitride properties

Hexagonal boron nitride is a layered material much like graphite (characterized by strong in-plane bonds and weak van der Waals interaction between layers), which can also be exfoliated to give flakes with atomically flat surfaces. Each layer of hBN is a hexagonal lattice consisting of boron and nitrogen atoms (figure 3). Since these two elements neighbor carbon on the periodic table, the lattice mismatch between hBN and graphene is only $\sim 1.8\%$ (hBN the longer of the two). In graphene, carbon atoms are held together through covalent bonds, but in hBN the boron and nitrogen atoms form ionic bonds. As a result, hBN has a large band gap of $\sim 6$ eV [76]. These properties make hBN a superior substrate for graphene over amorphously grown SiO$_2$. Transport measurements of graphene on hBN devices show an improvement of charge carrier mobility by a factor of three to ten compared with the usual graphene on SiO$_2$ devices [8, 10, 11]. Local measurement techniques are ideal for understanding this improvement and exploring new physical phenomena of this system on the microscopic level. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) are two convenient methods for doing so.
1.3. Principles of STM

Scanning tunneling microscopy exploits the quantum tunneling effect to image on the smallest scales achievable by any microscopy technique. To perform measurements, a sharp metal tip is held very close (typically sub-nanometer range) to the conducting sample of interest. In this configuration, electrons may tunnel through the vacuum barrier separating the tip and sample, resulting in a small (typically pA-nA range) electrical current between them. The tunneling current is exponentially sensitive to the separation between the tip and sample, permitting atomic resolution of crystalline samples. The tunnel current also depends on the density of states (DOS) of both the tip and sample. To good approximation, the tunneling current can be written as

\[ I \propto e^{-\left(\frac{z}{\hbar}\right)^2} \int_0^V \rho_T(E_F - eV + \epsilon) \rho_S(E_F + \epsilon) \, d\epsilon, \]

where \( z \) is the tip-sample separation, \( m \) is the electron mass, \( \Phi \) is the height of the tunnel barrier, \( \rho_T \) and \( \rho_S \) are DOS of the tip and the sample respectively, \( E_F \) is the Fermi energy and \( V \) is the bias between them [77].

1.3.1. Topography measurements. To obtain STM topography maps, the bias voltage between the tip and sample is fixed and the tip is scanned across the surface of the sample. The tunnel current between the tip and sample is held constant by an electrical feedback loop (thus, a constant tunneling resistance is maintained). The topography of the sample is then inferred by measuring how much the piezo controller must move the tip to maintain the constant tunneling resistance, which is exponentially sensitive to the tip-sample separation. In addition to fluctuations in sample height, the topography map is convolved with the integrated DOS of both the tip and sample (see equation (4)). Generally the tip DOS is flat, as the tip is a metal, and therefore does not influence the topography measurement. However, the sample DOS may contain energy dependent features that can influence the topography measurement. Therefore, all STM topography must be interpreted carefully with this in mind.

1.3.2. Spectroscopy measurements. Taking a derivative of the tunnel current with respect to the bias voltage yields

\[ \frac{dI}{dV} \propto \rho_T(E_F) \rho_S(E_F + eV), \]

indicating the differential conductance between the tip and sample is proportional to the product of their DOS. Again, by choosing a tip with constant DOS, \( dI/dV \) yields a measurement proportional to the DOS of the sample. Experimentally, the differential conductance is measured by turning off the feedback loop, holding the tip at the position and energy of interest, and adding a small AC bias voltage to the DC bias on the tip. The energy spectrum of interest can be mapped out by varying the DC tip bias as desired. This measurement technique is known as scanning tunneling spectroscopy.

It is important to note that STS yields a local measure of the density of states of the sample (LDOS), as opposed to transport measurements which probe the global density of states. LDOS can be defined as

\[ \rho(x, E_F + eV) = \lim_{\Delta V \to 0} \frac{1}{\Delta V} \sum_{E_F + eV} |\psi(x, E)|^2, \]

where \( x \) is the tip position, and \( \psi(x, E) \) is the electron’s wavefunction. The difference between the DOS and the LDOS is that the latter contains extra information about the electronic wavefunctions. One of the powerful features of STM is its ability to correlate local topographic and spectroscopic information of the sample.

1.3.3. Adatom manipulation. Additionally, the STM is capable of manipulating adatoms on the surface of a sample and constructing artificial structures consisting of atoms placed at arbitrary positions. The ‘quantum corral’ [78] of 48 iron adatoms on a copper(111) surface is an elegant demonstration of this method. By manipulating adatoms, different structures such as dimers, trimers and molecules can be created. For standard topography and spectroscopy measurements, the STM tip is kept far enough from the surface (controlled via the tunneling resistance) so as not to disturb the mobile surface adatoms. Adatoms may be manipulated along the surface by reducing the tip-adatom separation until a sufficient wavefunction overlap occurs, binding the adatom to the STM tip. Then the adatom is moved to the desired location and the tunneling resistance is quickly increased to place the adatom. This process may be repeated for multiple adatoms to create arbitrary configurations on a surface.

In sections 2–4 we will discuss how these three modes of STM operation are utilized to study the properties of graphene on hBN systems.

