Transition to Landau Levels in Graphene Quantum Dots

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We investigate the electronic eigenstates of graphene quantum dots of realistic size (i.e., up to 80 nm diameter) in the presence of a perpendicular magnetic field $B$. Numerical tight-binding calculations and Coulomb-blockade measurements performed near the Dirac point exhibit the transition from the linear density of states at $B = 0$ to the Landau level regime at high fields. Details of this transition sensitively depend on the underlying graphene lattice structure, bulk defects, and localization effects at the edges. Key to the understanding of the parametric evolution of the levels is the strength of the chiral-symmetry breaking $K-K'$ scattering. We show that the parametric variation of the level variance provides a quantitative measure for this scattering mechanism. We perform measurements of the parametric motion of Coulomb blockade peaks as a function of magnetic field and find good agreement. We thereby demonstrate that the magnetic-field dependence of graphene energy levels may serve as a sensitive indicator for the properties of graphene quantum dots and, in further consequence, for the validity of the Dirac-picture.

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I. INTRODUCTION

Graphene nanostructures attract increasing attention mainly due to their potential applications in high mobility electronics and solid state quantum information processing. In particular, low nuclear spin concentrations expected in graphene promise long spin lifetimes and make graphene quantum dots (QDs) interesting for spin-qubit operations. Moreover, graphene nanostructures may allow to investigate phenomena related to massless Dirac Fermions in reduced dimensions. Intensive research has been triggered by the unique electronic properties of graphene including the gapless linear dispersion, and the unique Landau level (LL) spectrum. Recent advances in fabricating width-modulated graphene nanoribbons have helped to overcome intrinsic difficulties in creating tunneling barriers and confining electrons in graphene, where transport is dominated by Klein tunneling-related phenomena. Graphene QDs have been fabricated and Coulomb blockade quantum confinement and charge detection have been demonstrated.

In this article, we focus on the eigenenergies of graphene quantum dots (see Fig. 1(a)) as a function of a perpendicular magnetic field. In graphene, the linear band crossing at the so-called Dirac point suggests a close connection between the dynamics of electrons and free, ultrarelativistic Dirac particles. One might therefore expect a magnetic-field dependence of quantum dot eigenenergies that closely mirrors that of massless Dirac particles. Indeed, this connection has been used recently to discuss the spectrum of ideal, circular graphene dots with smooth confinement. However, in more realistic models of finite graphene nanostructures, quantum confinement, edge effects, and lattice defects introduce a host of competing length scales absent from the simple Dirac picture. The magnetic-field dependence of the addition spectrum has been exploited in recent work to (approximately) pin down the electron-hole crossover point and disorder. In the present paper we report on a systematic study of the $B$-field dependence of electronic eigenstates of graphene quantum dots of experimentally realizable size (diameter $d \leq 80$ nm). We highlight the interplay of different length scales controlling the break-down of the chiral symmetry by $K-K'$ scattering. The latter is found to be key to the understanding of the diamagnetic spectrum. We find the $B$-field dependence of the level variance to be a sensitive measure for the strength of $K-K'$ scattering and obtain good agreement with experimental Coulomb blockade data.

The paper is organized as follows: we first briefly summarize the Dirac picture of Landau level formation for massless charged Dirac particles and discuss the length...
scales relevant to its applicability to finite-size graphene quantum dots (Sec. II). In Sec. III we present realistic simulations for graphene quantum dots with zigzag and armchair edges, with edge roughness as well as with a comparison between the calculated $B$-field dependence of the level variance and experimental data is given in Sec. IV, followed by a short summary (Sec. V).

II. THE DIRAC PICTURE AND ITS LIMITATIONS

The remarkable similarity of the low-energy band structure of graphene with the dispersion relation of a massless Dirac particle in two dimensions has been widely exploited in a variety of theoretical models for graphene. However, the applicability of such models requires careful consideration of competing effects that go beyond the simple, yet intriguing Dirac picture. A case in point is the diamagnetism, i.e., the magnetic response of a finite-size graphene quantum dot. It is of considerable interest to inquire into the applicability as well as the limitations of the well-known diamagnetic theory of charged massless Dirac fermions.

