Klein tunnelling and electron trapping in nanometre-scale graphene quantum dots

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1. Spiral pattern copper (111) reconstruction

In this section we briefly discuss the spiral pattern superlattice reconstruction of the Cu(111) underneath graphene which dominates the majority of our sample surface. Figure S1a displays a STM topograph from a typical CVD growth of graphene on single crystal Cu(111) [1,2]. A large wavelength Moiré superlattice is imaged due to the surface lattice constant mismatch between copper (111) (acu=2.55Å) and graphene (aG=2.46Å). We contrast this with the STM topograph in Fig. S1b of our epitaxially-grown graphene-Cu(111) samples
grown by a novel high-temperature CVD process [3]. The vast majority of the sample displays a long wavelength hexagonal superlattice of web-like spiral patterns as shown in Fig. S1b. (In addition to these spirals the majority surface is also decorated with bright features which we believe to be copper vacancies in the top-most layer of Cu(111).) Unlike the conventional Moiré patterns seen in Fig. S1a, these spiral patterns instead point to a dramatic reconstruction of the underlying Cu(111) whose topmost surface is epitaxially matched to the graphene lattice. Similar spiral reconstructions have been previously imaged with STM or theoretically calculated in graphene-Ru(0001) [4], epitaxial thin films of Cu-Ru(0001) [5, 6], and at the interface of Cu(111)/Ni(111) [7]. In all of these cases, the patterns arise when the surface or interface contains more atoms than the underlying bulk crystal (i.e. the topmost lattice constant is smaller). As the structure relaxes, it buckles and the spiral patterns emerge to minimize the surface energy. The presence of this surface reconstruction and the absence of a global Moiré structure strongly suggests that the graphene and topmost copper lattices are in perfect atomic registry.

Our graphene quantum dots (GQDs) are defined by rare patches of the Cu(111) substrate which are not epitaxially matched to graphene and thus do not reconstruct into these spiral patterns. For large GQDs, such as those shown in Fig. S2a,b and Fig. 1b of the main text, these patches display hexagonal Moiré patterns. Since the graphene is continuous and single-crystalline across the entire area of Fig. 1b, the differing Moiré patterns suggest that the Cu(111) in these patches are randomly oriented with respect to the graphene lattice above.

2. STM bias-dependent height of graphene quantum dots

Here we show that the apparent heights of the GQDs in STM topographs are not structural but are primarily due to variations in the local density of states (LDOS) on the GQDs. Figure
S1a shows a series of constant-current STM topographs on a GQD with radius \( R \approx 6.17 \) nm. At different tunneling bias energies, the apparent GQD height can either appear below \( (V_b = -200 \text{ mV}) \) or above \( (V_b = -350 \text{ eV}) \) the majority copper surface. There can be a significant difference between the two apparent heights \( (\sim 1.5\text{Å}) \) as seen in the line cuts shown in Fig. S1b. One can understand this by recalling that the tunneling current in STM measurements is proportional to the integrated LDOS [8]. Thus variations in the LDOS, for example due to the resonant states, can strongly affect the apparent STM tip height in STM topography. Importantly, we note that this energy-dependent topographic height is homogeneous inside of the GQD. This is a reflection of the homogeneous constant-height doping profile of the barrier substrate potential. The faint hexagonal pattern imaged inside the GQD is a Moiré pattern between graphene and the Cu(111).

3. Determination of Dirac point from \( dI/dV \) and field emission resonance spectroscopies

In this section we discuss how the Dirac point and, equivalently, the potential barrier height was measured on our GQDs and why field emission resonance (FER) spectroscopy was required. Figure S3 shows \( dI/dV \) spectra recorded on a GQD of radius \( R = 5.33 \) nm. At negative tunneling voltages, \( dI/dV \) curves probe the electronic valence band states and show a series of radial-dependent resonance peaks. Around the Fermi energy \( (E_F = 0 \text{ eV}) \) the curves display a graphene inelastic tunneling mode at \( \approx \pm 0.067 \text{ eV} \). At positive tunneling voltages, \( dI/dV \) curves probe the conduction band states and do not display any resonance peaks nor a clear signature of the ‘V’-shaped Dirac point. In cases where the Dirac point is close to inelastic tunneling modes, it can be difficult to ascertain the exact spot of the Dirac point [9]. Careful examination of our experimental \( dI/dV \) curves at the right edge of the positive inelastic tunneling mode (Fig. S3 inset) show a faint dip at \( E = h\omega_{ph} + E_{D}^{IN} \approx 0.208 \text{ eV} \). Since \( h\omega_{ph} \approx 0.067 \text{ eV} \), this would place the GQD Dirac point at \( E_{D}^{IN} \approx 0.14 \text{ eV} \). Outside
the barrier, the majority graphene-Cu(111) surface has a Dirac point of $E_D^{\text{OUT}} = -0.28$ eV, which yields a potential barrier height of $V_0 = E_D^{\text{IN}} - E_D^{\text{OUT}} = +0.42$ eV on the GQD.

