Electrically tunable resonant scattering in fluorinated bilayer graphene

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Adatom-decorated graphene offers a promising new path towards spintronics in the ultrathin limit. We combine experiment and theory to investigate the electronic properties of dilutely fluorinated bilayer graphene, where the fluorine adatoms covalently bond to the top graphene layer. We show that fluorine adatoms give rise to resonant impurity states near the charge neutrality point of the bilayer, leading to strong scattering of charge carriers and hopping conduction inside a field-induced band gap. Remarkably, the application of an electric field across the layers is shown to tune the resonant scattering amplitude from fluorine adatoms by nearly twofold. The experimental observations are well explained by a theoretical analysis combining Boltzmann transport equations and fully quantum-mechanical methods. This paradigm can be generalized to many bilayer graphene–adatom materials, and we envision that the realization of electrically tunable resonance may be a key advantage in graphene-based spintronic devices.

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Chemical functionalization is a powerful tool to engineer graphene for a broad range of application needs. The attachment of oxygen groups makes graphene soluble and fluorescent, and facilitates the formation of graphene nanocomposites [1–3]. Chemisorbed species increase the degree of sp3 bonding, drastically affecting graphene’s electrical conductivity, mechanical strength, and optical response, even in the very dilute limit [4–22]. The deposition of light adatoms, such as hydrogen and fluorine, endows graphene with intriguing magnetic and spintronic properties, including localized magnetic moments and enhanced spin–orbit coupling, which may enable the generation of large spin currents [16–19, 21–24].

Covalently bonded monovalent species, with orbitals close to the Dirac point of graphene systems, effectively decouple their carbon host from its neighbors, thereby simulating vacancies [25]. The latter are predicted to introduce power-law localized midgap states at the Dirac point [26–28], displaying anomalous divergent behavior of the density of states [29, 30]. These so-called resonant scatterers have a profound impact on charge carrier transport at all carrier densities, invalidating conventional transport pictures based on the weak disorder hypothesis [31–33]. In the high carrier density regime \(|n| \gg n_{rs}\), where \(n_{rs}\) denotes the areal density of resonant scatterers, the dc conductivity deviates from its typical behaviour \(\sigma \propto |n|\), acquiring a robust sublinear dependence, owing to a nonperturbative renormalization of s-wave phase shifts: \(\delta_{ss}(n) \approx \pi/2\ln(R\sqrt{\pi|n|})\), where \(R \approx 0.4\) nm is the scatterer range [18, 25, 31, 32].

Resonant scattering also plays an important role in metal spintronics [34], although such interactions are not easily tunable. Engineering tunable resonant interaction of charge carriers with atomic impurities in graphene \(\textit{in situ}\) would open new avenues, including the harnessing of spin relaxation [35] and the generation of robust spin currents through the extrinsic spin Hall effect [23, 24]. From the viewpoint of device scaling and operations, it is particular desirable to implement gate-controlled resonant interactions. A suitable candidate—so far overlooked—is bilayer graphene (BLG). Adatoms in BLG are likewise predicted to induce resonant scattering [32, 36, 37]. Moreover, the presence of two layers allows the mirror symmetry to be broken by an electric field perpendicular to the layers, opening up a band gap up to 250 meV [38–42]. The consequences of this extra degree of freedom for resonant scattering remain largely unexplored.

In this Rapid Communication, we report experimental observations of adatom-limited charge transport in BLG using fluorine adatoms as an example. Dual gating allows us to control the carrier type, density, and the perpendicular (bias) electric field independently. Both experiment and theory demonstrate that fluorine adatoms behave as resonant scatterers. Moreover, we show that the charge carrier scattering amplitude becomes strongly electron-hole asymmetric and is tunable over a large range \(\pm 20 - 30\%\) by controlling the carrier distribution between the two layers using a bias electric field. Once more, theory and experiment are found to be in excellent agreement. The demonstrated electric tunability of the resonant cross section offers a convenient tool to engineer desired charge–spin responses in graphene–adatom systems.

Bilayer graphene flakes are exfoliated from bulk highly ordered pyrolytic graphite (HOPG graphite) (ZYA grade, SPI supplies) onto prefabricated HfO2/Au bottom gate stacks [43], optically identified and confirmed by Raman spectroscopy. The flakes are then fluorinated in a CF4
After fluorination, van der Pauw or Hall bar devices are given in the Supplemental Material (SM) to monolayer graphene [17]. Discussions of the plasma graphene is substantially harder to fluorinate compared to carbon atoms in the top layer only [see Fig. 1(a)]. Bilayer transport measurements at temperatures ranging from 1.6 K to 200 K. A false color map of a four-terminal resistance $R$ in sample W38 as a function of the top and bottom gate voltages $V_{\text{bg}}$ and $V_{\text{bg}}$ is shown in Fig. 1 (d) and displays characteristics similar to that of a pristine bilayer [42]. This map enables us to extract the dependence of the sheet conductance $\sigma_s$ on the carrier density $n$ at fixed bias $D$ fields.

**Resonant impurity scattering.**—We first establish the resonant impurity nature of the fluorine adatoms. The rearrangement of electronic spectral weight due to the fluorination can be estimated through a calculation of the density of states (DOS) for a typical adatom concentration. To model the BLG system we employ a nearest-neighbor tight-binding Hamiltonian of $\pi$ electrons, supplemented with an on-site energy term $\pm V$ in the top (bottom) layer describing the effect of the $D$ field. Fluorine adatoms are modeled as vacancies in the top layer [25, 32]. The kernel polynomial method [46] is then used to accurately extract the DOS of a large lattice with $2 \times 14142^2$ carbon atoms. Details of the calculation are given in the Supplemental Material.

The calculated DOS is shown in Fig. 2(a). We note two prominent features. Firstly, in unbiased BLG, the DOS displays a sharp peak centered at zero energy (midgap state), already encountered in Refs. [32, 47]. Secondly, at nonzero bias field, new resonances pile up at the edges of the pseudogap, which is consistent with results obtained for a single vacancy [28]. Due to the broken layer symmetry, these resonances have different weights at $E_F \approx \pm V$, anticipating substantial electron-hole asymmetry (EHA).

Fig. 2(b) shows $\sigma_s(n)$ at $D = 0$ for samples W38, W02, W03, and Df at $T = 1.6$ K. Sample Df has a field effect mobility of $\mu \approx 1600 \text{ cm}^2/\text{Vs}$, which is comparable to that of a pristine bilayer in a similar geometry [42]. In contrast, fluorinated bilayers display much lower mobility: 172, 100, and 86 cm$^2$/Vs for W38, W02, and W03, respectively, which signals the dominance of adatom-induced scattering. Ferreira et al. [32] showed that in the high carrier density regime $n > n_F$ where quantum corrections are not dominant, a semiclassical description applies, and the resonant-scattering-limited sheet conductivity in unbiased BLG is given by

$$\sigma_s(n) = 2 \times \frac{\pi e^2 |n|}{4h n_F},$$

where an extra factor of 2 accounts for the one-sided fluorination of our samples. Since $\sigma_s$ is approximately insensitive to the scatterer radius, there is a single fitting parameter, $n_F$. Fits to Eq. 1 are plotted as dashed lines in Fig. 2(b) and describe data very well at high density [32]. The extracted $n_F$ are in good agreement with values obtained from Raman spectra for all samples (see Table I in Supplemental Material). Furthermore, in all samples we find an $n_F$-independent $\sigma_s \approx e^2/h$ in the low carrier density regime $n < n_F$, also in agreement with.

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**Figure 1:** Single-sided fluorinated BLG. (a) Schematic. Solid (dashed) lines represent the intralayer (interlayer) hopping terms. Fluorine adatoms bond to carbon hosts at random positions. (b) Optical micrograph of sample W02 showing the Au bottom gate (wide yellow stripe), four Au electrodes to the sample (dark gold) in van der Pauw geometry, and the top gate connected to two Au electrodes (yellow). (c) Raman spectra of pristine (plum), fluorinated (olive, from sample W02) and defluorinated (orange) BLG. The laser excitation wavelength is 488 nm. (d) The color map of a four-terminal resistance $R$ as a function of the top and bottom gate voltages. The black line corresponds to $n = 0$ and the white lines correspond to constant bias $D$ fields. $T = 10$ K. From W38.
theory. This observation is consistent with the formation of a narrow “impurity band” around the charge neutrality point (CNP) [32, 47] [see thick (orange) line in Fig. 2(a)].