The magnetic-field ($B$) dependence of the spectrum of free Dirac particles was first solved in an early paper by Rabi shortly after the Dirac equation was proposed. The Dirac equation for a massless particle with charge $q = -|e|$ in the presence of a potential $V(x)$ with time-like coupling and a perpendicular, homogeneous magnetic field $B = \nabla \times A = -By\nabla \times e_x$ reads

$$H_D = H_0 + H_B = v_F p \cdot \sigma + V(x)1 - \frac{q}{c} A \cdot \sigma.$$  \hspace{1cm} (1)

In the limiting case of strong magnetic field where $|qA/c| \gg |V(x)|$ the solution of Eq. (1) predicts the formation of Landau levels:

$$E_n^B(B) = \text{sgn}(n) \sqrt{2|e|hv_F^2|n|B}, \quad n \in \mathbb{Z}. \hspace{1cm} (2)$$

We explicitly label this reference spectrum with the superscript “D” (for Dirac equation). Equation (2) contains several remarkable features absent from non-relativistic diamagnetism: a ground state Landau level $n = 0$ the energy of which does not depend on $B$ at all. Higher Landau levels $n = \pm 1, \pm 2, \ldots$, are distributed symmetrically around $n = 0$, and feature a $\sqrt{B}$ rather than a linear dependence on $B$ known from non-relativistic diamagnetism. The high-field regime [Eq. (2)] is controlled by just two length scales, the (energy dependent) de Broglie wavelength $\lambda_F$ and the magnetic length $l_B = \sqrt{\hbar c/(eB)}$. The strong (weak) field regime is characterized by $l_B \ll \lambda_F$ ($l_B \gg \lambda_F$). In the limit of weak magnetic fields, Eq. (1) predicts the lowest-order energy corrections to scale linearly with $B$, unlike the conventional non-relativistic behavior ($\propto B^2$).

The ideal, infinitely extended graphene sheet can be described in nearest neighbor tight-binding approximation by the Hamiltonian:

$$H = \sum_{i,s} \phi_{i,s} V_i \phi_{i,s} - t \sum_{<i,j>,s} \phi_{i,s} \phi_{j,s} + h.c., \hspace{1cm} (3)$$

where the sum $(i,j)$ extends over pairs of adjacent lattice sites, $|\phi_{i,s}|$ is the tight-binding orbital with spin $s$ at lattice site $j$, $V_i$ is a locally varying potential, and $t$ (of the order of 2.8 eV) is the nearest neighbor hopping matrix element. In the numerical calculations we take into account second and third nearest neighbor couplings in addition to Eq. (3) in order to quantitatively account for the realistic band structure. Close to the Fermi energy, the band structure of Eq. (3) can be approximated (assuming that $V_i \ll t$) by a conical dispersion relation around the $K$ point:

$$E(k + k_F) = E(k_K) + k_\perp \cdot k + O(k_F^2) \approx v_F |k|, \hspace{1cm} (4)$$

where we have set $E(k_K) = 0$. Note that the above expansion ignores both the length scale of the graphene lattice constant $a = 1.4 \, \text{Å}$ and preferred directions of the lattice: due to the discrete lattice symmetry, the cone structure becomes squeezed along the $K-K'$ directions, an effect known as triangular warping. More importantly, the band structure features two non-equivalent cones at the $K$ and $K'$ points in the reciprocal lattice due to the sublattice (or chiral) symmetry. An expansion analogous to Eq. (4) holds near the $K'$ point. As long as the coupling between the $K$ and $K'$ points can be ignored, the band structure features two independent Dirac-like cones. Neglecting $K-K'$ coupling corresponds to the assumption that $V(x)$ varies sufficiently slowly on the length scale of the lattice constant such that the sublattice symmetry is preserved and high Fourier components that could couple $K$ and $K'$ are absent. In this case the separate expansion [Eq. (4)] for $K$ and $K'$ can be approximated by two Dirac Hamiltonians each of the form of Eq. (3):

$$H_0 = v_F \begin{pmatrix} \sigma \cdot p + V(x) & 0 \\ 0 & \sigma^* \cdot p + V(x) \end{pmatrix}. \hspace{1cm} (5)$$

Each Dirac Hamiltonian features a two-component spinor (corresponding to the pseudospin on one cone), giving the spinors [Eq. (5)] a total dimension of four. The wavefunctions at $K$ and $K'$ are related by time reversal symmetry.