2. Characterization of graphene on hBN devices

2.1. Topography

One of the drawbacks of graphene on silicon dioxide devices is that the oxide is thermally grown and is therefore amorphous.
This leads to an rms roughness on the order of 0.5 nm for SiO$_2$ surfaces. Since graphene tends to conform to its substrate [79], graphene on SiO$_2$ tends to exhibit a surface roughness of the same magnitude. However, graphene on hBN is expected to have very low surface roughness due to the atomically flat nature of the crystalline hBN surface. Experimentally, this can be clearly seen by comparing STM topography maps of graphene on hBN (figure 4(a)) and graphene on SiO$_2$ (figure 4(b)).

The histograms of these two images are shown in figure 4(c). Both curves are well fit by Gaussian distributions with standard deviations of 224.5 ± 0.9 pm for graphene on SiO$_2$ and 30.2 ± 0.2 pm for graphene on hBN. The surface roughness for graphene on hBN is similar to graphene on HOPG [80], suggesting it has reached its ultimate limit of flatness. This increased flatness helps expose electronic effects in graphene which would be obscured in rougher samples. While most of the effects discussed in this review benefit from increased graphene flattness, the most striking example of this is the local density of states oscillations from a step edge discussed in section 4.1.

2.1.1. Topographic moiré patterns. Interesting superstructures are observed when examining atomically resolved topography images of graphene on hBN figures (5(a)–(d)) [75, 81–85]. Longer wavelength hexagonal topography modulations are present in addition to the hexagonal structure of the graphene atomic lattice. This hexagonal superstructure, often referred to as a moiré pattern, occurs when two lattices with different lengths and/or orientations are placed on top of each other. Moiré patterns often form when graphene is grown on metal substrates [86]. Moiré patterns in graphene have also been observed when graphene is placed on other crystalline substrates such as HOPG [87], SiC [88], Cu [89], Ir [90], Ni [91], Pd [92], Pt [93], Rh [94], Ru [95]. The wavelengths of the two lattices, as well as their relative rotation, determines the wavelength of the moiré pattern. As shown in figures 6(a) and (b),

![Figure 5](image1.png)

Figure 5. (a)–(d) STM topography images of graphene on hBN with different relative lattice rotations (indicated on the image) exhibiting hexagonal superlattices. (e)–(h) Fourier transforms of (a)–(d) showing hexagonal moiré spots near the center of the image and atomic lattice points near the outer edges of the image. Reprinted with permission from Decker et al [82]. Copyright 2011 American Chemical Society.

![Figure 6](image2.png)

Figure 6. Moiré pattern schematic for graphene on hBN with different relative rotations. (a) The rotation is 8 degrees between the lattices. (b) The rotation is 14 degrees between the lattices giving a shorter moiré pattern. (c) Wavelength of the moiré pattern for graphene on hBN.
smaller rotation angles give longer period moiré wavelengths. For hexagonal crystals with identical lattice constants (such as twisted bilayer graphene), the moiré wavelength goes to infinity as the rotation angle approaches zero (perfect alignment). Since the lattice constant of hBN is about 1.8% longer than that of graphene, even perfect crystalline alignment of graphene on hBN exhibits a maximum moiré wavelength of about 14 nm [75].

2.2. Spectroscopy

2.2.1. Density of states. Early theoretical calculations predicted that a band gap of \( \sim 50 \) meV is opened in graphene on hBN [96, 97]. This calculation was based on a lowest-energy lattice configuration where the lattice mismatch is neglected and zero relative rotation is assumed. In this configuration, one sublattice of carbon atoms sits above boron atoms and the other sits above the center of a hexagon. This breaks the sublattice symmetry in graphene, and a band gap opens as a result. However, scanning probe measurements of graphene on hBN devices thus far have always shown a moiré pattern of no longer than 14 nm. These results are from both transferring of graphene on hBN flakes [75, 81, 82] and direct chemical vapor deposition growth of graphene on hBN [83–85]. These results suggest that the change in lattice constant needed for perfect stacking of graphene and hBN is not possible. Consequently, while at a particular site the A sublattice of graphene may sit above a boron atom, it will reside above a nitrogen within one period of the moiré pattern. Averaging over the entire sample restores sublattice symmetry, and is therefore not expected to open a sizable band gap [98, 99].

Reference [81] tests this prediction directly with STS. Figure 7(a) plots the \( dI/dV \) spectroscopy (which is proportional to the LDOS) of graphene on hBN as a function of STM tip bias. The \( dI/dV \) spectroscopy has a minimum near zero tip bias and increases nearly linearly with energy. This is in agreement with the linear density of states expected from the band structure of pristine graphene. This measurement does not exhibit a region of zero \( dI/dV \) at the charge neutrality point anticipated if there were a band gap opened due to the hBN substrate, further suggesting the absence of a sizable gap. Recent transport experiments have suggested the possibility of local lattice commensurability for very long moiré wavelengths, which could open spatially dependent band gaps [21, 23]. To date, STM work has been unable to conclusively address this issue.

2.2.2. Charge variation. Another drawback to graphene on SiO\(_2\) devices is that the substrate causes substantial charge inhomogeneity in the graphene. This manifests as electron and hole doped regions when the Fermi energy is tuned near the Dirac point. Scanning probe studies have mapped these charge puddles on SiO\(_2\) devices and found that they have a typical size scale on the order of 10 nm and a charge variation on the order of \( 10^{11} \) cm\(^{-2}\) [100–102]. Transport measurements [8, 10, 11] show that graphene on hBN devices exhibit greatly enhanced charge carrier mobility compared to graphene on SiO\(_2\) devices, indicative of reduced charge inhomogeneity. Scanning probe microscopy measurements of graphene on hBN samples permits direct visualization of this improvement [81, 82, 103]. Charge fluctuations resulting from impurities in the underlying substrate manifest themselves as local shifts.
in the energy of the Dirac point. Thus, these impurities act
as local dopants for the graphene. Figures 7(c) and (d) show
spatial maps of the energy of the Dirac point for graphene on
hBN and SiO₂, respectively. The blue (red) areas have excess
electrons (holes) compared with neutral graphene, so their
Dirac points are shifted to more negative (positive) energies.