More direct evidence of the impurity band is seen in the temperature-dependent resistance of the CNP under a finite bias field. Figure 3(a) plots $R_{\text{CNP}}(D)$—the sheet resistance of the CNP in sample W02—as a function of $D$ at selected temperatures $T = 1.6–200$ K, together with $R_{\text{CNP}}(D)$ of sample Df at $T = 1.6$ K. $R_{\text{CNP}}(D)$ of sample Df is similar to that of a pristine bilayer [42]. $R_{\text{CNP}}(D)$ of W02, on the other hand, rises much more slowly, pointing to additional conduction channels inside the band gap. To further understand the behavior of $R_{\text{CNP}}$, we plot in Fig. 3(b) its temperature dependence in both samples at $D = 0.93$ V/nm. The most remarkable difference between the two lies at high temperatures $T > 50$ K. In this regime, sample Df exhibits activated transport $R_1 \propto \exp(E_1/k_B T)$, with $E_1$ increasing with $D$ from 22.5 meV at $D = 0$ (data not shown) to 33.5 meV at $D = 0.93$ V/nm. These values are similar to pristine bilayers, where $\Delta = 2E_1$ approximates the bias-induced band gap in the large $D$ limit [42]. In contrast, similar analyses done on $R_{\text{CNP}}(T)$ of the three fluorinated bilayers yield roughly $D$-independent $E_1$, which is approximately 11–13 meV in all samples. We attribute this behavior to nearest-neighbor hopping among the fluorine-induced impurity states, as illustrated in the inset to Fig. 3(b), where $E_1$ is the half-width of the impurity band. This mechanism effectively shunts the band edge activation $\exp(\Delta/2k_B T)$ to result in a $D$-independent $R_{\text{CNP}}(T)$. Counting two impurity states per adatom [32], we independently estimate the bandwidth to be $\approx 10$ meV at $n_F \approx 4 \times 10^{12}$ cm$^{-2}$, which is in excellent agreement with the $E_1$ values extracted here.

Electric-field tuning of resonant scattering.—Next, we explore the role of a bias $D$ field in the carrier density regime $n > n_F$. Figure 4(a) plots $\sigma_s(n)$ of sample W02 at selected $D$’s from -2 to 2 V/nm, where $D > 0$ indicates field pointing towards the fluorine adatoms, as the inset of (a) shows. Pronounced EHA is observed. For electrons, $\sigma_s$ increases (decreases) when $D > 0$ ($D < 0$) and the opposite trend is observed for holes. This $D$-field tuning is further illustrated in Fig. 4(b), where we plot the normalized conductance change $\delta\sigma_s(D) \equiv \Delta\sigma_s(D)/\sigma_s(0) = [\sigma_s(D) - \sigma_s(0)]/\sigma_s(0)$ of the data in Fig. 4(a). Strikingly, in the high-density regime, $\delta\sigma_s(D)$ is roughly $n$-independent and ranges between -0.35 and 0.2 for $|D| < 2$ V/nm, i.e., the change of $\sigma_s$ is nearly twofold. Furthermore, $\delta\sigma_s(D)$ appears to be symmetric under $(n, D) \to (−n, −D)$. Similar $D$-field tuning of $\sigma_s(n)$ is observed on all three fluorinated samples, with the magnitude of $\delta\sigma_s(D)$ varying within a factor of 2 among them. Further examination of the EHA rules out an extrinsic mechanism due to nonuniform density distribution created by electrodes that screen a portion of the top gate. The detailed discussions are given in the Supplemental Material. Intuitively, the experimental observations suggest an increased weight of hole (electron) wave functions in the top layer under a positive (negative) $D$ field, and thus increased resonant impurity scattering.

To gain further insight into the strong $D$-field tuning of charge carrier transport, we solve analytically the Boltzmann transport equations for a BLG system with random short-range impurities constrained to one layer. We posit our investigations in the four-band continuum BLG–adatom Hamiltonian

$$\hat{H} = \begin{pmatrix} V + v_F \sigma \cdot \hat{p} & t_\perp \sigma_- \\ t_\perp \sigma_+ & -V + v_F \sigma \cdot \hat{p} \end{pmatrix} + \sum_i \left( v_i^0(r) \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \right),$$

(2)
where \( \mathbf{p} \) is the two-dimensional (2D) kinematic momentum operator around Dirac point \( K \), \( v_F \approx 10^6 \text{m/s} \) is the Fermi velocity, \( \sigma \) are Pauli matrices, with \( \sigma_z = \pm 1 \) describing states residing on the \( \alpha(\beta) \) sublattice, and \( \sigma_x = i \sigma_y \). The diagonal blocks in the first term on the right-hand side describe monolayers at a constant electrostatic energy, \( \pm V \) for top layer and bottom layer, respectively, whereas off-diagonal blocks contain the hopping processes \( A_2 = B_1 \) connecting the two layers \( (t_\perp \approx 0.45 \text{ eV}) [48] \). The bias potential \( V \) is determined from the experimental parameters according to \( V = -eDd/2\kappa \), where \( -e < 0 \) is the electron’s charge, \( d \approx 0.35 \text{ nm} \) is the layer separation, and \( \kappa = 4 \) is the phenomenological BLG effective permittivity [39, 49]. Diagonalization of the first term yields \( 2 + 2 \) bands separated by a gap: \( \Delta = 2|V|t_\perp/\sqrt{t_\perp^2 + 4V^2} \approx 2|V| \). Their dispersion relation reads \( \epsilon_{\pm \pm}(\pi) = \pm \sqrt{t_\perp^2/2 + \pi^2 + V^2} \pm \lambda^2(\pi) \), where \( \pi = v_F \mathbf{p} \) and \( \lambda^2(\pi) = \sqrt{t_\perp^2/4 + \pi^2} (t_\perp^2 + 4V^2) \). The second term is the scattering potential due to fluorine adatoms located in the top layer at random positions \( \{ \mathbf{r}_i \} \) with \( v_0(\mathbf{r}) = v_0 \delta(\mathbf{r} - \mathbf{r}_i) \). In the scattering problem, outgoing and incoming wavefunctions are related by the \( T \) matrix [50]. For delta-peak potentials, outgoing waves from a single impurity at the origin acquire the simple form \( \psi_{\text{out}}(\mathbf{r}) = \hat{G}_0(\mathbf{r}, E)\phi_k(\mathbf{r}) \), where \( \phi_k(\mathbf{r}) \) denotes free incoming wave solutions with momentum \( \mathbf{k} \), i.e., \( \hat{H}_0(\phi_k) = E\phi_k \), and \( \hat{G}_0(\mathbf{r}, E) \) is the propagator of pristine biased BLG, \( \hat{G}_0(\mathbf{r}, E) = \{ \mathbf{r} \}(-\hat{H}_0 + iv_0)^{-1}\hat{0} \) with \( v_0 \) a real infinitesimal. In the (resonant) scattering limit of interest \( v_0 \rightarrow \infty \), we easily find

\[
\hat{T}_{\text{ad}}(E) = - \sum_{\chi = A_2, B_2} [g_\chi(E)]^{-1} |\chi \rangle \langle \chi |,
\]

where \( g_\chi(E) = \langle \chi |\hat{G}(0, E)|\chi \rangle \). We evaluated \( g_\chi(E) \) in the entire parameter space (refer to Supplemental Material); in the intermediate regime \( \sqrt{t_\perp^2 + V^2} > |E| > |V| \) (typically \( \sim 0.05–0.5 \text{ eV} \)),

\[
g_{A_2}(E) = (V - E)[\Theta_{\lambda}(E) + (E + V)^2\Theta_{\text{reg}}(E)],
\]

\[
g_{B_2}(E) = \left( t_\perp^2 + V^2 - E^2 \right) (E + V)\Theta_{\text{reg}}(E)
\]

\[
+ (V - E)\Theta_{\lambda}(E),
\]

where

\[
\begin{align*}
\Theta_{\text{reg}}(E) &= \frac{1}{4\pi v_F E} \int_0^1 \left\{ \ln \left( \frac{A_+}{A_-} \right) - i\pi \right\} \frac{\psi(\Lambda)}{\Psi(\Lambda)} d\lambda, \\
\Theta_{\lambda}(E) &= \frac{1}{4\pi v_F E} \int_0^1 \left\{ \ln \left( \frac{A_+}{A_-} \right) + i\pi \right\} \frac{\psi(\Lambda)}{\Psi(\Lambda)} d\lambda.
\end{align*}
\]

In the above, \( A_{\pm} = \sqrt{4E^2V^2 + t_\perp^2 (E^2 - V^2) \pm (E^2 + V^2)} \), \( \Psi(x) = \sum_{p = \pm 1} A_p \ln(-p + x^2/[A_p]) \), and \( \Lambda = hv_F/R \) is the high-energy cutoff defining an effective potential range \( R \) [32]. Crucially, for non-zero bias field \( |V| > 0 \), the \( T \) matrix is sensitive to carrier polarity \( \pm|E| \) [see Eqs. (4)–(5)]. This feature results from the top-bottom layer asymmetry induced by the adatoms and, as argued below, is the origin of the strong EHA observed.