We now consider a finite-size system of linear dimension $d$, where $V(x)$ takes on the role of a confinement potential. With this additional length scale present, the Landau-level solution [Eq. (2)] is only valid in the strong magnetic field regime where $l_B \ll d$, while in the weak field regime, $l_B \gg d$, the spectrum will be determined by $V(x)$. For zero magnetic field, eigenstates $|\psi_K\rangle$ and $|\psi_{K'}\rangle$ localized at the $K$ and $K'$ points are degenerate. Turning on a magnetic field lifts this degeneracy without (to lowest order) introducing couplings between $K$ and $K'$. The degenerate subspace $\mathcal{V}_{K,K'}$ is
spanned by \( \{ |\psi_K\rangle, |\psi_{K'}\rangle \} \). Following first-order degenerate Rayleigh-Schrödinger perturbation theory, the perturbation matrix \( W \) describing the lowest order correction to the field-free spectrum of Eq. (4) takes the following form within \( \mathcal{V}_{KK'} \):

\[
W = \begin{pmatrix}
(H_B)_{KK} & 0 \\
0 & -(H_B)_{K'K'}
\end{pmatrix},
\]

(6)

where \( (H_B)_{KK} := \langle \psi_K | H_B | \psi_K \rangle = - (H_B)_{K'K'} \), and \( W \) is a \( 4 \times 4 \) matrix. For preserved \( K \)-\( K' \) symmetry, states at \( K \) and \( K' \) remain decoupled (i.e., \( | \psi_K \rangle V | \psi_{K'} \rangle =: \langle V \rangle_{K'K'} = 0 \)). The absence of \( K \)-\( K' \) coupling and the linear magnetic field dependence of \( (H_B)_{K'K'} \) for each decoupled Dirac cone implies that energy eigenvalues linearly cross the line \( B = 0 \) in pairs of two, forming an \( x \)-shaped intersection (see Fig. 2). This is in contrast to the nonrelativistic diamagnetic response \( \propto B^2 \) in the perturbative limit. It rather resembles the paramagnetic level splitting in conventional quantum dots when the magnetic field lifts a degeneracy. Examples of the latter are lifting of Kramers’ degeneracy or a symmetry-induced degeneracy as in circular quantum dots.

In order to quantitatively simulate the diamagnetic response of a finite-size graphene quantum dot in the presence of preserved chiral symmetry we invoke here the “trick” of introducing a chiral-symmetry preserving soft-wall potential pioneered by Berry and Mondragon 

\[
V(\mathbf{x}) = V_0 (e^{\Delta r(\mathbf{x})/\Delta d} - 1) \sigma_z,
\]

(7)

where \( \Delta r(\mathbf{x}) \) is the outward distance from the quantum dot boundary and \( \Delta d \) introduces an additional length scale controlling the preservation of chiral symmetry. We choose \( \Delta d = 24 \text{ Å} \) [see Fig. 1(a)] much larger than the lattice spacing \( (\Delta d \gg a \approx 1.42 \text{ Å}) \). Consequently, Eq. (7) varies slowly on the scale of the lattice constant, conserves chiral symmetry [to order \( (a/\Delta d)^2 \)] and provides a realization of the (approximately) \( K \)-\( K' \) decoupled diamagnetic perturbation [Eq. (7)]. We note that realizations of potentials of the form of Eq. (7) are, to our knowledge, currently experimentally not available. We employ a third-nearest neighbor tight-binding approximation (to correctly describe triangular warping) and simulate a 50\( \times \)50 nm graphene QD containing \( \approx 100,000 \) carbon atoms. The magnetic field is included by a Peierls phase factor. We use a Lanczos diagonalization in conjunction with an LU factorization to efficiently calculate the 500 eigenvalues closest to the Fermi edge [see Fig. 2].

