Theory of the Three Dimensional Quantum Hall Effect in Graphite

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We predict the existence of a three dimensional quantum Hall effect plateau in a graphite crystal subject to a magnetic field. The plateau has a Hall conductivity quantized at $\frac{4e^2}{h c_0}$ with $c_0$ the $c$-axis lattice constant. We analyze the three-dimensional Hofstadter problem of a realistic tight-binding Hamiltonian for graphite, find the gaps in the spectrum, and estimate the critical value of the magnetic field above which the Hall plateau appears. When the Fermi level is in the bulk Landau gap, Hall transport occurs through the appearance of chiral surface states. We estimate the magnetic field necessary for the appearance of the three dimensional quantum Hall Effect to be 15.4 T for electron carriers and 7.0 T for hole carriers.

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Recent advances in the fabrication of single graphene sheets as well as the striking initial experiments on the relativistic quantum Hall effect in graphene \cite{1,2} have generated intense interest in this remarkable material. Most of the theoretical and experimental research has focused on the properties of the low energy excitations close to half filling which have a Dirac spectrum with a speed of light of the order of $10^6$ m/s. The spin-unpolarized quantum Hall effect shows a sequence of plateaus at $\sigma_{xy} = (n + \frac{1}{2}) \times 4e^2/h$ consistent with the existence of two Dirac cones as well as a spin degeneracy \cite{1,2}.

The phenomenon of Hall conductivity quantization is however not restricted to two dimensions and can occur in bulk samples, albeit under more stringent conditions. It was first observed by Halperin \cite{3} that for a three-dimensional (3D) electron system in a periodic potential, if the Fermi level lies inside an energy gap, the conductivity tensor is necessarily of the form:

$$\sigma_{ij} = \frac{e^2}{2\pi h} \epsilon_{ijk} \hat{G}_k$$

(1)

where $\epsilon_{ijk}$ is the fully antisymmetric tensor and $\hat{G}$ is a reciprocal lattice vector of the potential which may or may not be zero. The periodic potential can be generated by either an underlying lattice or spontaneously by many-body effects through the formation of density waves.

The existence of the three dimensional quantum Hall effect (3DQHE) has not, however, been observed in any bulk materials, although the effect has been observed in stacked superlattices of 2D semiconductor layers, each exhibiting a 2DQHE, where the inter-layer tunneling is engineered away \cite{4}. The only current bulk material candidates for 3DQHE are the Bechgaard salts \cite{5,6}. The difficulty inherent in realizing the 3DQHE in a specific bulk material can be understood by considering the spectrum of an electron in a periodic potential under an applied magnetic field. In 2D, this Hofstadter problem \cite{7} results in magnetic energy bands. Associated with each band is an integer quantized Hall conductance; when the Fermi level lies in a gap, the observed Hall conductance is a sum over the contributions from each filled band. In 3D, the momentum component parallel to the magnetic field disperses freely and the very existence of such gaps is not guaranteed; indeed it is exceptional. Tilting the magnetic field away from the crystallographic axes helps \cite{8}, but does not guarantee, the opening of gaps.

In this paper we show that a true, bulk 3DQHE is realized in graphite under a large magnetic field parallel to the $c$-axis. Three factors conspire to render this possible: the large Landau gap of the integer quantum Hall state in graphene, the weak interplane hopping, and the Bernal stacking. We first give a physical argument for the existence of 3DQHE based on adiabatic continuity, then perform a full Hofstadter calculation in 3D of the band and surface states structure, using the realistic Johnson-Dresselhaus \cite{9,10} Hamiltonian for graphite, plus a magnetic field. We find the minimum magnetic
field necessary for a 3DQHE to be 15.4 T for electrons and 7.0 T for holes, and show that only one Hall plateau (Fig. 1) will be observed due to band closing in the higher Landau levels (LLs). Besides the obvious prediction of a plateau in off-diagonal conductive response, we also predict that a correlated chiral surface state occurs at the boundary of the sample. Based on the recent experimental focus on graphite [12] we believe our prediction is testable with current experimental techniques. Previous Hall plateaus observed in graphite [13, 14] are either even in B, or come in multiple sequences consistent with the graphene QHE plateaus [14, 15], and are hence different than our prediction of a single quantized Hall plateau of Hall conductivity twice as large as the one observed in graphene for Fermi level in the first Landau gap.