**Figure 4:** Tuning of charge carrier transport in \( D \)-field. (a) and (b) \( \sigma_\varepsilon(n) \) and normalized conductance change \( \delta\sigma_\varepsilon(D) \) for W02 at \( T = 1.6 \text{ K} \) and \( D = -2 \text{ V/nm} \) (cyan), -1 V/nm (plum), 0 V/nm (black), 1 V/nm (red), and 2 V/nm (blue). Positive \( D \) points towards the fluorine adatoms as illustrated in the inset of (a). (c) Calculated dc-conductivity \( \sigma_\varepsilon(n) \) for several inter-layer bias potentials corresponding to the \( D \)-field values in (a). Calculation only applies to \( n > n_F \). Other parameters in main text.

The effect of dilute random adatoms in dc-transport is encoded in the inverse transport relaxation time

\[
\frac{1}{\tau(\mathbf{k})} = \frac{2\pi n_F}{h} \int \frac{d^2k'}{(2\pi)^2} |\langle \phi_{\mathbf{k'}} |\hat{T}_{\text{ad}}(E) |\phi_{\mathbf{k}} \rangle|^2 \delta_{\mathbf{k}\mathbf{k'}}(E),
\]

where \( \delta_{\mathbf{k}\mathbf{k'}}(E) \equiv (1 - \cos \theta_{\mathbf{k}\mathbf{k'}})\delta(\epsilon_\mathbf{k} - \epsilon_{\mathbf{k'}}) \), \( \theta_{\mathbf{k}\mathbf{k'}} \) is the scattering angle, and \( \epsilon_{\mathbf{k}} \equiv \epsilon_{\mathbf{k}}^0 - (v_F \mathbf{k}) \) for \( E = \pm|E| \). The zero-temperature semiclassical dc-conductivity follows from \( \sigma_\varepsilon = (e^2/h)k_Fv(k_F)\tau(k_F) \), where \( v(k) = |\nabla k\epsilon_k|/h \) is the band velocity and \( k_F \) is the Fermi wave vector [51]. In order to unbiasedly extract the model parameters \( n_F \) and \( R \), we fit the 4-band expression to the \( D = 0 \) conductivity data in the electron sector \( n > 0 \) [see black curve in Fig. 4 (a)]. We obtain \( n_F \approx 1.6n_F^{\text{ram}} \) and \( R \approx 0.5 \text{ nm} \), where \( n_F^{\text{ram}} \) is obtained from the Raman spectra of this device (see above). These parameters are then employed to evaluate \( \sigma_\varepsilon(n) \) at all nonzero \( D \)-fields in Fig. 4 (c). The theory is seen to reproduce very well both the degree of EHA and the overall \( D \)-dependence observed in panel (a). This agreement is particularly remarkable as the strong scattering regime is characterized by a strong dependence of \( \tau^{-1}(\mathbf{k}) \) in the \( D \)-field and model parameters. This robust agreement is strong evidence that the \( D \)-field tuning of the resonant
adatom scattering amplitudes (3) is responsible for the observed conductance modulation. Because of the resonant nature of the adatoms, a twofold change of the scattering cross section can lead to very large tuning of other resonant properties, such as the spin Hall angle [23], giving BLG-based systems a distinct advantage in graphene-based spintronics.

In summary, through a joint experiment–theory effort, we have demonstrated that a perpendicular electric field achieves substantial tuning of the amplitude of resonant impurity scattering in one-sided fluorinated bilayer graphene. Our findings set the stage for exploring all-electric control of resonant scatterings that underlie novel spintronics effects in graphenic materials.

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I. FABRICATION AND CHARACTERIZATION OF FLUORINATED BILAYER GRAPHENE DEVICES

A. Fluorination of Bilayer Graphene

All samples were fluorinated in a plasma asher (Metal-line M4L) using CF4. Defluorination was done by annealing the sample in Ar/H2 flow at 360 °C for 12 hours. Compared to monolayer graphene, bilayer graphene is substantially harder to fluorinate, presumably due to a flatter topography. Three parameters, namely, the power p, the gas pressure P and the duration time T, control the fluorine coverage as well as the unintentional vacancy density. Empirical trials show that the ratio of fluorine density vs vacancy density is maximized to be roughly 4:1 under conditions of p=100 W and P=200mTorr (100 sccm of CF4 gas flow). At this setting, a T=5 min run produces approximately nF=1×10^{12}cm^{-2}.

B. Color Map of 4-Terminal Resistance

We attribute the resistance peak [black line in Fig. 1(d), main text] to the charge neutrality point (CNP). Tracking its evolution with V_{tg}, V_{bg} and the location of a minimum along the black line allows us to determine the gating efficiencies of the top and bottom gates α_{tg} and α_{bg}, respectively, and also the unintentional doping of the two gates, V^0_{tg} and V^0_{bg}, respectively. The total carrier density is n = α_{tg}(V_{tg} − V^0_{tg}) + α_{bg}(V_{bg} − V^0_{bg}), and the electric displacement field is D = (D_{tg} + D_{bg})/2, where D_{bg} = (α_{bg}e)/ε_{0}(V_{bg} − V^0_{bg})
and $D_{tg} = -(\alpha_{tg} \epsilon)/\varepsilon_0 (V_{tg} - V_{tg}^0)$. Table I lists the parameters of all devices used in this study.

|               | W38          | W02          | W03          | Df          |
|---------------|--------------|--------------|--------------|-------------|
| $\alpha_{tg} \times 10^{12}$ cm$^{-2}$V$^{-1}$ | 2.3          | 3.15         | 3.15         | 2.3         |
| $\alpha_{bg} \times 10^{12}$ cm$^{-2}$V$^{-1}$ | 2.44         | 3            | 3            | 0.065       |
| $V_{tg0}$ (V)  | -1.7         | -3.7         | -6           | -1.3        |
| $V_{bg0}$ (V)  | -0.2         | 0.6          | -3.1         | -7.7        |
| $I_D/I_G$      | 1.15         | 1.15         | 1.3          | 0.3         |
| $I_D/I_G^{\ast\ast}$ | 0.9          | 1.25         | 1.4          | N.A.        |
| $n_F \times 10^{12}$ cm$^{-2}$ | 2.2          | 3.8          | 4.4          | 0.6         |

Table I: Device characteristics for 3 dilute fluorinated bilayer graphene samples (W38, W03, and W02) and one defluorinated bilayer graphene sample (Df). Parameters are described in the text. ID/IG** indicates the expected ID/IG from resonant scattering fits.

C. Electron–Hole Assymetry

The density difference between the dual-gated portion of a bilayer and the area underneath the metal electrodes, whose density is only controlled by the backgate, can lead to bipolar junctions that are more resistive than unipolar junctions. Similar phenomena were studied in monolayers [1]. In our dual-gated bilayer, increasing $V_{bg}$ in the positive direction creates a n-doped region underneath the contact, which favors the conduction of electrons. This extrinsic electron–hole asymmetry carries the same sign as the $D$-field controlled resonant impurity scattering discussed in the main text since a positive $V_{bg}$ results in a positive $D$-field so care must be taken to differentiate between the two.

The junction induced electron–hole asymmetry becomes less important as the contact become less intrusive. Compared to conventional bar-like devices (pristine Bi 9-2 and Bi 5 shown in Fig. 1), fluorinated bilayer W02 shown in the main text [Fig. 1(c)] is a van der Pauw geometry with minimally intrusive voltage probes on the current path. Naturally, we expect a small impact from the junction effect on W02. In Fig. 1, we plot $R_{odd}$ vs electron density $n$ of the dual-gated area at fixed $n_{bg}$, using

$$R_{odd}(n_{bg}) = \frac{1}{2} \left[ R(n, n_{bg}) - R(-n, n_{bg}) \right],$$

as a measure of the electron–hole asymmetry [1]. Fig. 1(a)-(c) compare results from two pristine bilayer samples and the fluorinated W02 (in Fig. 4, main text). Bi 9-2 and Bi 5 use 300nm SiO$_2$ backgates so the carrier density and $D$ field range are smaller than that of W02.