The graphene on hBN sample exhibits much smaller shifts
in the Dirac point and hence much less charge variation than
the graphene on SiO₂ sample. Histograms of these two maps
(figure 7(b)) show that the FWHM value of the Dirac point
shift in graphene on hBN is 5.4 ± 0.2 meV, while for graphene
on SiO₂ it is 55.6 ± 0.7 meV. These fluctuations in energy can
be converted to the fluctuation in charge carrier densities using
the relation \( n \propto E^2 \) for graphene. The charge density fluctuations
are reduced by about two orders of magnitude when using hBN as a substrate rather than SiO₂. Suspended gra-
phene samples generally have even lower charge fluctuation,
however measuring such samples via STM is challenging as
the charged STM tip attracts the graphene sheet. Substrate
supported measurements, such as graphene on hBN, are much
more stable and are therefore more powerful probes of the
intrinsc graphene physics.

3. Superlattice Dirac points

3.1. Calculation of moiré wavelength

The hBN substrate creates a superlattice potential that has a
profound influence on the electronic properties of graphene.
In general, given a fractional lattice mismatch of \( \delta \) between
graphene and hBN and a relative rotation angle \( \phi \) between
the two lattices, the moiré wavelength \( \lambda \) is uniquely determined by

\[
\lambda = \frac{(1 + \delta) a}{\sqrt{2(1 + \delta)(1 - \cos(\phi)) + \delta^2}}, \tag{7}
\]

where \( a \) is the graphene lattice constant. The relative rotation
angle \( \theta \) of the moiré pattern with respect to the graphene lattice
is given by

\[
\tan(\theta) = \frac{\sin(\phi)}{(1 + \delta) - \cos(\phi)}. \tag{8}
\]

Figure 6(c) plots the superlattice wavelength as a function of
the angle \( \phi \) between the graphene and hBN lattices. The moiré
wavelength is only long for a small range of rotation angles
close to zero degrees. There is also a maximum wavelength of
about 14 nm given by the lattice mismatch \( \delta \) [75].

STM and conductive AFM measurements are able to clearly
detect this moiré pattern [21, 26, 27, 75, 81–85]. Figures 5(e)–
(h) show Fourier transforms of the topography measurements
shown in figures 5(a)–(d), where both the graphene lattice
and superlattice are visible. The rotation between these two
lattices matches that predicted by equation (8). These local
scanning probe measurements can be used to quickly and
accurately characterize the relative rotation angle between the
graphene and hBN lattices. Raman spectroscopy may also be
used to identify long wavelength moiré patterns, as the Raman
spectra of graphene is influenced by the interaction with the
hBN substrate [104].

3.2. Theoretical predictions for graphene on hBN

We discussed a model Hamiltonian for graphene on hBN in
section 1.1.3. The electronic effect of an hBN substrate on
the local density of states is modeled in [75] by considering
the interlayer hopping between the graphene and hBN lay-
ers. The potential strength \( V \) is estimated to be 0.06 eV from second order perturbation theory. The reciprocal superlattice vector \( G_1 = (4\pi / \sqrt{3} \lambda) (\cos \theta, \sin \theta) \) is determined by the rela-
tive rotation of the graphene and hBN lattices according to
equations (7) and (8). The two other superlattice wave vectors
are obtained by two rotations of 60°. The superlattice poten-
tial permits \( k \rightarrow -k \) backscattering processes along the direc-
tion of the reciprocal lattice vectors \( G_a \) which are normally
forbidden in bare graphene due to chirality. As long as the
potential maintains the sublattice symmetry of the graphene
layer, the chirality of the Dirac fermions prevents the opening
of a bandgap as is typical for such a process with Schrödinger
fermions. Instead, a new set of Dirac points is opened in the
valence and conduction bands at the energy where the periodic
potential connects the \( k \) and \( -k \) bands (that is, when \( 2k = G_a \)).
Assuming the linear band structure of graphene, we expect
this energy to be \( E = \hbar v_F |G| / 2 = 2\pi \hbar v_F / \sqrt{3} \lambda \). Figure 8 shows a tight-binding model calculation of the band structure of gra-
phene on hBN, where the new set of six valence band Dirac
points are visible in addition to the original Dirac point. There
are also six new Dirac points created in the conduction band.

Numerical calculations of the LDOS in the graphene layer
provide further evidence for these new Dirac points. As shown
in figure 9(a) for a variety of moiré wavelengths, the LDOS
exhibits two dips (superlattice Dirac points) symmetrically
placed about the original Dirac point. The dip in the LDOS in
the valence band is much stronger than the one in conduction
band due to the inclusion of next-nearest neighbor interlayer

![Figure 8. Band structure of graphene on hBN. In addition to the original Dirac point, there are six superlattice Dirac points shown in the valence band.](image)
coupling terms, which breaks electron-hole symmetry by inducing modulated hopping between different graphene sublattices [75]. As expected, the superlattice Dirac points move to higher energies with increasing rotation between the graphene and hBN lattices (shorter wavelength moiré patterns).