Graphite is a layered material consisting of weakly coupled parallel graphene layers in an ABABAB configuration known as Bernal stacking [16], as depicted in Fig. 1. We let initially the inter-layer hopping to zero and place a large number of uncoupled stacked graphene layers in a strong magnetic field perpendicular to their surface. Each layer exhibits a relativistic quantum Hall Effect as previously described with a LL energy \( E_n = \pm n\hbar v / \ell \), where \( \ell = \sqrt{\hbar e / B} \) is the magnetic length, \( n = 0, 1, \ldots \), and \( v \approx 10^6 \text{ m/s} \). Typical values of the gap are roughly 0.1 eV for \( B = 10 \text{T} \) and 0.25 eV for \( B > 40 \text{T} \), thus making graphene the first system to exhibit quantized Hall conductance at room-temperature. If we place the Fermi level in the first Landau gap, our system of uncoupled graphene layers trivially exhibits a 3DQHE, with the bulk enveloped by a sheath of chiral surface states as in Fig. 1. For uncoupled layers, there is no \( k_z \) dispersion. We now adiabatically turn on intralayer hopping, which causes almost all LLs to disperse with \( k_z \). The exception are the zero modes which are stable in an idealized model due to particle-hole symmetry, as we show below. By adiabatic continuity, the sheath of chiral states (and hence the 3DQHE) must be stable as long as the Landau gap does not collapse.

We first show that the statement above is true for a simplified toy-model of graphite. If we introduce a parameter \( x \) which interpolates between uncoupled graphene layers (\( x = 0 \)) and graphite (\( x = 1 \)), the minimal Hamiltonian of our system is a \( 4 \times 4 \) Hermitian matrix acting on the lattice spinor \((\psi_A, \psi_B, \psi_C, \psi_D)\), where \((A,B)\) and \((C,D)\) are the two inequivalent sites of the lower and upper graphene layers in the Bernal stacking, respectively. Its nonzero independent elements are \( H_{AB} = -H_{BD} = \frac{2\pi}{\sqrt{c/eB}} t_{\|} a_0 k_\perp \), and \( H_{AC} = -2x t_{\perp} \cos \left( \frac{\pi}{2} k_z c_0 \right) \). The in-plane hopping is \( t_{\|} = 3.16 \text{ eV} \), \( t_{\perp} = 0.39 \text{ eV} \) is the interlayer (A-C) hopping in graphite (\( x = 1 \)) [16], and \( a_0 = 2.456 \text{ Å} \) is the graphite lattice constant (in-plane A-A distance). The c-axis lattice constant is \( c_0 = 6.74 \text{ Å} \) (the distance between consecutive lattice planes equal to \( \frac{1}{2} c_0 \)), and \( k_\pm = k_x \pm ik_y \). The in-plane dispersion is expanded about the point \( K = (\frac{4\pi}{3a_0}, 0, 0) \), which is the Dirac point in graphene. In a uniform magnetic field, adopting the symmetric gauge \( \vec{A} = \frac{\vec{B}}{2}(y, x, 0) \), the Kohn-Luttinger substitution \( k_\pm \rightarrow k \pm ik_y + \frac{c_0}{\sqrt{c/eB}} (A_x \pm iA_y) \) [17]. In the specific case of \( (x = 1) \) this model is the same as the one used in [18]. Let \( b^\dagger, b \) be creation and annihilation Landau Level operators (with \([b, b^\dagger] = 1\)), and introduce the notation \( c_z = \cos(\frac{1}{2} k_z c_0) \). The Hamiltonian is

\[
H(x) = \begin{pmatrix}
0 & -\epsilon t_{\|} b & -2x t_{\perp} c_z & 0 \\
-\epsilon t_{\|} b^\dagger & 0 & 0 & 0 \\
-2x t_{\perp} c_z & 0 & 0 & -\epsilon t_{\|} b^\dagger \\
0 & 0 & -\epsilon t_{\|} b & 0
\end{pmatrix} \tag{2}
\]