On the pristine devices, $R_{odd}$ increases with the magnitude of $n_{bg}$ and reverses sign in the vicinity of $n_{bg} = 0$, as expected from the junction effect. Furthermore, $R_{odd}$ decreases with increasing $n$ and tends toward zero at high $n$. In comparison, $R_{odd}$ in W02, which is non-zero because it does exhibit electron–hole asymmetry, does not correlate with $n_{bg}$ and shows no dependence on $n$. This rules out the junction effect as the origin of the reported electron–hole asymmetry tuning.

II. SOLUTION OF THE SCATTERING PROBLEM

A. Propagator of Biased Bilayer Graphene

In this section we provide the derivation of the propagator of low-energy quasi-particles in Bernal-stacked bilayer graphene in the presence of a perpendicular electric field. For our purposes it is sufficient to consider the following minimal Hamiltonian describing $\pi$-electrons in the $K$ valley [3]

$$\hat{H}_K = \begin{pmatrix} B_2 & V & 0 & V \\ -V & A_1 & V & 0 \\ 0 & -V & A_2 & 0 \\ -t_\perp & -V & 0 & A_2 \end{pmatrix},$$

(1)

where $\hat{p} \equiv v_F(\hat{p}_x + i\hat{p}_y)$ [here $\hat{p} = -(i\hbar \mathbf{v})$ is the 2D momentum operator and $v_F \approx 10^6$ m$^{-1}$ is the Fermi velocity], $t_\perp$ denotes the inter-layer hopping, and $V$ is half the energy difference between the layers as induced by a perpendicular electric field [4]. Hereafter we set $\hbar = 1$. The dispersion relations of the four bands associated with $\hat{H}_K$ read as

$$\epsilon^{\pm}(\mathbf{\pi}) = \pm \sqrt{\frac{t^2_\perp}{2} + \mathbf{\pi}^2 + V^2} \pm \sqrt{\frac{t^4_\perp}{4} + \mathbf{\pi}^2 (t^2_\perp + 4V^2)},$$

(2)
Usually $|V|$ is small, and thus $\Delta \simeq 2|V|$ is a good approximation. Depending on the position of the Fermi level, three spectral regions must be considered:

- **Region I**: $|V| > |E| > \Delta/2$, the “Mexican hat” region. Here, the Fermi level crosses the band $\epsilon^{\pm}$ twice.
- **Region II**: $E_H > |E| > \Delta/2$, the intermediate density region where the Fermi level crosses $\epsilon^{\pm}$ at a single point.
- **Region III**: $\Lambda > |E| > E_H$, the high-energy region where the Fermi level crosses $\epsilon^{\pm}$ and $\epsilon^{\pm}$ at a single point.

In the above, $\pm E_H = \pm \sqrt{t_{\perp}^2 + V^2}$ denotes the maximum (minimum) of the band $\epsilon^{\pm}$ and $\Lambda$ a cutoff of the low-energy theory (see below). In what follows we compute the propagator in coordinate space in regions I–III.

The resolvent operator $G(z) \equiv (z - i \mu_K)^{-1}$ has a simple representation in momentum space:

\[
G(z, \pi) = \left[ z - \frac{t_{\perp}}{2} (\sigma_z \otimes \sigma_z - \sigma_0 \otimes \sigma_z) \right. \\
\left. - |\pi| |\sigma_x \otimes (n' \cdot \sigma) - V\sigma_x \otimes \sigma_z|^{-1} \right], \tag{3}
\]

where $n' = (\cos \theta_p, -\sin \theta_p)^t$, $\sigma_\alpha$ are Pauli matrices ($\alpha = x, y, z$), and $\sigma_0$ is the $2 \times 2$ identity. The matrix inversion in (3) is straightforward. We obtain

\[
G(z, \pi) = \frac{1}{D(z, \pi)} D^{(4)}(z, \pi), \tag{4}
\]

where

\[
D(z, \pi) \equiv - \prod_{\lambda, \lambda' = \pm 1} \left[ z - \epsilon^{\lambda \lambda'}(\pi) \right] = -\pi^4 + 2\pi^2(z^2 + V^2) + (z^2 - V^2)(t_{\perp}^2 - z^2 + V^2), \tag{5}
\]

and $D^{(4)}(z, \pi)$ is the matrix

\[
D^{(4)}(z, \pi) = \begin{pmatrix}
\Xi_{1+}(z, \pi) & \pi^2 e^{2i\theta_p t_{\perp}} & \pi e^{i\theta_p t_{\perp}}(z + V) & \pi e^{i\theta_p} \Upsilon_{+}(z, \pi) \\
\pi^2 e^{2i\theta_p t_{\perp}} & \Xi_{1-}(z, \pi) & \pi e^{-i\theta_p} \Upsilon_{-}(z, \pi) & \pi e^{-i\theta_p} t_{\perp}(z - V) \\
\pi e^{-i\theta_p} t_{\perp}(z + V) & \pi e^{i\theta_p} \Upsilon_{-}(\pi) & \Xi_{2+}(z, \pi) & t_{\perp}(z^2 - V^2) \\
\pi e^{-i\theta_p} \Upsilon_{+}(z, \pi) & t_{\perp}(z - V) & \pi e^{i\theta_p} t_{\perp} & \Xi_{2-}(z, \pi)
\end{pmatrix}. \tag{6}
\]

Figure 1: A close look into the electron–hole asymmetry. $R_{\text{total}}$ vs electron density $n$ at selected $n_{bg}$ for pristine bilayers Bi 9-2, Bi 5 and fluorinated bilayer W02. (Bi9-2 and Bi 5 were reported in Ref. [2]). The magnification of the y-axis is adjusted to account for the geometry difference between the three measurements, ensuring a fair comparison. Positive $n_{bg}$ corresponds to electrons. Insets are optical micrographs of the devices. The graphene flake is outlined in each image. Black dots indicate voltage probes used. In Bi9-2 and Bi 5, the voltage probes are fairly invasive with pronounced junction effect. They are minimally invasive in W02.

where $\pi = v_F p \equiv v_F p (\cos \theta_p, \sin \theta_p)^t$. The presence of a bias potential opens a gap $\Delta = 2|V t_{\perp}|/\sqrt{4V^2 + t_{\perp}^2}$. 

\[n_{bg}(1\times10^{12}\text{cm}^{-2})\]
In the above we have also defined the following quantities

\[ \Upsilon_\pm (\pi) = \pi^2 - (z \pm V)^2, \]
\[ \Xi_{1\pm} (\pi) = (t_\perp^2 + V^2 - z^2)(z \pm V) + \pi^2(z \mp \pi), \]
\[ \Xi_{2\pm} (\pi) = (z \pm V) \Upsilon_\mp (z, \pi). \]

The propagator in coordinate space is obtained from (4) via inverse Fourier transform

\[ G(z, r' - r) = \int \frac{dp}{4\pi^2} e^{ip(r-r')} G(z, v_F p). \]

In order to evaluate the above integral we use differentiation under the integral sign, that is,

\[ G(z, r - r') = D^{(4)} \left( z, \frac{\nabla}{i} \right) \Lambda_0^{(4)}(z, r - r'), \]

with

\[ \Lambda_0^{(4)}(z, r - r') = \int \frac{dp}{4\pi^2} e^{ip(r-r')} D(z, p) = \int_0^\infty dp p J_0(p)|r-r'|/2\pi \quad D(z, v_F p). \]

We note that the operation (11) is strictly valid for \(|r-r'| \neq 0\), where the inverse Fourier transform (10) converges for all matrix components of \( G \). The one-dimensional integral in Eq. (12) can be solved using standard methods (we provide a derivation in the Appendix A). One obtains

\[ \Lambda_0^{(4)}(E, \mathbf{r}) = \frac{1}{4v_F^2} \frac{1}{A_- + A_+} \times \]
\[ \begin{cases} -iH_0(p_+, r) + \frac{2}{\pi} K_0(p_- r), & A_+ > 0 \text{(regions II)} \\ -iH_0(p_-, r) + iH_0(p_- r), & A_- < 0 \text{(regions I and III)} \end{cases}, \]

where \( p_{\pm} = \sqrt{|A_{\pm}|/v_F} \) and

\[ A_\pm = \pm (E^2 + V^2) + \sqrt{4E^2V^2 + t_\perp^2(E^2 - V^2)}. \]

In the above, \( H_0(.) \) [\( K_0(.) \)] denotes the zeroth order first kind Hankel [second kind modified Bessel] function. In region II, \( \Lambda_0^{(4)}(E, \mathbf{r}) \) contains one propagating mode \( H_0(p_+, r) \)—representing outgoing cylindrical waves with momentum \( p_+ \)—and one evanescent wave \( K_0(p_- r) \). Regions I and III admit two (real) propagating solutions as the Fermi level intersects the electronic bands at two distinct points [namely, \( E = \epsilon^{\pm-}(v_F p_+) \) and \( E = \epsilon^{\pm+}(v_F p_-) \)] in region I and \( E = \epsilon^{\pm-}(v_F p_+) \) and \( E = \epsilon^{\pm+}(v_F p_-) \) in region III).