3.3. Experimental signatures

STS measurements exhibit similar dips in the LDOS symmetrically placed about the original Dirac point figure 9(b) [75], providing evidence for the existence of the superlattice Dirac points. The same electron-hole asymmetry is observed in these measurements as predicted by the numerical calculations. In [75], seven different rotation angles of graphene on hBN were measured. Only moiré wavelengths longer than 2 nm were measured due to the smeared spectroscopy resolution for energies outside the range of $\pm 1$ V. Figure 9(c) plots the measured energies of the superlattice Dirac points in these samples as a function of moiré wavelength. The black curve plots the expected dispersion from the assumed linear graphene band structure, and is closely matched to the experimental results. Electrical transport measurements for nearly aligned graphene on hBN devices also show sharp increases in resistance when the Fermi energy is tuned to the new superlattice Dirac points [21, 26, 27, 84], providing further evidence of the reduced density of states there.

3.3.1. Dirac point movement. Figure 10(a) tracks the evolution of the LDOS as a function of gate voltage (which changes the chemical potential) for a 13.4 nm moiré pattern. Two dips in the LDOS, highlighted by white dotted lines, move in parallel with changing gate voltage. The upper dip is due to the original Dirac point, and the lower dip is due to the valence band superlattice Dirac point (the conduction band superlattice Dirac point is too weak to observe). The parallel movement of these features provides evidence that the new dip in the LDOS of graphene on hBN is a feature of the band structure. The gate dependence of the original Dirac point is given by the equation

$$E_0 = h\nu_F\sqrt{2\alpha\pi(V_g - V_o)/g_v}$$  \hspace{1cm} (9)$$

where $V_g$ is the gate voltage, $V_0$ is the offset voltage, $\alpha$ is the coupling to the gate and $g_v$ is the valley degeneracy. Near the original Dirac point ($\sim -15$ V in figure 10(a)), the valley degeneracy is $g_v = 2$, and the resulting square root movement of the Dirac point gives a Fermi velocity of $v_F = v_F^0 = 0.94 \pm 0.02 \times 10^6$ m s$^{-1}$.
When the Fermi energy is tuned near the superlattice Dirac point in the valence band ($\sim -50$ V in figure 10(a)), the linearly vanishing density of states gives a second square root-dependent movement of the Dirac point, which does not occur for the case of bare graphene. Here, the valley degeneracy is $g_v = 6$ due to the three reciprocal superlattice vectors $G_a$ in each of the two Dirac cones. The superlattice Dirac cones are predicted to be anisotropic with constant energy contours given by ellipses rather than circles. Therefore, the Fermi velocity in equation (9) must be modified to $v_F = \sqrt{v_F^0 v_F^*}$ where $v_F^0$ is the unmodified Fermi velocity parallel to $G_a$ and $v_F^*$ is the reduced Fermi velocity perpendicular to $G_a$. A fit of the movement of the Dirac point when the Fermi energy is tuned near the superlattice Dirac point gives a reduced Fermi velocity for the new electrons and holes of $v_F^* = 0.5 \pm 0.1 \times 10^6$ m s$^{-1}$. Figure 10(b) plots the movement of the Dirac point around that range of Fermi energies, and shows the second square root dependence of the Dirac point motion near the superlattice Dirac point. The red dotted line plots the expected Dirac point movement for bare graphene. Roughly speaking, the new superlattice Dirac cones are about twice as wide as the original Dirac cone.

3.3.2. Periodic charge variation. The presence of the periodic potential leads to a matching spatial variation in the LDOS [75, 105]. Theoretical calculations predict strong spatial modification in the LDOS at energies above (below) the conduction (valence) band superlattice Dirac point, but little modification at energies near the original Dirac point figure 11(d)–(f). Furthermore, the relative strength of the hexagonal LDOS variation inverts between the valence and conduction bands. In the valence band the perimeters of the hexagons exhibit an enhanced LDOS, whereas in the conduction band the centers of the hexagons exhibit an enhanced LDOS. This hexagonal LDOS modulation spatially mirrors the periodic potential from the hBN substrate. Figure 11(a)–(c) shows the corresponding experimental results, which exhibit behavior similar to the theoretical predictions.

3.4. Other periodic potentials

Similar superlattices can exist in graphene devices placed on other substrates [86–95]. The most noteworthy is graphene grown on metallic Ir(111). The graphene layers grow with near perfect crystalline alignment with the underlying Ir, and due to the slight mismatch in lattice constants a 2.53 nm hexagonal moiré pattern is formed. Angle resolved photoemission (ARPES) measurements have shown superlattice Dirac points similar to those in graphene on hBN [106], although these samples lack the ability to tune the wavelength of the superlattice and thus the energy of these superlattice Dirac points. Furthermore, due to the metallic nature of the Ir(111) substrate, gated transport measurements probing carrier dynamics in the graphene layer alone are not possible. While measurements of graphene on other crystalline substrates have shown similar moiré patterns, they have yet to exhibit the existence of replica Dirac cones in the band structure, likely due to the coupling strength between the graphene and substrate [106].

Twisted bilayer graphene exhibits similar moiré patterns in STM topography as well. In this case, the lower graphene layer can be modeled as providing the periodic potential for the upper layer. Twisted graphene bilayers are strongly coupled, and thus instead of opening superlattice Dirac points, the band structure consists of two neighboring Dirac cones at half-filling, connected by new van Hove singularities. The energy of these van Hove singularities scales with the rotation between the layers. Numerous STM studies have shown the existence of these van Hove singularities and explored their properties [107–109].