In the limit of weak magnetic fields, we find that our numerical results, indeed, follow the linear \( B \)-field dependence of the energy eigenvalues as predicted by perturbation theory [Eq. (6)] [see Fig. 2(b)]. Residual deviations from the perfect sub-lattice symmetry (due to the finite width \( \Delta d \) of the confinement) appear as minute energy splittings between near-degenerate levels in the \( B \to 0 \) limit. The resulting level splitting at \( B = 0 \) is, however, very small (\( 120 \mu \text{ eV} \)), i.e., two orders of magnitude below the mean level spacing (\( \approx 10 \text{ meV} \)).

Turning now to the high-field limit, \( l_B \ll d \), the influence of confinement effects should be diminished and the formation of Landau levels following the Dirac picture [Eq. (1)] is expected. The transition from low to high magnetic fields drastically changes the density of states (DOS). The depletion of the DOS near \( E = 0 \) at low fields,

\[
\rho(E) = \frac{d^2}{2(hv_F)^2} |E|,
\]

(8)
is replaced, for increasing \( B \), by an increasing number of eigenstates moving towards the Landau level at \( E^D_0 \), which is located at the Dirac point [see Fig. 2(a)]. More specifically, all graphene levels with energies in between the two first Landau levels, \( E^D_0 < E < E^D_1 \), adiabatically converge to the level at \( E^D_0 = 0 \). As we have shown recently, this unique feature can be used to pin down the energetic position of the Dirac point in the experiment and thus of the electron-hole crossover region in real graphene quantum dot devices.

Even though, at low fields, chiral symmetry is approximately preserved by the potential in Eq. (7), a large num-
FIG. 3: (color online) Typical eigenstates (plotted is the absolute square of the wavefunction) of a graphene quantum dot with smooth confinement [see Fig. 1(a) and Eq. (7)] at high magnetic field (B=25 T), corresponding to the zeroth (a, b) and first (c, d) Landau level. Symbols (▲, ▼, ■, ♦) correspond to those in Fig. 2(a).

ber of sizeable avoided crossings appear at higher magnetic fields as the magnetic length is reduced to $l_B \ll d$. Edge states that couple to bulk states or to other edge states become prevalent. The complicated pattern in Fig. 2(a), (c) of many avoided crossings near the first Landau energy $E = E_D^{E\pm 1}$ reflects this interplay between magnetic bulk and edge states. Levels with eigenenergies that follow the predicted values for the Landau levels, $E_D^n$, are localized in the interior of the quantum dot and well separated from the edges. Conversely, the states with energies in between the values $E_D^n$ should be strongly influenced by the spatial confinement in the quantum dot. Wave functions corresponding to energy levels close to $n = 0$ and $n = 1$ Landau levels [Fig. 3(a, c)] as well as those in between $n = 0$ and $n = \pm 1$ [Fig. 3(b)] and between $n = 1$ and $n = 2$ [Fig. 3(d)] confirm these expectations.

Apparently, the typical level splittings at the avoided crossings [Fig. 3(b, c)] are dramatically enhanced in the high-field regime. This is due to the fact that, as compared to the low-field case, the amplitudes of wave functions are enhanced at the dot boundary [see Fig. 3(b)]. Since, in addition, the lattice symmetry is broken right at the boundary, these edge states do have an increased coupling strength to all other states in the sample. Following the Wigner-von Neumann non-crossing rule, this increased coupling strength leads to increased level splittings at the crossing point.

FIG. 4: (color online) Same as Fig. 2, but for a quantum dot with atomically sharp zigzag and armchair boundaries. The solid line in (b) is a fit to Eq. (10), the dashed line (corresponding to $V_{KK'} = 0$) is inserted as guide to the eye. The evolution of one eigenenergy with magnetic field is drawn with a thick green line as guide to the eye in (a), (c). The arrow in (c) marks a kink in the magnetic field dependence of this state (see text).