However, as this faint dip could not be unambiguously attributed to the GQD Dirac point, and in order to make a good comparison to theoretical calculations, FER spectroscopy was required as a secondary measurement of the barrier height. As shown in Fig. 1d of the main text, $dz/dV$ curves recorded on and off the GQDs reveal a positive shift of $+0.42$ eV of the FER peaks recorded on the GQD. The correspondence between the peaks on each curve can also be shown by plotting the substrate $dz/dV$ spectra shifted by $+0.42$ eV (Fig. S4a). It is then clear from Fig. S4a that the three sets of FER peaks on and off the GQD are aligned after this shift. (The unpaired peak on the GQD (blue) curve at $E \approx 2.75$ eV only ever appears on GQDs and is independent of GQD size.) We note that the first set of peaks (named $1'$ and $1''$) appear split on both sets of curves measured on and off the GQD and can be fit with closely-spaced Lorentzians (Fig. S4b). A similar closely-spaced peak structure in the lowest FER resonance has been reported previously in [10].

4. Massless Dirac particle incident on a potential step

In this section we derive the solutions to the Dirac Hamiltonian in the presence of a radial step potential, a problem which has attracted much theoretical attention [11–16]. To model our system we begin with the linearized graphene Hamiltonian [17] but allow for finite doping to shift the Dirac point, $E_D$, away from the Fermi energy, $E_F$, which, for undoped graphene, $E_D = E_F$. For $E_D < E_F$ ($E_D > E_F$), the graphene is said to be $n$-doped ($p$-doped). In what follows we set $E_F = 0$ and we will focus on the dynamics near a single Dirac cone at $K_+$,

$$\mathcal{H}_0 = v_F \sigma \cdot p + E_D \sigma_0, \quad (S.1)$$

where $v_F \approx 10^6$ m/s is the Fermi velocity of graphene, and $\sigma_0$ is the identity matrix. Focusing on a single Dirac cone is valid since intervalley scattering between Dirac cones ($K/K'$) is
generally not observed on the GQDs (for the exception see Fig. S7) and the experimental potential step occurs over a distance \( L \sim 1 \text{ nm} \approx 4a \) (where \( a = 0.246 \text{ nm} \) is the graphene lattice constant). This is much shorter than the Fermi wavelength (\( \lambda_{\text{IN}} = 29.5 \text{ nm}; \lambda_{\text{OUT}} = 14.8 \text{ nm} \)) and so the step potential model is valid [11–16]. For a circular barrier of radius \( R \) the potential is given by,

\[
V = V(r)\sigma_0 = V_0\Theta(R - r)\sigma_0. \quad (S.2)
\]

where

\[
V(r) = \begin{cases} 
V_0, & \text{for } r \leq R \\
0, & \text{for } r > R.
\end{cases} \quad (S.3)
\]

The effect of the barrier is to raise (\( V_0 > 0 \)) or lower (\( V_0 < 0 \)) the Dirac point in graphene (Fig. 1a, main text), creating a circular NPN or PNP junction. The full Hamiltonian is then given by \( \mathcal{H} = \mathcal{H}_0 + \mathcal{V} \),

\[
\mathcal{H} = v_F\sigma \cdot \mathbf{p} + [V(r) + E_D]\sigma_0 = \begin{pmatrix} V(r) + E_D & v_Fp_- \\
v_Fp_+ & V(r) + E_D \end{pmatrix}, \quad (S.4)
\]

where \( p_\pm = p_x \pm ip_y \). We can put this into circular coordinates by writing the canonical momentum operators as

\[
p_\pm = \frac{\hbar}{i} e^{i\phi} \left( \partial_r \pm \frac{i}{r} \partial_\phi \right). \quad (S.5)
\]

Applying the Hamiltonian Eq. (S.4) on a two-component wavefunction, \( \psi = (A, B)^T \), yields a set of coupled eigenvalue equations

\[
\begin{align*}
\xi A &= \frac{\hbar v_F}{i} e^{-i\phi} \left( \partial_r - \frac{i}{r} \partial_\phi \right) B, \\
\xi B &= \frac{\hbar v_F}{i} e^{+i\phi} \left( \partial_r + \frac{i}{r} \partial_\phi \right) A,
\end{align*} \quad (S.6, S.7)
\]

where \( \xi = E - E_D - V(r) \).

We now seek the proper eigenfunction solutions. Since the potential has radial symmetry
one would immediately seek out solutions that conserve angular momentum, $L_z = (r \times p)_z$. However, it turns out $L_z$ is not a good quantum number since $[L_z, \mathcal{H}] = i\hbar \varepsilon_{xyz} \sigma_z p_y$, where $\varepsilon_{xyz}$ is the Levi-Civita symbol [16]. If one instead looks at the $z$-component of the total angular momentum, $J_z = L_z + \frac{\hbar}{2} \sigma_z$, including the sublattice isospin $\sigma$, then one can easily find that $[J_z, \mathcal{H}] = 0$. We thus look for eigenfunctions of $J_z = L_z + \frac{\hbar}{2} \sigma_z$ with eigenvalues $m = l + 1/2 = \pm 1/2, \pm 3/2, \ldots$, where $l = 0, \pm 1, \pm 2, \ldots$.