4. Unique electronic effects in graphene on hBN

In addition to the new electronic effects in graphene that are direct consequences of the hBN substrate, the cleaner charge environment and flat surface also allow the observation of intrinsic electronic properties of graphene which are normally obscured by the dirty and rough SiO$_2$ substrate. For most rotation angles between the graphene and hBN lattices, the band structure renormalization from the hBN substrate is negligible at low energies and therefore does not interfere with the detection of graphene’s intrinsic electronic properties.

4.1. LDOS oscillations

For a uniform area of a given sample the electron wavefunctions can be represented as plane waves, therefore no spatial variation of the LDOS is expected. However, defects in the sample can scatter electrons, creating standing waves which can be detected as oscillations in the LDOS. The ‘quantum corral’ [78] experiment of 48 iron adatoms on a copper(111) surface is an excellent example, where scattering from a circle of adatoms on a metallic surface creates concentric rings of LDOS within the circle.

4.11. Oscillation wavelength. LDOS oscillations in monolayer graphene, as compared to those observed in noble metals, are about an order of magnitude longer in wavelength and
The latter. For graphene on SiO2 samples, LDOS oscillations explains the former feature, and the pseudospin quantum num-
ber of Fermi circles decay more quickly. These properties result from the peculiar nature of the graphene band structure. As shown in figure 13(a), when an electron with momentum k is scattered, due to conservation of energy and the momentum component parallel to the step, the resulting wave will have momentum k within the constant energy circle centered in the same valley. Since the step edge is not an atomic-scale defect, it cannot provide the large momentum transfer required for intervalley scattering. The scattered electron wave with momentum k interferes with the incident wave with momentum k.

The wavelength of the resulted standing wave can be calculated by considering k − k′, which is a small number since it is the result of an intravalley scattering process. The small scattering wave vector corresponds to long wavelength LDOS oscillations. Conversely, similarly scattering on noble metal surfaces has much shorter wavelength LDOS oscillations. Unlike graphene, which has small constant energy circles near its Fermi energy, noble metals usually have a large Fermi surface (large constant energy circles), so small momentum transfer scattering and hence long wavelength LDOS oscillations are not possible. Figure 13(a) also explains the observed behavior of the wavelength as a function of the energy shown in figure 12. The diameter of the constant energy contour shrinks towards the Darwin point, thus k − k′ decreases and the wavelength of the LDOS oscillations increases. Figure 13(b) plots the line profiles of the oscillations (black curves) from the panels in figure 12 (tip voltage increases from top to bottom). The wavelength of the LDOS oscillations clearly increases as the energy approaches the Darwin point, as expected.

4.12. Oscillation decay. Additionally, the amplitude of the LDOS oscillations decreases as a function of distance from the step edge at all energies. This feature can be explained by considering the relative contributions of incoming and reflected waves as a function of angle with respect to the step edge. Pairs of incoming and reflected waves create oscillations
with varying wavelengths as a function of angle. Most of these contributions away from normal incidence tend to cancel each other far from the edge, resulting in a decreasing oscillation amplitude as a function of distance. Similar decay behavior has been seen in noble metals [111, 112]. However, the pseudospin quantum number forbids direct backscattering in graphene (an allowed process in noble metals) [113]. As a result, the LDOS oscillations decay faster than comparable oscillations in noble metals [110, 114]. Theoretical calculations accounting for these factors (blue curves in figure 13(b)) show good agreement with experimental measurements.

4.2. Manipulation of atomic adsorbents

Coulomb potentials can be formed in graphene by depositing charged impurities on the graphene surface. Work in this field has been done with cobalt, calcium and potassium atoms deposited in situ via electron beam evaporation [115–118]. While it is possible to measure the electronic influence of these adatoms on SiO2 [116], the intrinsic electronic response of graphene to individual charged impurities can be obscured by the inhomogeneous charge environment. The flatter surface of the hBN substrate allows for easier manipulation of adsorbed charged impurities and the cleaner charge environment allows interpretation of the intrinsic electronic response of graphene to these impurities. Adatom monomers may be manipulated into dimers and trimers via diffusion or direct surface manipulation with the STM tip, and these larger charge impurities may be further manipulated on the surface with the STM tip as well.

4.2.1. Coulomb impurities. Wang et al explored the electronic effects of a single Coulomb impurity on graphene [117]. Coulomb impurities are formed via electron beam evaporation of Co atoms onto the surface of graphene. These surface adatoms are manipulated into Co trimers on the atomically flat and clean graphene on hBN surface using an STM tip. The trimer configuration is chosen as it is the fewest adatom system which exhibits charge toggling via a back gate electrode and charge state stability in the presence of an STM tip. Figure 14(a)–(e) shows the process of manipulating Co monomers on graphene on hBN into a Co trimer, while figure 14(f) shows a zoomed-in topography image of the Co trimer. The dI/dV spectroscopy (figure 14(g)) taken with the tip directly above the Co trimer exhibits the characteristic R and S states previously found in Co monomers on graphene on SiO2 [116]. The R state arises from local cobalt-graphene hybridization, and the S state is due to tip-induced ionization of the trimer.

Figure 15 shows maps of the dI/dV spectroscopy response of graphene to a Co trimer in three different charge states at a sample voltage of +0.3 eV, achieved by varying the back gate voltage. The clean charge environment from the hBN
substrate ensures the spectroscopy response represents the intrinsic electronic behavior of graphene. The combination of the tip and back gate is capable of charging the Co trimer by one electron. For large positive gate voltages figure 15(b) the Co trimer is always uncharged, and for large negative gate voltages figure 15(c) the Co trimer is always charged with one electron for all positions of the tip. At intermediate gate voltages figure 15(a) the Co trimer is in a bistable configuration, where the charge of the trimer can be changed by one electron depending on whether the tip is inside or outside the ring feature surrounding the trimer.