III. REALISTIC GRAPHENE QUANTUM DOTS

A. Clean dots with sharp edges

We turn now to realistic graphene quantum dots where the nanostructures are terminated by atomically sharp edges, either of armchair or zigzag shape [Fig. 1(b)]. Following recent estimates for passivation of the dangling carbon bonds at the edges of graphene samples (e.g., by attached hydrogen), we set the potential of the outermost carbon atoms to 1.7 eV. Although in this case many of the surface states present in a perfect zigzag boundary remain suppressed, such a confining potential leads to substantial changes in the energy level spectrum [see Fig. 4(a)] as compared to the model potential in Eq. (7). Most importantly, in the low-field regime [see Fig. 4(b)] the linear $B$-field dependence of the level splitting resembling the nonrelativistic diamagnetic response. This is due to the presence of sizable avoided crossings near $B = 0$ as a result of broken chiral symmetry at the edges (chiral symmetry is not conserved upon reflection at atomically sharp zigzag edges). In terms of perturbation theory, the confining potential $V$ now includes a (small) coupling term $\langle V \rangle_{KK'} := \langle \psi_K | V | \psi_{K'} \rangle$ in the subspace $\psi_{KK'}$. The
p perturbation matrix thus becomes

\[
W = \begin{pmatrix}
\langle H_B \rangle_{KK} & \langle V \rangle_{KK'} \\
\langle V \rangle_{KK'} & -\langle H_B \rangle_{KK}
\end{pmatrix},
\]

with eigenvalues

\[
\varepsilon = \pm \sqrt{\langle H_B \rangle_{KK}^2 + (\Delta\varepsilon/2)^2}, \quad \Delta\varepsilon = 2 |\langle V_{KK'} \rangle|.
\]

The coupling between \(K\) and \(K'\) cones thus leads, according to the Wigner-von Neumann non-crossing rule\(^{26}\) to avoided crossing with level splittings \(\Delta\varepsilon\) [see Fig. 4(b)] proportional to the coupling strength \(V_{KK'}\) between the two Dirac cones. Conversely, a fit to Eq. \((10)\) yields a sensitive indicator for the amount of \(K-K'\) scattering in the quantum dot.

For high magnetic fields [see Fig. 4(c)], the presence of \(V_{KK'}\) coupling lead to a large number of correlated avoided crossings when the edge states move towards the zeroth bulk Landau level. In other words avoided crossings appear when the energy of eigenstates evolving towards the \(E_b\) level “pass” through the energy \(E'_b(B)\) of the first Landau level [Fig. 4(c)]. Due to a large number of avoided crossings, there are no states continuously following the first Landau level. We rather observe a bundle of states sequentially moving along the characteristic energy of the first Landau level, much like in a relay [see Fig. 4(c)]. Such an interrelated sequence of avoided crossings is well-known from atomic physics as “diabatic ridge” - riding states localized on potential barriers.\(^{33}\) A direct consequence is that the evolution of eigenstates for an increasing magnetic field [see green highlighted line in Fig. 4(a)] features sharp “kinks” when crossing the ridge following the first Landau level [see arrow in Fig. 4(c)]. As the state is transiently trapped by the ridge, it moves away from the Dirac point, and continues again monotonically towards the Dirac point once clear of the ridge. These kinks due to the ridge riding mechanism have been observed in the experiment\(^{23}\) serving as an additional indicator for the position of the lowest Landau level and the electron-hole crossover.

The present results show that the atomically sharp edges do destroy the linear \(B\)-dependence of the energy levels at weak fields, but they do apparently not destroy the square-root \(B\)-dependence at very high fields. The linear \(B\) dependence results from the fragile suppression of \(K-K'\) scattering \((\propto \langle V \rangle_{KK'})\) between the Dirac cones while the square-root dependence results from the much more robust dispersion relation of the individual cone. Therefore, Landau levels survive the introduction of sharp boundaries much better than the energy levels at weak fields. In turn, even when in the experiment a Dirac-like Landau level spectrum is recorded, many other features of the same graphene sample may very well show large deviations from predictions based on Dirac theory.
ridges between the Landau level energies which were absent for edge scattering [see dotted lines in Fig. 5(a,c)]. The corresponding eigenstates near these new ridges [see Fig. 5(b), marked by ▼ in Fig. 5(a)] are pinned to a single defect, where the lattice symmetry and thus also the chiral symmetry are broken. Such localized states can therefore be expected to behave differently from the bulk Landau levels. The resulting new ridges feature a very weak quasi-linear magnetic field dependence. We therefore conjecture that these structures are due to avoided crossings with such localized defect states. While the energetic positions of more complicated defects in experiment (e.g., Stone-Wales defects, or attached nitrogen molecules) may be shifted energetically, we expect the same linear $B$-field dependence as long as the states are localized. Such localized states with weak magnetic field dependence were also observed experimentally in Coulomb blockade measurements.