We can then separate variables in the wavefunctions $A$ and $B$ by making the ansatz [11–16]

$$
\psi = e^{im\phi} \begin{pmatrix} \chi_A(r) e^{-i\phi/2} \\ i\chi_B(r) e^{i\phi/2} \end{pmatrix} = e^{i(m-1/2)\phi} \begin{pmatrix} \chi_A(r) \\ i\chi_B(r)e^{i\phi} \end{pmatrix},
$$

(S.8)

where $(m - 1/2) = l$ is an integer. Note that the phase factor of $e^{\mp i\phi/2}$ in the sublattice A and B wavefunctions derives from the honeycomb structure of graphene and is responsible for the $\pi$ Berry phase of graphene electrons [17]. Using this form of the wavefunction leads to

$$
\xi \chi_A = \hbar v_F \left( \partial_r + \frac{m - 1/2}{r} \right) \chi_B
$$

(S.9)

$$
\xi \chi_B = -\hbar v_F \left( \partial_r - \frac{m + 1/2}{r} \right) \chi_A.
$$

(S.10)

We can de-couple these by applying each equation to the other. This gives two separate Bessel equations of order $(m - 1/2)$ and $(m + 1/2)$, respectively, where $m = \pm 1/2, \pm 3/2, \pm 5/2, \ldots$ is an odd half-integer,

$$
0 = \left\{ \partial_r^2 + \frac{1}{r} \partial_r - \frac{(m - 1/2)^2}{r^2} + \kappa^2 \right\} \chi_A(r)
$$

(S.11)

$$
0 = \left\{ \partial_r^2 + \frac{1}{r} \partial_r - \frac{(m + 1/2)^2}{r^2} + \kappa^2 \right\} \chi_B(r).
$$

(S.12)
Here

\[ \kappa = \begin{cases} 
q = \frac{E - E_D - V_0}{\hbar v_F}, & \text{for } r \leq R, \\
k = \frac{E - E_D}{\hbar v_F}, & \text{for } r > R.
\end{cases} \tag{S.13} \]

For clarity, in the following we choose to perform the infinite sums and expansions over the integer \( l = m - 1/2 \) before replacing the explicit \( m \)-dependence at the very end. We solve the radial Klein tunneling problem using the geometry of [11, 15, 16]. An electron is incident in the \( x \)-direction. The Jacobi-Anger expansion [18] of the incident plane wave is

\[ \psi_i = \frac{e^{ikx}}{\sqrt{2}} \left( \frac{1}{\alpha} \right) = \frac{e^{ikr \cos \phi}}{\sqrt{2}} \left( \frac{1}{\alpha} \right) = \frac{1}{\sqrt{2}} \sum_{l=-\infty}^{\infty} i^l J_l(kr) e^{il\phi} \left( \frac{1}{\alpha} \right), \tag{S.14} \]

where \( l \) is an integer, \( J_l \) is the Bessel function of the first kind, and \( \alpha = \text{sgn}(E - E_D) \) takes care of the proper sign of the sublattice-B wavefunction for electrons/holes [17]. We can rewrite the infinite sum for the sublattice-B wavefunction to match the right side of Eq. (S.8)

\[ \psi_i = \frac{1}{\sqrt{2}} \sum_{l=-\infty}^{\infty} i^l \left\{ J_l(kr) e^{il\phi} \left( \frac{1}{0} \right) + i\alpha J_{l+1}(kr) e^{i(l+1)\phi} \left( 0 \right) \right\} \tag{S.15} \]

\[ \psi_i = \frac{1}{\sqrt{2}} \sum_{l=-\infty}^{\infty} i^l \left( J_l(kr) e^{il\phi} \right) \tag{S.16} \]

Outside the barrier, the reflected wave (at \( r \to \infty \)) should behave as an outgoing free particle (\( \sim e^{-ikr} \)) and so the solution of Eqs. (S.11) an (S.12) is given by Hankel’s function of the first kind, \( H_l^{(1)}(kr) \),

\[ \psi_r = \frac{1}{\sqrt{2}} \sum_{l=-\infty}^{\infty} i^l R_l \left( \frac{H_l^{(1)}(kr) e^{il\phi}}{i\alpha H_{l+1}^{(1)}(kr) e^{i(l+1)\phi}} \right) \tag{S.17} \]

and the \( R_l \)’s are the \( l \)-dependent reflection coefficients.
The transmitted electron inside the barrier must have a wavefunction that is finite at $r = 0$ and so is satisfied by Bessel’s function of the first kind, $J_l(qr)$,