4.2.2. Atomic collapse. Among its many incredible properties, graphene can serve as a low-energy testbed for mimicking high-energy phenomena, such as Klein tunneling [59–61] and atomic collapse [118]. The latter is a prediction that highly charged atomic nuclei are unstable due to relativistic quantum effects. Specifically, if the nuclear charge $Z$ exceeds a critical value $Z_c$, the electron wavefunction falls towards the nucleus and the positron component escapes to infinity [119–122]. In contrast, subcritical nuclei have stable atomic bound states. For real atoms, $Z_c \sim 170$ can only be achieved through colliding heavy atoms, and interpretation of the results is challenging. Results from these efforts remain ambiguous [123, 124]. However, in graphene $Z_c$ is instead of the order one due to the relativistic nature of the charge carriers, as well as the large effective fine-structure constant [125–127]. In this case, holes play the role of positrons. Near ‘artificial nuclei’ on graphene of charge greater than $Z_c$, a spatially extended electronic resonance corresponding to the electron-like part of the wave function is expected just below the Dirac point. Reference [118] explores this prediction by assembling artificial nuclei of different charge via spatial manipulation of adsorbed Ca dimers.

The insets of figures 16(a)–(e) show STM topography of clusters of Ca dimers ranging from one to five dimers arranged via an STM tip on the surface of graphene on hBN. The main panels show $dI/dV$ spectroscopy taken at a varying range of distances from the cluster center. As the number of dimers in the cluster is increased a bound-state resonance develops near the Dirac point, and drops below the Dirac point energy for a cluster of five dimers. This resonance represents the atomic collapse state. Despite the spatial separation and asymmetric placement of these dimers, spatial maps of the quasi-bound state resonance intensity in the region surrounding the dimer cluster is highly symmetric and extends greater than 10 nm from the cluster center. This provides evidence that the dimer cluster behaves as a single artificial nucleus, and that the graphene charge carriers are spatially separated from the dimers.

Figures 16(f)–(j) plot simulated $dI/dV$ spectroscopy next to the corresponding experimental data. The simulations are calculated assuming a two-dimensional continuum Dirac model for graphene in the presence of a Coulomb potential. The only essential fitting parameter is $Z/Z_c$. $Z$ is the effective screened charge seen by the graphene charge carriers. $Z_c$ in graphene is $Z_c = \frac{\hbar \nu}{2e^2} \sim 0.25$. The best fit values for $Z/Z_c$ are given in figures 16(f)–(j).

4.3. Magnetic field effects

Local measurements of graphene on hBN in a magnetic field show very well developed Landau levels owing to the reduced charge environment due to the hBN substrate [128–131]. Furthermore, new many-body effects, which were previously smeared in graphene on SiO$_2$, are accessible in the cleaner graphene on hBN samples.

Reference [128] provides a study of graphene on hBN in magnetic fields from 0 to 8 T. The LLs are extremely sharp and are well developed at fields as small as 2 T, as shown in the $dI/dV$ spectroscopy in figure 17(d). The energy of the LLs as a function of magnetic field behaves as expected for bare graphene, where the linear dispersion gives $E_N = E_0 + sgn(N) \sqrt{2e\nu_B\Delta B}$, where $E_0$ is the energy of the Dirac point.

Figures 17(a) and (b) track the $dI/dV$ spectroscopy as a function of gate voltage and magnetic field. The LLs become sharper and more step-like with increasing magnetic field. The staircase pattern results from partially-filled LLs being pinned at the Fermi energy. A quick transition to the next LL is made when the prior LL is filled. The overall behavior of the gate dependent spectroscopy is consistent with the theoretical simulation shown in figure 17(c). Furthermore, at large gate voltages, and thus large charge carrier density, the simulation provides a good quantitative fit to the experimental results as evidenced by the yellow theory curves overlayed above the experimental data. However, at low carrier densities the simulated peak positions are poorly matched to the experimental data.

The low density deviations provide evidence for the breakdown of the single particle behavior assumed in the theoretical simulation. This result shows the importance of accounting...
Figure 16. (a)–(e) $dI/dV$ spectroscopy taken at varying distances from the center of Ca clusters. Insets show topography of the Ca clusters and indicate the number of adatoms in the cluster. (f)–(j) Theoretical $dI/dV$ predictions for comparable measurements. The black dotted line marks the Dirac point energy in all panels. Red arrows indicate the atomic collapse state. From Wang et al 2013 [118]. Reprinted with permission from AAAS.
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for many-body interactions at low densities. Plotting $E$ as a function of $NB$ for different carrier densities reveals that the LL dispersion remains linear even at very low densities, however the slope changes as a function of carrier density. This implies that while the graphene energy dispersion always remains linear, the Dirac cone is squeezed due to interaction effects at low densities (figure 18(a)). Figure 18(b) plots the Fermi velocity fit over a range of carrier densities for both an electron and hole doped region. Both indicate a renormalized Fermi velocity at low carrier densities, with measured low density values over 30% larger than the bare graphene velocity. Transport measurements of suspended graphene devices have revealed similar physics, although without the ability to tune excitation energy and carrier density separately [132].