Next, we show how to compute the propagator at the origin, \( G(E, \mathbf{r} = 0) \). This quantity plays a central role in scattering from short-range impurities (Sec. II B). Combining Eqs. (4)-(6) and (10) we obtain

\[ G(E, 0) = \int_0^\infty dp \frac{p}{2\pi D(E, p) + i\eta} \begin{bmatrix} \Xi_{1+}(v_F p) & 0 & 0 & 0 \\ 0 & \Xi_{1-}(v_F p) & 0 & 0 \\ 0 & 0 & \Xi_{2+}(v_F p) & t_\perp(E^2 - V^2) \\ 0 & 0 & t_\perp(E^2 - V^2) & \Xi_{2-}(v_F p) \end{bmatrix}. \]

Since the matrix entries on the RHS are of the form \( a + bp^2 \) we are lead to the following type of integrals

\[ \Theta(E) = \int_0^\infty dp \frac{p}{2\pi D(E, p) + i\eta}, \]
\[ \Theta_A(E) = \int_0^{\frac{1}{v_F^2}} dp \frac{p^3}{2\pi D(E, p) + i\eta}, \]

with \( \eta \) a real infinitesimal. We notice that the terms \( bp^2 \) result in logarithmically divergent integrals and hence a cut-off was introduced in \( \Theta_A(E) \). It is useful to recast the denominator in the following form

\[ \frac{1}{D(E, p) + i\eta} = \frac{1}{A_- + A_+} \times \frac{1}{A_- + v_F^2 p^2 + is_0 \mp + A_+ - v_F^2 p^2 + i0^+}, \]

where \( s_- \equiv \text{sign}(A_-) \). Inserting (18) into (16)-(17), and making use of the Sokhotski–Plemelj formula, we arrive at

\[ \Theta(E) = \frac{1}{4\pi v_F^2} \frac{1}{A_- + A_+} \times \]
\[ \begin{cases} \ln \left( \frac{A_+}{A_-} \right) - i\pi, & A_- \geq 0 \\ \ln \left( \frac{A_-}{A_+} \right), & A_- < 0 \end{cases}. \]
We remark that the local density of states (LDOS) can be obtained through a very similar calculation, according to \( \rho_{\beta_L}(E) = \frac{-1}{\pi} \text{Im} G^+(E,0) \), with \( G^+(E,0) \equiv G(E + i0^+,0) \). The different form of the analytic continuation leads to somewhat different expressions (see Appendix B for details). The LDOS of a representative system is shown in Fig. 2.

\[
\Theta_L(E) = -\frac{1}{4\pi v_F^2} \frac{1}{A_+ + A_-} \times
\begin{cases}
\Psi_+(\frac{A}{v_F}) + i\pi A_+ , & A_+ \geq 0 \\
\Psi_-(\frac{A}{v_F}) + i\pi (A_+ + A_-) , & A_- < 0 , 
\end{cases} 
\]

where

\[
\Psi_\pm(x) = A_- \ln \left( \pm 1 + \frac{v_F^2 x^2}{|A_-|} \right) + A_+ \ln \left( -1 + \frac{v_F^2 x^2}{A_+} \right),
\]

encodes the cutoff-sensitive component. The non-zero entries of Eq. (15) become

\[
G(E,0)_{11} = \left( t_+^2 + V^2 - E^2 \right) + (E + V) \Theta(E) + v_F^2 (E - V) \Theta(E), \quad (22)
\]

\[
G(E,0)_{22} = \left( t_+^2 + V^2 - E^2 \right) + (E - V) \Theta(E) + v_F^2 (E + V) \Theta(E), \quad (23)
\]

\[
G(E,0)_{33} = t_+ (E^2 - V^2) \Theta(E), \quad (24)
\]

\[
G(E,0)_{43} = t_+ (E^2 - V^2) \Theta(E), \quad (25)
\]

\[
G(E,0)_{3,4} = (E + V) \left[ v_F^2 \Theta(E) - (E - V)^2 \Theta(E) \right], \quad (26)
\]

\[
G(E,0)_{4,4} = (E - V) \left[ v_F^2 \Theta(E) - (E + V)^2 \Theta(E) \right]. \quad (27)
\]

We remark that the local density of states (LDOS) can be obtained through a very similar calculation, according to \( \rho_{\beta_L}(E) = \frac{-1}{\pi} \text{Im} G^+(E,0) \), with \( G^+(E,0) \equiv G(E + i0^+,0) \). The different form of the analytic continuation leads to somewhat different expressions (see Appendix B for details). The LDOS of a representative system is shown in Fig. 2.

\[
\Psi_k(r) = \phi_k(r) + G(E,r) V \Psi_k(0), \quad (28)
\]

where \( \phi_k(r) \) stands for the incident wave of energy \( E \) and momentum \( k \), whereas \( \Psi_k(r) \) represents the full 'incident + scattered' wavefunction. Setting \( r = 0 \) in the LS equation results in

\[
\Psi_k(0) = [I - G(E,0)V]^{-1} \phi_k(0), \quad (29)
\]

where \( G(E,0) \) has been computed earlier (refer to Sec. II A). The scattered wavefunction \( \Delta \Psi_k(r) \equiv \Psi_k(r) - \phi_k(r) \) is obtained by substituting (29) into the RHS of Eq. (28), i.e.,

\[
\Delta \Psi_k(r) = G(E,r) V [I - G(E,0)V]^{-1} \phi_k(0) . \quad (30)
\]

Local electrostatic potentials are described by a diagonal matrix in the sublattice space [5]

\[
V = V_0 \begin{bmatrix} a & 0 & 0 & 0 \\
0 & b & 0 & 0 \\
0 & 0 & c & 0 \\
0 & 0 & 0 & d \end{bmatrix}, \quad (31)
\]

where \( V_0 \equiv S v_0 \) with \( S \) encoding the areal range of the potential and \( v_0 \) its strength. Denoting \( g_{n_1,n_2} \equiv [G(E,0)]_{n_1,n_2} \) and inserting the potential matrix (31) into the LS equation (30) we obtain

\[
\Delta \Psi_k(r) = G(E,r) V_0 \begin{bmatrix} a & 0 & 0 & 0 \\
0 & b & 0 & 0 \\
0 & 0 & c & 0 \\
0 & 0 & 0 & d \end{bmatrix} 
\begin{bmatrix} a & 0 & 0 & 0 \\
0 & b & 0 & 0 \\
0 & 0 & c & 0 \\
0 & 0 & 0 & d \end{bmatrix} \phi_k(0) \quad (32)
\]

where

\[
\Phi(E) = V_0^{-1} - d g_{44} - c [g_{43} + d (g_{44}^2 - g_{33} g_{44}) V_0] . \quad (33)
\]

Below we show how to compute the scattering flux for the particular case: \( b,c,d = 0 \) and \( c = 1 \). The latter represents a potential localized on atom \( B_2 \), for which the intervalley terms have been artificially set to zero (see also remark [5]). Despite its simplicity, this model already contains the basic physics underpinning the electron–hole asymmetry observed in the experiments. For such a toy model,
the scattered component reads

$$\Delta \Psi_k(r)|_{B_2} = G(E,r) \begin{bmatrix} \frac{1}{V_0 - g_{11}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \phi_k(0). \quad (34)$$