$$\psi_t = \frac{1}{\sqrt{2}} \sum_{l=-\infty}^{\infty} i^l T_l \left( J_l(qr)e^{il\phi} + \alpha' J_{l+1}(qr)e^{i(l+1)\phi} \right),$$  \hspace{1cm} (S.18)

where the $T_l$’s are the $l$-dependent transmission coefficients and $\alpha' = \text{sgn}(E - E_D - V_0)$ takes care of the proper sign of the sublattice-B wavefunction for electrons/holes inside the barrier. Continuity of the wavefunction at the boundary of the barrier

$$\psi_t(kR) + \psi_r(kR) = \psi_t(qR)$$  \hspace{1cm} (S.19)

and matching coefficients term-by-term leads to the determination of the reflection and transmission coefficients

$$R_l = \frac{-J_l(qR)J_{l+1}(kR) + \alpha' J_l(kR)J_{l+1}(qR)}{J_l(qR)H_{l+1}^{(1)}(kR) - \alpha' J_{l+1}(qR)H_{l}^{(1)}(kR)}$$ \hspace{1cm} (S.20)

$$T_l = \frac{J_l(kR)H_{l+1}^{(1)}(kR) - J_{l+1}(kR)H_{l}^{(1)}(kR)}{J_l(qR)H_{l+1}^{(1)}(kR) - \alpha' J_{l+1}(qR)H_{l}^{(1)}(kR)}.$$  \hspace{1cm} (S.21)

Note that both $R_l$ and $T_l$ have the same denominator. Resonant states—which coincide at the same energy $E$ both inside and outside the barrier—occur when the denominator vanishes, i.e. $R_l$ and $T_l$ are sharply-peaked. Thus the resonance condition is

$$0 = J_l(qR)H_{l+1}^{(1)}(kR) - \alpha' J_{l+1}(qR)H_{l}^{(1)}(kR),$$  \hspace{1cm} (S.22)

which was previously calculated in $[13, 15, 16]$. 
It is now useful to return the explicit $m$-dependence,

$$R_m = \frac{-J_{m-1/2}(qR)J_{m+1/2}(kR) + \alpha' J_{m-1/2}(kR)J_{m+1/2}(qR)}{J_{m-1/2}(qR)H_{m+1/2}^{(1)}(kR) - \alpha' J_{m+1/2}(qR)H_{m-1/2}^{(1)}(kR)} \quad (S.23)$$

and

$$T_m = \frac{J_{m-1/2}(kR)H_{m+1/2}^{(1)}(kR) - J_{m+1/2}(kR)H_{m-1/2}^{(1)}(kR)}{J_{m-1/2}(qR)H_{m+1/2}^{(1)}(kR) - \alpha' J_{m+1/2}(qR)H_{m-1/2}^{(1)}(kR)}. \quad (S.24)$$

Recalling that $Z_{-n} = (-1)^n Z_n$ (where $Z_n$ is a Bessel or Hankel function), one sees immediately that $R_m = R_{-m}$ and $T_m = T_{-m}$ and that the resonant states are twofold degenerate for $m \to -m$. This degeneracy is not due to the circular symmetry of the barrier, but instead is a result of the Kramer’s degeneracy due to time-reversal invariance of the Hamiltonian in Eq. (S.4) (ref. [14]).

In summary, the incident, reflected, and transmitted wavefunctions can be written, replacing the explicit total angular momentum $m$ number,

$$\psi_i = \frac{1}{\sqrt{2}} \sum_{m=\pm1/2,\pm3/2,...} i^{m-1/2} e^{im\phi} \begin{pmatrix} J_{m-1/2}(kR)e^{-i\phi/2} \\ i\alpha J_{m+1/2}(kR)e^{i\phi/2} \end{pmatrix} \quad (S.26)$$

$$\psi_r = \frac{1}{\sqrt{2}} \sum_{m=\pm1/2,\pm3/2,...} i^{m-1/2} R_m e^{im\phi} \begin{pmatrix} H_{m-1/2}^{(1)}(kR)e^{-i\phi/2} \\ i\alpha H_{m+1/2}^{(1)}(kR)e^{i\phi/2} \end{pmatrix} \quad (S.27)$$

$$\psi_t = \frac{1}{\sqrt{2}} \sum_{m=\pm1/2,\pm3/2,...} i^{m-1/2} T_m e^{im\phi} \begin{pmatrix} J_{m-1/2}(qR)e^{-i\phi/2} \\ i\alpha' J_{m+1/2}(qR)e^{i\phi/2} \end{pmatrix} \quad (S.28)$$

We can image these states by calculating $|\Psi(r, E)|^2 \propto LDOS(r, E)$, where $\Psi$ is the total wavefunction, both inside and outside the barrier.
In Fig. 3b of the main text we plot the radial (or “angular”) average of this quantity

\[
\langle |\Psi|^2 \rangle = \frac{1}{2\pi} \int_0^{2\pi} |\Psi|^2 d\phi.
\]  

(S.29)