5. Electrical transport measurements

In prior sections we discussed, from the perspective of STM and STS measurements, the benefits of an hBN substrate for graphene devices and the new physics which becomes accessible as a result. In the following section we highlight a few of the recent transport experiments that require either the ultra low charge variation provided by the hBN substrate or the superlattice Dirac points created by the periodic potential. Important insights into the novel physics observed in these transport experiments have come directly from results of STM measurements of graphene on hBN.

5.1. Integer quantum hall effect

Due to the spin and valley degeneracy of graphene, each Landau level is four fold degenerate (in bilayer graphene, the lowest energy Landau level is eight-fold degenerate). This provides an ideal test bed for exploring the rich physics of multicomponent quantum Hall effects [133]. In the early transport experiments where SiO$_2$ was the common choice of substrate, quantum Hall measurements showed Hall conductance plateaus at $\sigma_{xy} = \pm (N+1/2)4e^2/h$ for monolayer
graphene and $\sigma_{xy} = \pm 4N e^2/h(N \neq 0)$ for bilayer graphene [134–136]. Broken symmetry effects such as Zeeman splitting, long range Coulomb interaction, and lattice scale electron-electron interactions have been shown to partially lift the degeneracy in suspended graphene [137, 138] and graphene on SiO$_2$ [139] under high magnetic field. However, due to the fragile device structure of suspended samples and the dirty charge environment of the SiO$_2$ substrate, studying broken symmetry states in these samples is challenging. With hBN as the substrate, these states can be readily observed and the full four-fold degeneracy can be easily lifted at lower magnetic fields, hence all the integer filling factors can be observed [8]. Figure 19 shows the LL development with increasing magnetic field for graphene on hBN. The darkest regions of the LL fan correspond to the $N=0, 1, 2$, etc. LLs, while the four-fold broken symmetry states begin to emerge at fields above $B = 7$ T.

To understand the origin of the broken symmetry states, Young et al performed tilted magnetic field measurements of graphene on hBN devices [15]. In this type of measurement, the sample is tilted at different angles relative to the magnetic field. The overall field strength is changed to keep the perpendicular component of the field constant. Since graphene is only one atom thick, the in-plane field couples to the system only through the electron spin. By measuring how the energy gaps of different quantum Hall states evolve as a function of in-plane field (or total field, since the perpendicular field is fixed), one can gain important insights into the spin structure of the broken symmetry states.

With this technique, Young et al found that the symmetry broken order of the zeroth Landau level is different from higher Landau levels. At filling factor $\nu = 0$, the zeroth Landau level is half filled, and an insulating state is present. The resistance of this state is found to decrease with increasing total magnetic field, which signifies that the ground state at $\nu = 0$ is not spin polarized, instead, it has a broken valley symmetry origin. Therefore, the ground state is valley polarized. On the other hand, energy gaps at half fillings of higher Landau levels, such as $\nu = 4, 8, 12$, etc. increase with total magnetic field, indicating that the ground states are spin polarized. To further confirm these broken symmetry assignments, Young et al examined energy gaps at quarter fillings, such as $\nu = -1$ from the zeroth Landau level and $\nu = -3$ and $\nu = -5$ from the first Landau level in the hole side. They found that as expected, $\nu = -1$ state is spin polarized as the gap size increases with total magnetic field, while $\nu = -3$ and $\nu = -5$ gaps in general show minimal dependence on the total magnetic field. Behavior deviating from this was also observed in some samples studied, indicating more work is necessary to gain a full understanding of the underlying physics.

5.2. Fractional quantum hall effect

The fractional quantum Hall effect has been observed by Dean et al [17] with high quality graphene on hBN samples. Figure 20 illustrates magnetoresistance and Hall resistance results in a magnetic field of $B = 35$ T. Previously, this many-body interaction effect could only be observed in high quality suspended devices [137, 138]. Compared with the suspended structure, hBN supported devices are more robust and easier to electrically contact and measure. Therefore, it is possible to make multi-terminal devices on hBN substrates. Another advantage of the supported structure is that higher carrier density can be achieved by applying larger gate voltages, which is problematic for suspended devices because they tend to break.

In their devices, Dean et al found quantum Hall states at fractional filling of $1/3$ and other equivalent states, such as $2/3$ and $4/3$ in the $\nu = 0$ and $\nu = 1$ Landau levels, respectively. The presence of these states can be understood within the picture of composite fermions [140, 141]. The absence of the $5/3$ state in these devices is intriguing, since it should be the closest analogue to the $1/3$ state in conventional semiconductors. The absence of the $5/3$ state is presumably due to some remaining symmetry from the original four fold degeneracy. In contrast, all multiples of the $1/3$ fractions are observed in the second LL. This may signify the importance of density dependent electron–electron interactions.

5.3. Double layer devices

Graphene on hBN heterostructures can be repeated vertically to form multilayered devices. The simplest version of this type of structure is two layers of graphene separated by hBN. Ponomarenko et al showed that with high carrier density ($n > 10^{13}$ cm$^{-2}$) induced in the bottom graphene layer, the top graphene layer shows a diverging resistance at the charge neutrality point [20]. Interestingly, this diverging resistance
can be strongly suppressed by a small perpendicular magnetic field \( B < 0.1 \) T (figure 21), a signature of anti-localization. The authors reasoned that the bottom layer graphene with high charge density screens the electrostatic potential from the SiO\(_2\) substrate. Therefore, the electron-hole puddles in the top graphene layer are further reduced compared with simple graphene on hBN devices. With this further improved charge homogeneity, a very low charge carrier density of \( \sim 10^{10} \) cm\(^{-2}\) can be reached and the graphene resistance reaches the threshold value for localization, i.e. \( \hbar/4e^2 \), where the factor of four accounts for the doubly degenerate spin and valley quantum numbers. However, this interpretation of the result is still under debate \[22, 142\] and a complete understanding of this phenomenon is still lacking.