In the low field regime, we observe a significant change in the $B$-evolution of eigenenergies: avoided crossings become asymmetric [see Fig. 5(b)]. The reason is that the $K - K'$ splitting introduced by the lattice vacancies is strong enough to yield different matrix elements for $\langle H \rangle_{KK'}$ and $\langle H \rangle_{K'K'}$: consequently, the slope of both eigenvalues of Eq. (9) is different [see Fig. 5(b)]. To illustrate that the diamagnetic spectrum, in particular the avoided crossing distribution, is due to the chiral symmetry breaking induced by the defects, we present as counter example the spectrum for sublattice preserving double vacancies. As such double vacancies replace an entire unit cell in the hexagonal lattice, they conserve the A-B lattice symmetry and do not act on the $K - K'$ symmetry. We find, indeed, that for the same number of defects as previously considered for the case of single vacancies (Fig. 5), only avoided crossings with comparatively small energy splittings appear in the energy level diagram (Fig. 7), resembling much more closely Fig. 3. This clearly proves that it is the breaking of the chiral symmetry and not the presence of defects per se which is responsible for the break-down of the Dirac picture for graphene quantum dots.

C. Dots with edge disorder

We consider now a clean graphene quantum dot with atomically sharp but disordered edges. We connect short straight edge segments (with a random length between 0.5-3 nm) to obtain a polygon-shaped boundary [see Fig. 1(c)] with a disorder amplitude of $|\delta d| \leq 2$ nm. $\delta d$ is thus (at energies close to the Dirac point) smaller than the wavelength $\lambda_F$ of the confined particles as well as the magnetic length, but larger than the lattice constant. Since rough boundaries, just like bulk defects, have the property to localize states, we expect similar signatures of these two types of disorder. Indeed, in the low field regime, dots with rough edges feature a similar pattern of fluctuating energy levels as dots with single-lattice defects (compare Fig. 8 and Fig. 5). The spectra are so similar that it is difficult to distinguish between bulk and edge disorder breaking the $K - K'$ symmetry. Also in the high-field regime, the evolution towards the Landau
levels features the correlated sequence of avoided crossings reflecting the diabatic ridges [see Fig. 5(c)]. Wave functions of eigenstates at these energies display patterns which are very similar to those for the clean system [compare Fig. 3(a) and Fig. 6(d)]. In particular, states near Landau levels localize in the interior of the dot, and thus are not influenced by edge disorder. Likewise, the kink pattern at the crossing of the ridges is robust against edge disorder. While the inclusion of edge disorder does not give rise to qualitatively new effects on the eigenenergy spectrum in the high-field regime, differentiating between edge and bulk disorder might become possible by probing the different scaling behavior for bulk and edge with the size of the graphene quantum dot.

It is instructive to directly contrast the level splitting $\Delta \varepsilon$ of an avoided crossing [Eq. (10)] due to finite $K - K'$ coupling for different scenarios: (i) chiral-symmetry preserving confinement [Fig. 8(a)], (ii) clean graphene quantum dots with atomically sharp edges [Fig. 8(b)] and (iii) disordered graphene quantum dots [Figs. 8(c),d)]. Graphene dots with both edge and bulk roughness feature similar behavior as dots with only one type of roughness [compare Fig. 8(c) and Fig. 8(d)]. We observe an increase in the absolute size of the average level splitting ($\Delta \varepsilon$) due to $K - K'$ coupling at the edges and impurities. In scenario (i) $\langle \Delta \varepsilon \rangle$ is at least one order of magnitude smaller than the mean level spacing $\langle \delta \varepsilon \rangle$, $\langle \Delta \varepsilon \rangle \ll \langle \delta \varepsilon \rangle$. In (ii) where $\langle \Delta \varepsilon \rangle < \langle \delta \varepsilon \rangle$ a first-order perturbative treatment of $K - K'$ coupling correctly describes the level repulsion. For localization at defects (iii) where $\langle \Delta \varepsilon \rangle \lesssim \langle \delta \varepsilon \rangle$ level pairs at $K$ and $K'$ feature different quadratic dependences on $B$, i.e., they can not be accurately treated with only first order perturbation theory.