The radially-averaged wavefunction squared inside and outside the barrier is then given by

\[
\langle |\Psi(r, E)|^2 \rangle_{\text{in}} = \frac{1}{2} \sum_{m=\pm1/2, \pm3/2, \ldots} |T_m|^2 \left( J_{m-1/2}^2(qr) + J_{m+1/2}^2(qr) \right)
\]

(S.30)

\[
\langle |\Psi(r, E)|^2 \rangle_{\text{out}} = \frac{1}{2} \sum_{m=\pm1/2, \pm3/2, \ldots} \left( |L_-(kr)|^2 + |L_+(kr)|^2 \right),
\]

(S.31)

where we used the short-hand notation

\[
L_-(kr) = J_{m-1/2}(kr) + R_m H_{m-1/2}^{(1)}(kr)
\]

(S.32)

\[
L_+(kr) = J_{m+1/2}(kr) + R_m H_{m+1/2}^{(1)}(kr)
\]

(S.33)

We calculate the above quantities up to a maximum angular momentum quantum number of \(|m_{\text{max}}| = 61/2\). To account for the (negative) \(\hbar\omega_{\text{ph}} \approx 0.067\) eV shift of the resonant energies due to the graphene inelastic tunneling channel [9] that is present in the experimental data, we use a Dirac point of \(E_D' = E_D^{\text{OUT}} - \hbar\omega_{\text{ph}} = -0.28 - 0.067 = -0.347\) eV in our calculations. Here, \(E_D^{\text{OUT}}\) is the Dirac point measured outside the GQD where there is very little to no signal from the inelastic mode (Fig. 2a).

If only a single mode \(m\) is excited then Eqs. (S.30, S.31) can be written as [15, 16]

\[
\langle |\Psi(m, r, E)|^2 \rangle_{\text{in}} = \frac{1}{2} |T_m|^2 \left( J_{m-1/2}^2(qr) + J_{m+1/2}^2(qr) \right) \quad \text{for } r \leq R
\]

(S.34)

\[
\langle |\Psi(m, r, E)|^2 \rangle_{\text{out}} = \frac{1}{2} \left( |L_-(kr)|^2 + |L_+(kr)|^2 \right) \quad \text{for } r > R
\]

(S.35)

The above are used to calculate the partial local density of states (pLDOS) maps displayed in Fig. 3d in the main text.
5. **Massless spinless boson incident on a circular step**

As a comparison to the previous section, we consider now a hypothetical graphene electron that has been stripped of its sublattice spinor structure and instead has a scalar wavefunction [19]. Such spinor-less, Klein-Gordon solutions have been used effectively to model bound states in finite-sized graphene islands (i.e. hard wall confinement, \(|V_0| \to \infty\), and \(\psi(r = R) = 0\)) in past STM experiments [20–23]. However, as shown in Fig. 3a-c in the main text, such spinor-less solutions cannot describe the quasibound states for moderate barrier heights. Below we describe the derivation used to calculate the simulation in Fig. 3c.

Recall that relativistic spinless particles are described by the second-order Klein-Gordon equation

\[
[E - V(r)]^2 \psi(r) = \left[p^2 c^2 + m_e^2 c^4\right] \psi(r),
\]

where \(m_e\) is the electron mass and \(c\) is the speed of light in vacuum.

To describe our hypothetical scalar graphene electron at low energies we set the effective electron mass to zero, \(m_e = 0\), \(c = v_F\), and we measure the energy relative to the Dirac point, \(E_D\), to account for finite doping. Setting \(p = -i\hbar \nabla\) gives,

\[
[E - E_D - V(r)]^2 \psi(r) = -\hbar^2 v_F^2 \nabla^2 \psi(r),
\]

where the potential, \(V(r)\), is given in Eq. (S.3). In the absence of isospin, the orbital angular momentum is conserved and so we look for solutions of the form \(\psi(r, \phi) = e^{il\phi} \chi(r)\), where \(l\) is an integer angular momentum quantum number. As in the previous section, in radial coordinates this can be written

\[
0 = \left\{ \partial_r^2 + \frac{1}{r} \partial_r - \frac{l^2}{r^2} + \kappa^2 \right\} \chi(r),
\]

which reproduces Eq. (S.11). We can then inherit the solutions for the sublattice-A wave-

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function from the previous section

\[ \psi_i = \sum_{l=-\infty}^{\infty} i^l J_l(kr) e^{il\phi}, \tag{S.39} \]
\[ \psi_r = \sum_{l=-\infty}^{\infty} i^l R_l H_l^{(1)}(kr) e^{il\phi}, \tag{S.40} \]
\[ \psi_t = \sum_{l=-\infty}^{\infty} i^l T_l J_l(qr) e^{il\phi}, \tag{S.41} \]

where, as before, \( R_l \) \((T_l)\) are the reflection (transmission) coefficients. In order to solve for the two unknown expansion coefficients, \( R_l \) and \( T_l \), we match both the wavefunction and its first derivative at the boundary,

\[ \psi_i(kR) + \psi_r(kR) = \psi_t(qR) \tag{S.42} \]
\[ \partial_r \psi_i(kr)\big|_{r=R} + \partial_r \psi_r(kr)\big|_{r=R} = \partial_r \psi_t(qr)\big|_{r=R}. \tag{S.43} \]