A similar device structure has also been measured by Hunt et al, where the graphene on hBN heterostructure sits atop a thick piece of graphite, which is contacted separately to act as a back gate \[21\]. This device geometry provides an even flatter and cleaner environment for the top layer of graphene than devices using a single layer of graphene as the substrate for the graphene on hBN heterostructure, as the thick graphite gate is able to better screen charge inhomogeneities in the SiO\(_2\). These devices have exhibited full spin and sublattice symmetry breaking in the graphene, as evidenced by the presence of...
the $\nu = 5/3$ fractional quantum Hall state. They also exhibit a band gap at the charge neutrality point, whose size increases with moiré wavelength. Recent theoretical studies have worked to explain these phenomena [143, 144]. STM topography was used in this experiment to confirm the very long moiré wavelengths determined by transport measurements, as well as to measure the shorter moiré wavelengths which were inaccessible for the range of carrier densities probed.

### 5.4. Hofstadter butterfly

Probing the behavior of superlattice Dirac points in a magnetic field proves challenging for most STM experiments, where only modest magnetic fields may be applied. Transport experiments can be used in conjunction with STM results to probe the interplay between periodic potentials and magnetic fields. Long wavelength superlattice potentials found in nearly aligned graphene on hBN samples provide a unique platform for studying charge carriers where the wavelength of the periodic potential is on the order of the magnetic length. As outlined in section 1.1.2, the unusual energy level dispersion of LLs in graphene follows $E_N = \text{sgn}(N) \sqrt{2e\hbar^2 NB}$, with $E_N$ referenced to the Dirac point energy. Superlattice Dirac points exhibit their own electron and hole carriers, whose energies also break into Landau levels with a similar dispersion in a magnetic field. Transport experiments have shown Landau fans originating from both the original and superlattice Dirac points [21, 26, 27, 84]. At low magnetic field, Landau fans originating from the superlattice Dirac points are only accessible through back gate tuning for very long wavelength moiré patterns, where the superlattice Dirac points are closest to the original Dirac point. As the magnetic field is increased, Landau levels from the original and superlattice bands intersect for $\phi/\phi_0 = 1/q$, where $q$ is an integer. The resulting Landau levels create a recursive structure known as the ‘Hofstadter butterfly’ spectrum [21, 26, 27, 145]. Long wavelength periodic potentials formed by graphene on hBN allow the observation of this Hofstadter butterfly spectrum at magnetic fields accessible in the lab, which must be able to fill more than one flux quantum quantum per superlattice unit cell. Figure 22(a) shows one such measurement for a nearly perfectly aligned graphene on hBN device. Figure 22(b) provides a theoretical calculation for the system, indicting which broken symmetry states of the original and superlattice Dirac points are found experimentally.

![Figure 22. (a) Magnetococonductance of graphene on hBN with near perfect rotational alignment. Landau level fans originate from the original Dirac point (around $V_g = 0$ V) and from the superlattice Dirac points (around $V_g = \pm 1.5$ V). (b) Theoretical calculation similar to (a). Black lines represent gaps requiring no broken symmetry. Blue and red are broken symmetry states of the original and superlattice Landau fans, respectively. Gaps intersect for $\phi/\phi_0 = 1/q$, where $q$ is an integer. From Hunt et al [21]. Reprinted with permission from AAAS.]
6. Conclusion

We have reviewed the properties of graphene on hBN devices from the perspective of scanning tunneling microscopy. Graphene on hBN provides, to date, the most convenient structure for achieving clean graphene devices. Graphene on hBN devices show charge impurity densities approaching suspended graphene devices, but are much easier to fabricate and contact electrically, and are much more physically robust. Furthermore, the hBN substrate acts as a periodic potential for graphene, opening new Dirac points in the electronic band structure which may be exploited to create novel devices. Scanning tunneling microscopy is an ideal tool for understanding the improvement of the hBN substrate over the standard SiO2 substrate as it provides a direct probe of the charge landscape in the graphene. Furthermore, STM provides direct experimental access to local electronic properties of graphene on hBN which are much more difficult or impossible to observe in graphene on SiO2 devices. These results can be used to aid the understanding of novel global transport experiments which exploit the benefits of the hBN substrate.

Graphene on hBN heterostructures represent an important family of devices which will be used for the discovery of new physics of these heterostructures. With greatly improved transfer techniques [49, 146] which never require polymers or chemicals to touch the interfaces of the 2D materials, device cleanliness is nearing its ultimate limit. Consequently, the electronic properties of such heterostructures may be studied in the ballistic regime, in the absence of virtually all disorder. Adding other van der Waals materials to these heterostructures [147] and tuning the relative rotations and stacking orders amongst the crystalline layers will enable the development of an innumerable number of novel device characteristics. This ability to combine two-dimensional materials into heterostructures is already showing promise for the creation of novel structures with tailored properties such as tunneling transistors and photovoltaic devices [36, 147–149]. Furthermore, with advances in the direct growth of these layers on top of each other [84, 150–153], there is great hope for industry scalable devices utilizing the incredible properties discovered in laboratory settings. Local probe measurements have and will be an invaluable tool for understanding the local physics of these heterostructures.

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