**Solution in Region II**

To make further progress we need the form of the incident wave. Taking the incoming momentum along the $x$ axis, and assuming for simplicity $|V| \leq |E| \leq E_H$ (region II), we have

$$\phi_k(0)|_{II} = \mathcal{N}(E) \begin{bmatrix} \frac{\nu_F k}{E-V} \\ \frac{(E-V)(t_+^2 + V^2 - E^2) + \nu_F^2 k^2(E + V)}{\nu_F k t_+ (E-V)} \\ \frac{\nu_F^2 k^2 - (E-V)^2}{t_+ (E-V)} \\ 1 \end{bmatrix},$$

with $\mathcal{N}(E)$ a normalization factor, whose form does not need to be specified. Altogether we have

$$\Delta \Psi_k(r)|_{B_2} = \mathcal{N}(E) G(E,r) \begin{bmatrix} \frac{\nu_F k}{E-V} \frac{1}{V_0 - g_{11}(E)} \\ 0 \\ 0 \\ 0 \end{bmatrix}. \quad (36)$$

All that is left is to “propagate” the wave by acting with $G(E,r)$. The propagator reads [refer to Eqs. (10)-(13)]

$$G(z,r) = D^{(4)}(z,\mathbf{\nabla}) \Lambda^{(4)}_0(z,r), \quad (37)$$

where $D^{(4)}$ is obtained from Eq. (6) replacing $\pi e^{\pm i\theta_p} \rightarrow v_F (\hat{p}_x \pm i \hat{p}_y)$ and

$$\Lambda^{(4)}_0(z,r)|_{II} = \frac{1}{4v_F^2} \frac{1}{A_+ + A_-} \left[ -iH_0 \left( v_F^{-1} \sqrt{A_+} |r| \right) + \frac{2}{\pi} K_0 \left( v_F^{-1} \sqrt{A_-} |r| \right) \right]. \quad (38)$$

Inserting this expression into (37), and using $H_0(x) \rightarrow \sqrt{\frac{2}{\pi x}} e^{i(x-\frac{\pi}{4})}$ for $x \gg 1$, we finally arrive at

$$\Delta \Psi_k(r,\theta)|_{B_2} \xrightarrow{r \gg 1} - i \frac{\mathcal{N}(E)}{8v_F^2 \sqrt{4E^2V^2 + t_+^2 (E^2 - V^2)}} \sqrt{\frac{2}{\pi i k r}} e^{ikr} D^{(4)}(E, v_F k e^{i\theta}) \begin{bmatrix} \frac{\nu_F k}{E-V} \frac{1}{V_0 - g_{11}(E)} \\ 0 \\ 0 \\ 0 \end{bmatrix}, \quad (39)$$

where we have identified the wavevector at the point of observation [i.e., $k' = kr/r = k(\cos \theta, \sin \theta)$]. Equation (39) gives the exact asymptotic form of the scattered wavefunctions in the energy range $|V| \leq |E| \leq E_H$.

According to the definition of differential cross section [14] it follows that

$$\sigma(\theta) = r \left| \frac{v_n(r,\theta)}{v_{in}} \right|. \quad (40)$$
where $v_{in} \left[ v_{n}(r, \theta) \right]$ is the velocity of the incident wave [scattered wave], that is

$$v_{in} = v_{F}\langle \phi_{k}(0) | \left( \begin{array}{cccc} 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{array} \right) | \phi_{k}(0) \rangle,$$

$$v_{n}(r, \theta) = v_{F}\langle \Delta\Psi_{k} | \left( \begin{array}{cccc} 0 & 0 & 0 & e^{i\theta} \\ 0 & 0 & e^{-i\theta} & 0 \\ e^{-i\theta} & 0 & 0 & 0 \end{array} \right) | \Delta\Psi_{k} \rangle.$$

Substitution of (39) and (35) into the above expressions and subsequent use of (40) gives after somewhat lengthy but simple algebra:

$$\sigma(\theta)_{|E|\leq E_{H}} = \frac{1}{32\pi k} \frac{1}{4E_{V}^{2}V^{2} + \tau_{\perp}^{2}(E^{2} - V^{2})} \left( \frac{\hbar^{2}k^{2}t_{\perp}}{\sqrt{4E_{V}^{2}V^{2} + \tau_{\perp}^{2}(E^{2} - V^{2})}} \right)^{2} \frac{\Gamma(k, E, V)}{g_{11}(E) - \frac{\hbar^{2}}{2v_{F}} \Gamma(k, E, -V)},$$

where

$$\Gamma(k, E, V) = t_{\perp}^{2}v_{F}k^{2}(E + V) + \left[ v_{F}k^{2} - (E + V)^{2} \right] \left[ (E - V)(v_{F}k)^{2} + (E + V)(V^{2} + \tau_{\perp}^{2} - E^{2}) \right].$$

The factor that controls the electron–hole asymmetry is easily identified:

$$\chi(E) = \frac{1}{g_{11}(E) - \frac{\hbar^{2}}{2v_{F}} \Gamma(k, E, -V)} \Gamma(k, E, V).$$

Remarkably, when the resonant scattering limit $V_{0} \to \infty$ is taken at nonzero bias $V \neq 0$, the $E \to -E$ invariance is not recovered. This is to be contrasted to the case of (i) resonant impurities acting on both layers, and (ii) resonant impurities in monolayer graphene, for which cross sections are electron–hole symmetric [6].

Solution in Regions I and III

In regions I and III, Eq. (18) admits two propagating poles because $A_{-} < 0$. This occurs because the Fermi level crosses the electronic bands at two distinct Fermi points; see Eq. (2) and comments therein. As a consequence the scalar propagator [Eq. (12)] is given by a superposition of two cylindrical waves (see Appendix A)

$$\Lambda_{0}^{(4)}(z, r)_{|E|>E_{H}} = \frac{1}{8v_{F}^{2}} \frac{1}{4E^{2}V^{2} + \tau_{\perp}^{2}(E^{2} - V^{2})} \left[ -iH_{0}(k_{+}|r|) + iH_{0}(k_{-}|r|) \right],$$

where

$$k_{\pm} = \frac{1}{v_{F}} \sqrt{(E^{2} + V^{2}) \pm \sqrt{4E^{2}V^{2} + \tau_{\perp}^{2}(E^{2} - V^{2})}}$$

denote the Fermi momenta. The expression for the propagator evaluated at the origin also changes because $A_{-} < 0$ [refer to Eqs. (19)-(20)]. The wavefunction of incident particles therefore admits two (degenerate) solutions.
where act as resonant impurities with a range conductivity limited by fluorine adatoms located in the

\[ \Delta \Psi_k (r, \theta) \bigg|_{B_2} = \sum_{\lambda=\pm} \Delta \Psi_k^{(\lambda)} (r, \theta) \bigg|_{B_2}, \]

(49)

with

Similar expressions hold for incoming waves with incoming momentum \( k_- \). The explicit form of \( \sigma_{\pm}(\theta) \) is

\[ \sigma_{\pm}(\theta) |_{k=\pm} \equiv \sigma_{\pm}(\theta) = \sigma_{++}(\theta) + \sigma_{+-}(\theta), \]

(51)

\[ \sigma_{\pm}(\theta) = r \frac{v_n^{\pm}}{|v_m(k_\pm)|}, \]

(52)

where

\[ v_n^{\pm}(r, \theta) = v_F \langle \Delta \Psi_k^{(\pm)} \rangle \begin{pmatrix} 0 & 0 & 0 & e^{i \theta} \\ 0 & 0 & e^{-i \theta} & 0 \\ e^{i \theta} & 0 & 0 \\ e^{-i \theta} & 0 & 0 \end{pmatrix} | \Delta \Psi_k^{(\pm)} \rangle. \]

(53)

\[ \sigma_{\pm}(\theta) \bigg|_{B_2} = \frac{1}{32 \pi k_\pm} \frac{1}{4 E^2 V^2 + t_2^2 (E^2 - V^2)} \frac{(k^2 t_2 k_\pm^2)^2}{\Gamma(k_\pm, E, V) + \Gamma(k_T, E, V)} \frac{\Gamma(k_\pm, E, -V)}{g_{11}(E) - \frac{k_2}{S V_0}}. \]

(54)