**IV. COMPARISON WITH EXPERIMENT: LEVEL SPACING FLUCTUATIONS**

For a comparison with the experimental data of the magnetic response of graphene quantum dots we pursue two strategies: in a direct approach we compare our models with the observed parametric $B$-field evolution of individual Coulomb blockade peaks. Alternatively, we identify the $B$-field dependence of the level spacing fluctuations (variance) as a robust measure for the degree of disorder in a graphene quantum dot. Specifically, we define the rescaled (or unfolded) variance $\sigma_\varepsilon$ of the distribution of neighboring energy level spacings $\delta \varepsilon$ as

$$\sigma_\varepsilon := \frac{1}{\langle \delta \varepsilon \rangle} \sqrt{\langle (\delta \varepsilon)^2 \rangle - \langle \delta \varepsilon \rangle^2}. \quad (11)$$

Since switching on a magnetic field $B$ leaves the number of states unchanged, $\langle \delta \varepsilon \rangle$ is (approximately) independent of $B$, while higher moments of the level distribution are drastically affected. At $B = 0$, pairs of energy levels are split by the characteristic energy $\Delta \varepsilon$ of the avoided level crossings. However, as long as $\langle \Delta \varepsilon \rangle$ [Eq. (10)] is small compared to the mean level spacing $\langle \delta \varepsilon \rangle$, the level sequence alternates between small and large spacings, while spacings of the order of $\delta \varepsilon$ are unlikely. We thus expect for magnetic field $B = 0$ a comparatively large variance $\sigma_\varepsilon$. For increasing $|B|$ the levels become more equally

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**FIG. 8**: (color online) Same as Fig. 4 for a quantum dot featuring rough edges (with a roughness amplitude $\delta d = \pm 2$ nm). Symbols mark the states for which the corresponding wavefunction is shown in Fig. 6.

**FIG. 9**: (color online) (Avoided) crossings for (a) soft edge s, (b) hard edges, (c) rough edges, and (d) rough edges plus bulk disorder. The level splitting is (a) 0.1 meV, (b) 2 meV,(c) 3 meV, and (d) 2.5 meV.
spaced, leading to a decrease in $\sigma_z$. Correspondingly, the variance $\sigma_z$ of the level spacings should feature a peak at $B = 0$. The numerical results for the dependence of $\sigma_z$ on $B$ for different disorder strength (i.e., different $|V_{K-K'}|$) are shown in Fig. 10. Our data display a pronounced peak of $\sigma_z$ for the clean flake slowly decreasing for increasing number of single-vacancy defects (i.e., for increasing $K-K'$ scattering) [see Fig. 11(a)]. Note that both the peak height at $B = 0$ and the overall value of $\sigma_z$ decrease with increasing disorder. The latter can be explained by the emerging localized states that feature a regular spacing (and hence a suppressed variance $\sigma_z$). For comparison we also show $\sigma_z$ for double vacancies preserving chiral symmetry. [see Fig. 11(b), note the different scales]. Accordingly, $\sigma_z$ is, indeed, strongly dependent on the amount of $K-K'$ scatterers, not on the number of defects per se.