Matching these term-by-term gives the scattering coefficients for a scalar graphene electron

\[ R_l = \frac{-kJ_l(qR)J'_l(kR) + qJ_l(kR)J'_l(qR)}{kJ_l(qR)H'_l(kR) - qJ'_l(qR)H_l(kR)}, \tag{S.44} \]
\[ T_l = \frac{kJ_l(kR)H'_l(qR) - kJ'_l(kR)H_l(kR)}{kJ_l(qR)H'_l(kR) - qJ'_l(qR)H_l(kR)}. \tag{S.45} \]

(Note that \( H_l \) refers to Hankel’s function of the first kind.) The resonance condition occurs when the denominator vanishes,

\[ 0 = kJ_l(qR)H'_l(kR) - qJ'_l(qR)H_l(kR). \tag{S.46} \]

One could also easily derive this by comparing the Dirac equation boundary condition, Eq.
where primes on the Bessel and Hankel functions denote first derivatives with respect to the radial coordinate and $H_I$ is Hankel’s function of the first kind.

6. Assignment of angular momentum modes to experimental data

The angular momentum quantum numbers in Fig. 3d of the main text were assigned to particular resonant modes in the experimental $dI/dV$ map in Fig. 3a by a close comparison with the solution of the continuum Dirac equation (see Section 4). Figure S5 reproduces Fig. 3 of the main text with pertinent features in the experimental data highlighted with oval symbols (Fig. S5a). These features consist of a series of peaks in the LDOS that shift from the center of the GQD and move towards the edges with decreasing energy as well as subtle features in the center of the GQD which appear as a vertical oval with “mouse ears” (see yellow dotted triangular region in Fig. 3a of the main text). By simply superimposing these symbols from experiment over the continuum Dirac solution, one finds a very good correspondence between experiment and Dirac theory (Fig. S5b). Notably, this process fails for the Klein-Gordon solution which describes electrons with a spinless, gap-less, linear dispersion (Fig. S5c). Calculating the individual resonant $m$-modes (using Eqs. S.34, S.35) both strong and subtle features can then be assigned to the resonance of a particular angular momentum mode (Fig. S5d). We note that the “double-lobes” in the structure of the $|m| = 1/2$ mode, in theory, appear closer in energy than is found in experiment
(shown schematically with black arrows in Fig. S5b,d). This may indicate that the lowest resonant mode is more sensitive to the asymmetry in the GQD shape and/or its specific edge terminations (zigzag, armchair).

7. **Sublattice symmetry and asymmetry**

Inspection of the solutions to the Dirac equation for the radial square potential, Section 4 Eqs. (S.23-25), shows that the resonant m-states have different radial wavefunctions on each sublattice. For example, for \( m = 1/2 \), the radial solutions inside the dot give

\[
\psi_{1/2} = \frac{1}{\sqrt{2}} T_{1/2} \begin{pmatrix} J_0(qr) \\ i\alpha' J_1(qr)e^{i\phi} \end{pmatrix}, \tag{S.50}
\]

which gives a spatial probability density of

\[
|\psi_{1/2}|^2 = |T_{1/2}|^2 (J_0^2(qr) f_A + J_1^2(qr) f_B), \tag{S.51}
\]

where \( f_A, f_B \) are atomic triangular lattices describing the \( A, B \) sublattices of graphene. Since the Bessel functions \( J_0 \) and \( J_1 \) have different spatial geometries, one would surmise that the resonant mode creates a sublattice asymmetry. However, as mentioned in Section 4, the resonant states are twofold degenerate. A similar calculation for \( m = -1/2 \) gives

\[
|\psi_{-1/2}|^2 = |T_{-1/2}|^2 (J_{-1}^2(qr) f_A + J_0^2(qr) f_B) = |T_{1/2}|^2 (J_1^2(qr) f_A + J_0^2(qr) f_B), \tag{S.52}
\]

where

\[
|\psi_{-1/2}|^2 = |T_{-1/2}|^2 (J_{-1}^2(qr) f_A + J_0^2(qr) f_B) = |T_{1/2}|^2 (J_1^2(qr) f_A + J_0^2(qr) f_B), \tag{S.53}
\]
where in the last line we used that $T_m = T_{-m}$ and $J_m^2 = J_{-m}^2$. Since the two resonant states are degenerate, what is recorded with $dI/dV$ mapping is given by the sum,

$$|\psi_{\text{tot}}|^2 = |\psi_{1/2}|^2 + |\psi_{-1/2}|^2 \tag{S.54}$$

$$|\psi_{\text{tot}}|^2 = |T_{1/2}|^2 \left( J_0^2(qr) + J_1^2(qr) \right) (f_A + f_B), \tag{S.55}$$

and so the wavefunctions have equal amplitudes, and thus should appear as a honeycomb lattice.