III. BOLTZMANN TRANSPORT FORMULATION IN BIASED BILAYER GRAPHENE

In this section we compute the Boltzmann de-

conductivity limited by fluorine adatoms located in the top layer. As discussed in the main text, fluorine adatoms act as resonant impurities with a range \( R \sim 0.4 \text{ nm} \). Such short-range impurities with \( R \gtrsim a_0 \)—where \( a_0 \) de-

notes the carbon-carbon distance—are well described by a potential matrix

\[ \nu^{(\top)} = V_0 \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \]

(55)

with the resonant limit \( V_0 \to \infty \) taken when appropriate [6]. The solution of the respective scattering problem is
In deriving the above formulae we have used the relations between the centres (computed in Sec. II) according to

\[ \sigma_{\text{dc}}(k_F) = \frac{2e^2}{h} \times \begin{cases} \frac{k_F}{n_{\text{ad}} \Sigma(k_F)} & \text{, region II} \\ \sum_{s=\pm} \frac{k_F^{(s)}}{n_{\text{ad}} \Sigma(k_F^{(s)})} & \text{, otherwise} \end{cases} \]  

(57)

with \( n_{\text{ad}} \) denoting the areal density of adatoms. The transport cross section is given by

\[ \Sigma(k_F^{(s)}) = \int_{0}^{2\pi} d\theta (1 - \cos \theta) |\sigma_s(\theta)|^2, \]  

(58)

given by Eq. (32) with \( a = d = 1 \) and \( b = c = 0 \). For example, in region II, one finds

\[ E(n) = \text{sign}(n) \times \begin{cases} \sqrt{\frac{h^2 v_F^2 \pi |n|}{2} + \frac{t_1^2}{4} + V^2 - \sqrt{\frac{t_1^4}{4} + h^2 v_F^2 \pi |n| (t_1^2 + 4V^2)}} & , |V| \leq |E(n)| \leq E_H \\ \sqrt{\frac{h^2 v_F^2 \pi |n|}{2} - V^2} - t_1 V^2 & , |E(n)| > E_H \end{cases} \]  

(59)

These expressions were used to make the plots of the dc-conductivity shown in the main text.
The density of states is formally given by
\[ \rho(E) = \frac{1}{D} \text{Tr} \delta(E - \hat{H}) , \]  
where \( \hat{H} \) is tight-binding Hamiltonian [8] and \( D \) is the dimension of the Hilbert space (i.e., number of lattice sites).

In the KPM approach, the—non-periodic—target function \( f(x) \) is expressed in terms of a complete set of orthogonal polynomials. First-kind Chebyshev polynomials \( \{T_n(x)\}_{n \in \mathbb{N}_0} \) are usually the best choice for systems with bounded spectrum [9, 46]. The use of Chebyshev polynomials requires rescaling the spectrum into the interval \( x \in [-1 : 1] \), where a polynomial expansion \( f(x) = \sum \alpha_n T_n(x) \) is defined with the following scalar product:
\[ \alpha_n \equiv \langle T_n | f \rangle = \int_{-1}^{1} \frac{dx}{\pi \sqrt{1 - x^2}} T_n(x) f(x) . \]  

Application to the average DOS [Eq. (61)] is straightforward and results in
\[ \rho(\epsilon) = \frac{2}{D \pi \sqrt{1 - \epsilon^2}} \sum_{n=0}^{\infty} \frac{1}{1 + \delta_{n,0}} \mu_n T_n(\epsilon) , \]  
where \( \epsilon \in [-1 : 1] \) is the rescaled energy, and the Chebyshev moments are given by \( \mu_n = \text{Tr} T_n(\hat{H}) \), where \( \hat{H} = \hat{H}/W \) and \( W \) is the half bandwidth of the biased bilayer system. In the KPM, the infinite sum in (63) is truncated and a kernel \( \{g_n\}_{n=0...N-1} \) is introduced to damp Gibbs oscillations [7]
\[ \rho_{\text{KPM}}(\epsilon) = \frac{2}{D \pi \sqrt{1 - \epsilon^2}} \sum_{n=0}^{N-1} \frac{g_n}{1 + \delta_{n,0}} \mu_n T_n(\epsilon) , \]  
where \( N \) depends on the desired resolution \( \eta \), usually \( N \propto W/\eta \). For the DOS we use the Jackson kernel due to its superior performance close to the Dirac point [6]
\[ g_n = \frac{(N-n+1) \cos \left( \frac{\pi n}{N+1} \right) + \cot \left( \frac{\pi}{N+1} \right) \sin \left( \frac{\pi n}{N+1} \right)}{N+1} . \]  

Finally, to compute the moments \( \mu_n \) efficiently we make use of the stochastic trace evaluation (STE) technique [10]. For large sparse matrices, the STE amounts to replace the trace \( \text{Tr} \) in Eq. (61) by the average with respect to a single random vector \( |R\rangle = \sum_{i=1...D} \chi_i |i\rangle \), that is, \( \text{Tr} T_n(\hat{H}) \rightarrow \langle R | T_n(\hat{H}) | R \rangle \). The latter is essential exact for large sparse systems because fluctuations can be shown to be of the order of \( D^{-1/2} \).

As explained in the main text, we model resonant adatoms by removing the corresponding \( p_z \) orbitals to
of Chebyshev polynomials, we rescale the energy variable so that \( \hat{\epsilon}_x = (i/\hbar)[\hat{H}, \hat{x}] \) is the \( x \)-th component of the velocity operator, \( g_s = 2 \) is a spin degeneracy factor, and \( \Omega \) stands for the area. In order to write \( \sigma_{dc}(E) \) in terms of Chebyshev polynomials, we rescale the energy variable and operators in (66) to get

\[
\sigma_{dc}(\epsilon) = \frac{\pi g_s \hbar e^2}{\Omega} \text{Tr} \left[ \hat{v}_x \delta(\epsilon - \hat{H}) \hat{v}_x \delta(\epsilon - \hat{H}) \right].
\]  

(67)

The above formula has support in the interval \([-1 : 1]\) and can now be written in terms of a KPM expansion as

\[
\sigma_{\text{KPM}}(\epsilon) = \frac{2g_s \hbar e^2}{\pi \Omega (1 - \epsilon^2)} \sum_{n,m=0}^{N-1} \Delta_{nm} \left[ T_{n+m}(\epsilon) + T_{|n-m|}(\epsilon) \right],
\]  

(68)

where the expansion coefficients

\[
\Delta_{nm} = \frac{g_n}{1 + \delta_{n,0}} + \frac{g_m}{1 + \delta_{m,0}} \text{Tr} \left[ \hat{v}_x T_n(\hat{H}) \hat{v}_x T_m(\hat{H}) \right],
\]  

(69)

are computed with the STE technique, and a Lorentz kernel [7]

\[
g_n = \frac{\sinh[\tilde{\eta}(N - n)]}{\sinh(\tilde{\eta}N)},
\]  

(70)

is used to approximate the delta functions appearing in Eq. (67) by Lorentzians with resolution \( \eta \equiv \tilde{\eta}W \). The computational cost of evaluating the matrix expansion coefficients in Eq. (69) is now substantially higher than computing DOS moments \( \mu_n = \text{Tr}T_n(\hat{H}) \), which in practice limits the size of systems we can tackle.

In Fig. 5 we show the Kubo dc-conductivity for a BLG system with \( \sim 20 \) million atoms [15]. The results disclose a conductivity plateau in the pseudo-gap region due to an impurity band formation, as found earlier in Ref. [6]. More importantly, the bias potential is seen to originate electron–hole asymmetry only for impurities restricted to a single layer, as discussed in the main text. Remarkably—away from the Dirac point—the conductivity displays the exact same trends as predicted by the semi-classical calculations. In particular, the linear response calculation shows that the increase of the conductivity upon increasing the bias field saturates in the electron sector \( (E_F > 0) \), exactly as predicted by the 4-band semi-classical model (Sec. III). The opposite trends are observed upon reversal of the bias sign (not shown), again as predicted by the semi-classical calculation.

Figure 5: Kubo dc-conductivity of a BLG system with \( D = 2 \times 3200^2 \) carbon atoms at selected bias values for 0.5% vacancy concentration [[(top panel) vacancies distributed in the right layer; (bottom panel) vacancies distributed in the both layers]. The calculation has \( N^2 = 1000^2 \) Chebyshev expansion coefficients and kernel resolution \( \eta = 15 \) meV. Other parameters as in Fig. 4.