The decrease in peak height with increasing $K-K'$ scattering should thus provide a robust and sensitive measure for $K-K'$ scattering present in the experiment. To test this conjecture, we have measured the evolution of 42 Coulomb blockade peaks with magnetic field. We follow the parametric motion of the peak positions, and hence the eigenstate energies, as a function of magnetic field $B \in [-2, 2\text{T}]$. To compare with our numerical results, we take into account a charging energy of 13 meV (determined independently) as well as spin (by Zeeman splitting). We observe, indeed, a quadratic $B$-field dependence rather than the linear dependence predicted for conserved $K-K'$ symmetry of the Dirac equation. Our experimental data can be well described by Eq. (11) [see Fig. 11(a)]. For pairs of consecutive Coulomb blockade resonances belonging to the same avoided-crossing, we find a mismatch in slopes, in agreement with our numerical findings for the rough-edged quantum dot [compare Fig. 11(a) and Fig. 9(c,d)]. This has important consequences for the interpretation of experimental data: the roughness present in the experimental dot does not allow to disentangle $K$ and $K'$ states. To be more quantitative, we compare our simulations for the level variance with experimental data. We indeed find good agreement as confirmed by a noticeable peak also in the experimental data for $\sigma_z(B)$ [see Fig. 11(b)]. The offset between the two data sets in Fig. 11(b) is attributed to statistical fluctuations in charging energy and in the number of localized states for different values of the back gate voltage. By using the edge roughness $\delta d$ as the only adjustable parameter, we can match the measured $\sigma_z(B)$ very well with our numerical simulation [see lines in Fig. 11(b)]. Good agreement is found for an edge roughness of about $\delta d \approx 0.5 \pm 0.2$ nm, or a $K-K'$ scatterer concentration in the bulk $n_i \approx (3.5 \pm 1) \times 10^{-4}$, both of which are well within expectation. We emphasize that, although we can quantify the resulting overall strength of $K-K'$ coupling in our experimental quantum dot, we cannot disentangle whether the observed $K-K'$ scattering comes from edge roughness, lattice defects, or disorder through flake-substrate interactions with a length scale comparable to the lattice constant.

V. CONCLUSIONS

We have investigated the evolution of eigenstates in graphene quantum dots with increasing magnetic field. Concentrating on the energy regime around the Dirac point, we observe a smooth transition from a linear density of states to the emergence of Landau levels. At high field strength, we find that Landau levels follow the square-root dependence of the Dirac equation, manifested in the energy level diagram by sequences of corre-
lated avoided crossings along “diabatic ridges”. These
ridges lead to characteristic kinks in the evolution of
energy states that cross a Landau level. Appearing
also in Coulomb blockade measurements, these kinks can
be used to experimentally pin down the electron-hole
crossover point. In the perturbative regime of small
magnetic fields, we find that the linear dependence on B
predicted by the model of massless Dirac fermions disap-
ppears when the chiral symmetry is broken. Even perfect
armchair and zigzag edges are sufficient to break the sub-
lattice symmetry giving rise to avoided crossings with a
quadratic dependence on B instead. A similar effect is
observed for lattice defects: single lattice vacancies break
the K − K′ symmetry and thus result in avoided cross-
ings with substantial level splittings (even for defect con-
centrations as low as 1 in 20,000). By comparison with
double vacancies which conserve the sublattice symmetry
we show explicitly that it is not the presence of disorder
per se which leads to deviations from predictions by the
Dirac equation, but the breaking of chiral symmetry.

We compare our theoretical predictions with experi-
mental results on the parametric B-field evolution of
Coulomb blockade peaks. As a quantitative indicator
for the strength of K − K′ scattering, we calculate the
variance σ of the level spacing distribution as a function
of magnetic field. We observe a peak in the variance at
B = 0 due to level correlations near avoided crossings.
We find quantitative agreement between the measured
and the calculated data for σ, which enables us to pin-
point the amount of K − K′ scattering present in our
experimental flake. The present results provide a sen-
tive indicator for the quality of the graphene dot and
demonstrate the limits of the Dirac picture in describing
the experiment.

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The measured graphene quantum dot had a similar geometry as the dot described in Refs. 31,44. By changing the potential of the back gate electrode ($V_G$) a region of suppressed current between $V_G = 10$ V and 45 V was found. From measurements of Coulomb blockade peaks in this region (with $\approx 150$ Coulomb peaks) a charging energy of $\approx 13$ meV was extracted. For more details about the measurements see Refs. 31,44.