In an attempt to understand the apparent sublattice asymmetry in Fig. 5a,b of the main text we use the above discussion to simulate the resonant modes for the N1 state ($m = \pm 1/2$) and the N2 state ($m = \pm 3/2$) for a graphene quantum dot of $R = 2.76$ nm, $V_0 = +0.42$ eV, and Dirac point $E_D' = E_D - \hbar \omega_{ph} = -0.347$ eV. The constituent $m$-mode simulations and their sums are shown in Figs. S6a, b for the N1, N2 resonant states, respectively. The sum of the degenerate $m$-modes (Figs. S6c,d) indeed display a honeycomb lattice. This differs from the experimental $dI/dV$ maps (Figs. S6e,f) which instead display a sublattice asymmetry. While the origin of this apparent sublattice asymmetry is currently not well understood, we do not believe it is due to an artifact of the STM tip as the simultaneously-recorded topography maps (Figs. S7a,c) display a clear honeycomb lattice (cf. [24]) and reproducible $dI/dV$ spectra (Fig. 5d) displaying the graphene inelastic mode [9].

8. Linear dispersion for resonant Klein states

In this section we show that, by making a simple estimation, the resonant energies for all our GQDs follow a linear dispersion curve. We do this by assuming that the quantum wells perfectly trap the electrons, i.e. the wavefunction vanishes at GQD radius, $\psi(r = R) = 0$. This is the well-known particle-in-a-box problem [20–23]. The solutions are the Bessel functions of the first kind, $0 = J_n(k_{n,i}r)$, where the perfect trapping potential enforces the quantization condition $k_{n,i} = x_{n,i}/R$ where $x_{n,i}$ is the $i$th zero of the $n$th Bessel function. In
Fig. S8 we plot the resonant energies for all 15 GQD measured as a function of these $k_{n,i}$ for the four lowest Bessel zeros ($i = 1$ and $n = 0, 1, 2, 3$). The resonant energies were corrected for the negative shift of $\hbar \omega_{ph} \approx 0.067$ eV (when applicable) due to the phonon-assisted inelastic tunneling mode inside the GQD [9]. In Fig. S8 we plot the corrected energies $E' = E_{\exp} + \hbar \omega_{ph}$, where $E_{\exp}$ is the experimentally observed resonant energy. Error bars of $\pm \hbar \omega_{ph}/2$ were used for states that displayed this inelastic mode and $\pm \hbar \omega_{ph}$ for those that did not.

Figure S8 shows a clear linear dispersion relation for the resonant states on the GQDs. A linear fit gives a value for the Fermi velocity of $v_F = (0.86 \pm 0.05) \times 10^6$ m/s, which, considering the crudeness of the perfect trapping approximation, is in fair agreement with the bulk photoemission value of $v_F^{\text{ARPES}} = (1.04 \pm 0.03) \times 10^6$ m/s (ref. [3]). The $y$-intercept of the linear fit gives a value for Dirac point inside the GQD of $E_D^{\text{fit}} = 0.098 \pm 0.035$ eV, which is close (with error) to the expected value of $E_D^{\text{IN}} \approx 0.14$ eV from $dI/dV$ spectroscopy and field emission resonance (FER) peak shifts (see main text).
Fig. S8 we plot the resonant energies for all 15 GQD measured as a function of these $k_{n,i}$ for the four lowest Bessel zeros ($i = 1$ and $n = 0, 1, 2, 3$). The resonant energies were corrected for the negative shift of $\Delta \phi \approx 0.067$ eV (when applicable) due to the phonon-assisted inelastic tunneling mode inside the GQD [9]. In Fig. S8 we plot the corrected energies $E_0 = E_{\text{exp}} + \Delta \phi$, where $E_{\text{exp}}$ is the experimentally observed resonant energy. Error bars of $\pm \Delta \phi/2$ were used for states that displayed this inelastic mode and $\pm \Delta \phi$ for those that did not.

Figure S8 shows a clear linear dispersion relation for the resonant states on the GQDs. A linear fit gives a value for the Fermi velocity of $v_F = (0.86 \pm 0.05) \times 10^6$ m/s, which, considering the crudeness of the perfect trapping approximation, is in fair agreement with the bulk photoemission value of $v_{\text{ARPES}} = (1.04 \pm 0.03) \times 10^6$ m/s (ref. [3]). The $y$-intercept of the linear fit gives a value for Dirac point inside the GQD of $E_{\text{fit}}D = 0.098 \pm 0.035$ eV, which is close (with error) to the expected value of $E_{\text{IN}D} = 0.14$ eV from $dI/dV$ spectroscopy and field emission resonance (FER) peak shifts (see main text).