Next we discuss the application of KPM to the calculation of the dc-conductivity. The starting point is the Kubo formula at zero temperature [11]

\[
\sigma_{dc}(E) = \frac{\pi g_s \hbar e^2}{\Omega} \text{Tr} \left[ \hat{v}_x \delta(E - \hat{H}) \hat{v}_x \delta(E - \hat{H}) \right],
\]  

(66)

which they hybridize [6]. The average DOS of real-size bilayer graphene system with dilute vacancies in the top layer computed with this powerful technique is shown in Fig. 4 for several values of the bias inter-layer potential.

**DC-Conductivity**

In Fig. 5 we show the Kubo dc-conductivity for a BLG system with \( \sim 20 \) million atoms [15]. The results disclose a conductivity plateau in the pseudo-gap region due to an impurity band formation, as found earlier in Ref. [6]. More importantly, the bias potential is seen to originate electron–hole asymmetry only for impurities restricted to a single layer, as discussed in the main text. Remarkably—away from the Dirac point—the conductivity displays the exact same trends as predicted by the semi-classical calculations. In particular, the linear response calculation shows that the increase of the conductivity upon increasing the bias field saturates in the electron sector \( (E_F > 0) \), exactly as predicted by the 4-band semi-classical model (Sec. III). The opposite trends are observed upon reversal of the bias sign (not shown), again as predicted by the semi-classical calculation.
V. APPENDIX A: CALCULATION OF THE PROPAGATOR IN COORDINATE SPACE

For completeness we show how to compute the integral

\[ \Lambda_0^{(4)}(u) = \int_0^\infty \frac{dp}{2\pi} \frac{J_0(pu)}{D(z,v_F p) + i\eta}, \quad u \equiv |u| > 0. \]  

(71)

The sign of the infinitesimal \( \eta \) is chosen as to guarantee that \( \Lambda_0^{(4)}(u) \) represents an outgoing wave. Using Eq. (18) we split the integral into two contributions \( \Lambda_0^{(4)}(u) = \Lambda_0^+(u) + \Lambda_0^-(u) \), where

\[ \Lambda_0^+(u) = \int_0^\infty \frac{dp}{2\pi a} \frac{J_0(pu)}{A_+ + v_F^2 p^2 + i0^+}, \]

(72)

and \( a = A_+ + A_- \) is a constant. The cases \( A_- \geq 0 \) have to be considered separately. When \( A_- > 0 \) (region II), the term \( \Lambda_0^-(u) \) reads

\[ \Lambda_0^-(u) = \int_0^\infty \frac{dp}{2\pi a} \frac{J_0(pu)}{A_- + v_F^2 p^2 + i0^+} = \frac{1}{a} K_0(\sqrt{A_-} u). \]

(73)

In the above we have made use of

\[ \int_0^\infty \frac{dp}{p^2 + z^2} = K_0(zu), \quad \text{for } Re z > 0, \]

(see, e.g., Eq. EH II 96(58), Ref. [12]), whereas for \( A_- < 0 \) (regions I and III) one finds [13]

\[ \Lambda_0^-(u) = \int_0^\infty \frac{dp}{2\pi a - |A_-| + v_F^2 p^2 + i0^+} = \frac{i\pi}{2a} H_0(\sqrt{|A_-|} u). \]

(74)

The term \( \Lambda_0^+(u) \) has the same form in all regions since \( A_+ > 0 \). We find

\[ \Lambda_0^+(u) = \int_0^\infty \frac{dp}{2\pi a} \frac{J_0(pu)}{A_+ - v_F^2 p^2 + i0^+} = \frac{i\pi}{2a} H_0(\sqrt{A_+} u). \]

(75)

The meaning of all these terms is clear. Eqs. (74)-(75) represent propagating waves with the characteristic two-dimensional asymptotic behavior \( \propto e^{ik_\perp \sqrt{k_\perp u}} \), whereas (73) encodes an evanescent mode.

VI. APPENDIX B: CALCULATION OF THE PRISTINE LDOS

The local density of states (LDOS) is formally given by

\[ \rho(E) = \frac{1}{\pi} \text{Im} \log \{|G(z,0)_{11}, ..., G(z,0)_{4,4}\}|_{z \rightarrow E + i0^+}. \]

(76)

From Eq. (4) we obtain the LDOS as an integral over the momentum variable

\[ \rho(E) = -\frac{1}{\pi} \text{Im} \int_{0}^{\infty} \frac{dp}{2\pi} \prod_{\lambda,\lambda' = \pm 1} \left[ E - e^{i\lambda' p} (v_F p) + i0^+ \right] \times \text{diag} \{|\Xi_{1+}(v_F p), \Xi_{1-}(v_F p), \Xi_{2+}(v_F p), \Xi_{2-}(v_F p)\} \].

(77)

Using the Sokhotski–Plemelj formula and evaluating the imaginary part we get after straightforward integrations

\[ \rho(E)_{1,1} = \left( t_1^2 + V^2 - E^2 \right)(E + V)\Phi^+ + (E - V)\Phi^- \]

(78)

\[ \rho(E)_{2,2} = \left( t_2^2 + V^2 - E^2 \right)(E - V)\Phi^+ + (E + V)\Phi^- \]

(79)

\[ \rho(E)_{3,3} = (E + V) \left[ \Phi_+^0 - (E - V)^2 \Phi^+ \right] \]

(80)

\[ \rho(E)_{4,4} = (E - V) \left[ \Phi_+^0 - (E + V)^2 \Phi^- \right] \]

(81)

with

\[ \Phi_+^0 = \frac{s_E}{4\pi v_F^2} \frac{1}{A_+ + A_-} \times \begin{cases} 1, & |V| \leq |E| \leq E_H \\ A_+ \end{cases}, \quad \begin{cases} 2, & \frac{\Delta}{2} < |E| < |V| \\ A_+ - A_- \end{cases}, \quad \begin{cases} 0, & |E| > E_H \\ A_+ + A_- \end{cases} \]

(82)
Explicitly,

\[
\Phi^+_{\Lambda} = \frac{s_E}{8 \pi v_F^2} \sqrt{4 E^2 V^2 + t_\perp^2 (E^2 - V^2)} \left\{ \begin{array}{ll}
\frac{1}{E^2 + V^2 + \sqrt{4 E^2 V^2 + t_\perp^2 (E^2 - V^2)}} & , |V| \leq |E| \leq E_H \\
\frac{2}{2 (E^2 + V^2)} & , \frac{\Delta}{2} < |E| < |V| \\
0 & , |E| > E_H
\end{array} \right. 
\]

where \(a(h)^\dagger_{i,L} \) creates quasiparticles in site \( i \) in sublattice \( A(B) \) at bottom/top layer \( L = 1, 2, t(t_\perp) \) is the \( A-B \) intra(inter)-layer hopping integral, and \( 2V \) is the potential difference across the layers. To distinguish electron–hole asymmetry induced by defects from band structure effects, intra- and inter-layer second-next-neighbor hoppings have been neglected [4].

[9] Chebyshev and Fourier Spectral Methods, Second Revised Edition, J. P. Boyd (Dover Publications, 2001).
[10] T. Itaka, and T. Ebisuaki, Phys. Rev. E 69, 057701 (2004).
[11] G. D. Mahan, Many-particle Physics, 3rd ed. (Springer, New York, 2000).
[12] I.S. Gradshteyn and I.M. Ryzhik. Table of Integrals, Series, and Products, 7th Edition (Elsevier, Academic Press, 2007)

[13] To obtain this result we make use of the analytic continuation

\[
\int_{0}^{\infty} dp \frac{J_0(p|r|)}{z^2 + p^2} \bigg|_{z = -ip_F + 0^+} = K_0(-ip_F |r| + 0^+) , \quad (83)
\]

where \( p_F = \sqrt{4 E_L} \). To express the result in terms of Hankel functions we use the connecting formula \( K_0(w) = \frac{i}{2} H_0(iw) \) [valid for \( -\pi < \text{Arg}(w) \leq \pi/2 \) (see e.g., http://dlmf.nist.gov/10.27)] to obtain the desired result

\[
\Lambda_0(r) = \frac{i \pi}{2} H_0(p_F |r|) . \quad (84)
\]

[14] L. L. Schif, Quantum Mechanics, 3rd ed. (McGraw–Hill, New York, 1968).
[15] In order to reach the diffusive regime we have artificially increased the concentration of impurities as compared to the experimental determined values.