Figure S1: a, STM topography image ($V_b = 0.6$ V, $I = 1$ nA) of graphene grown on single crystal Cu(111) by the typical CVD process showing the typical Moire pattern. b, STM topograph ($V_b = -0.02$ V, $I = 80$ pA) of our epitaxial graphene-Cu(111) foil detailing the spiral pattern reconstruction of the Cu(111) substrate underneath graphene. The bright, atomic features (~50-80 pm tall) peppering the surface are vacancies in the Cu(111) substrate.
Figure S2: a, STM topographs of a GQD recorded at two different tunneling voltages ($I = 80$ pA in both) showing that the variations in the apparent heights of the GQDs in the main text are not structural, but are due to strong variations in the local density of states. The hexagonal pattern inside the GQD is a Moiré pattern which does not disperse with energy. b, Linecuts of the topographs in a show that the height difference can be as much as 1.5 Å.
Figure S3: Experimental \( \frac{dI}{dV} \) spectra recorded on a GQD of radius \( R = 5.33 \) nm. (Set-point conditions: \( V_b = -0.8 \) V, \( I_s = 150 \) pA.) Curves have been vertically offset for clarity. Spectra display resonance peaks at negative energies pertaining to quasibound valence band (filled) states as well as a gap-like graphene inelastic tunneling mode at \( \pm \hbar \omega_{\text{ph}} \approx 0.067 \) eV around the Fermi energy (\( E_F = 0 \) eV). At positive energies there are no resonance peaks and no clear ‘V’-shaped Dirac point. Inset: A zoom-in view of the spectra near the positive edge of the graphene inelastic tunneling mode. A subtle drop in the \( \frac{dI}{dV} \) curves is seen at energy \( E = \hbar \omega_{\text{ph}} + E_{\text{IN}}^D = 0.208 \) eV yielding a GQD Dirac point of \( E_{\text{IN}}^D \approx +0.14 \) eV.
Figure S4: a, The same experimental dZ/dV spectra from Fig. 1d of the main text displaying field emission resonance (FER) peaks on and off a GQD. Here the spectra have been vertically offset and the substrate curve (red) has been shifted in energy by +0.42 eV to make a better visual correspondence between the salient features in the two spectra. The chief peaks in both spectra are well-aligned after this energy shift, confirming the value of the GQD barrier height energy of $V_0 = +0.42$ eV. The lone unpaired peak at $E \approx 2.75$ eV on the GQD (blue) spectra is only measured on GQDs. b, Detailed view of the closely-spaced peaks in the lowest FER peak (deemed 1’ and 1”) on the GQD (top, blue curve) and off the GQD (bottom, red curve) and fitting results using Lorentzian functions. Note that the spectra recorded off the GQD in b has not been shifted in energy. (Setpoint conditions: $V_s = 1$ V, $I_s = 150$ pA.)
Figure S5: a, Radially averaged spectroscopic $dI/dV$ map of a GQD of radius $R = 5.93$ nm. Key features in the map have been highlighted by colours pertaining to individual angular momentum quantum numbers in d. b, Solution of the continuum Dirac equation for a circular barrier of radius $R = 5.93$ nm and step height $V_0 = +0.42$ eV. The coloured symbols from a have been superimposed over the solution, showing excellent agreement. Only the $|m| = 1/2$ features (white ovals) have been slightly shifted closer in energy (displayed with black arrows) to match theory. c, Solution of the Klein-Gordon equation for a circular barrier as in b. A translation of the experimental features onto this solution shows no agreement. d, Decomposition of the Dirac solution for the four lowest resonant modes. Key features in the maps have been highlighted and colour-coded by the angular momentum quantum number $m$. 
Figure S6: Local density of states (LDOS) simulations of the (a) N1 ($m = \pm 1/2$) and (b) N2 ($m = \pm 3/2$) resonant modes for a GQD of radius $R = 2.76$ nm and potential barrier $V_0 = +0.42$ eV. A clear sublattice asymmetry is imaged. The sum of the degenerate $m$ modes in a, b are shown in c, d and display a restoration of the honeycomb sublattice symmetry. For comparison, corresponding experimental constant-current $dI/dV$ maps of a GQD of radius $R = 2.76$ nm are shown in e, f. Note the sublattice asymmetry in the experimental maps which appear as a triangular lattice. Dashed lines in a-d outline the edge of the GQD.
Figure S7: Simultaneously acquired STM topographies and dI/dV maps of the N1 (a and b) and N2 (c and d) resonant modes for the GQD displayed in Fig. 5 of the main text. e-h, The corresponding 2D Fourier transforms of the real-space STM images in a-d. Graphene atomic Bragg peaks are highlighted with blue circles. Interestingly, the dI/dV map of the N1 mode in f shows a clear (\(\sqrt{3} \times \sqrt{3}\))R30 pattern indicative of intervalley scattering. (Tunneling conditions: \(V_b = -0.367\) V, \(I = 150\) pA in a, b; \(V_b = -0.608\) V, \(I = 150\) pA in c, d.)
Figure S8: A plot of the resonant energies and corresponding wavevectors (using the perfect trapping approximation) for every GQD in this study. We plot the four lowest resonant energies, N1-N4. The results of the linear fit are shown.
References