with \( \epsilon = B/B_0 \) and \( B_0 = (hc/e)/3\pi a_0^2 = 7275 \text{ T} \), and is diagonalized in a basis \( \psi = (|n\rangle, |n + 1\rangle, |n\rangle, |n - 1\rangle) \), for \( n > 0 \). We obtain below the 4 LL energies \( E_n \) as

\[
E_n = \pm \left[ (n + \frac{1}{2}) e^2 t_{\|}^2 + 2x^2 t_{\perp}^2 c_z^2 \right.
\]

\[
\pm \sqrt{4 e^4 t_{\|}^4 + 4 (n + \frac{1}{2}) x^2 e^2 t_{\|}^2 t_{\perp}^2 c_z^2 + 4x^4 t_{\perp}^4 c_z^4} \right]^{1/2},
\]

This spectrum has explicit particle-hole symmetry. For \( n = 0 \) there are eigenvalues at \( \pm (e^2 t_{\|}^2 + 4x^2 t_{\perp}^2 c_z^2)^{1/2} \) and a doubly degenerate level at \( E_0 = 0 \). (All levels receive an additional double degeneracy owing to the existence of the inequivalent \( K \) point.) The next Landau bands are the lowest two energy levels of \( n = 1 \). Using this spectrum we find that the gap between the zero mode...
and the LL above or below it cannot collapse upon interpolating between \( x = 0 \) and \( x = 1 \) for any value of the magnetic field. As such, by adiabatic continuity, the Hall conductance when the Fermi level is in the 3D gap (with doubling for the two spins) is:

\[
\sigma_{xy} = \frac{4e^2}{h} \int \frac{d^2k}{(2\pi)^2} \text{Im} \left\langle \frac{\partial \psi}{\partial k_x} \frac{\partial \psi}{\partial k_y} \right\rangle = (2n+1) \frac{4e^2}{h} \int \frac{dk_y}{2\pi} = (2n+1) \times \frac{4e^2}{hc_0}. \tag{4}
\]

For the Fermi level between the zero mode and the first LL, \( n = 0 \) and \( \sigma_{xy} = \pm \frac{4e^2}{hc_0} \). The Bernal stacking of graphite accounts for the extra factor of 2 relative to graphene and \( \int \frac{d^2k}{(2\pi)^2} \text{Im} \left\langle \frac{\partial \psi}{\partial k_x} \frac{\partial \psi}{\partial k_y} \right\rangle = 2n+1 \) is the TKNN integer \([19]\) of the relativistic graphene bands when the Fermi level is placed in the \( n \)th bulk gap. We observe that the gap between the first and the second LL in graphite closes for any realistic value of the \( B \) field (Fig. \ref{fig:fig1}), and hence higher \( n \) plateaus will not be observed. Zeeman splitting could give rise to a \( \sigma_{xy} = 0 \) plateau, but is smeared by the dispersion of the zero mode in the realistic graphite model used below, and hence the predicted Hall conductance is sketched in Fig. \ref{fig:fig1}.

The existence of a full gap in the 3D LL spectrum is an artifact of the toy model involving only \( t_{\parallel} \) and \( t_\perp \). It derives from the presence of a flat, twofold degenerate band at the Fermi level along the HK spines of the Brillouin zone. The Bernal stacking is crucial, for if the individual graphene planes were stacked identically, all LLs would acquire a \( k_z \)-dependent contribution to their energies \(-2t_\perp \cos(k_zc_b)\), and would then overlap at all but extremely high magnetic fields \([20]\). More realistic models for graphite, such as the Slonczewski-Weiss-McClure (SWMC) model \([21, 22]\) or that of Johnson and Dresselhaus (JD) \([9, 10]\), contain small \( c \)-axis B-B (D-D) hopping terms, through the open hexagons of the CD (AB) plane. Their value is small on the scale of nearest neighbor hopping – only 10 meV, leading to a bandwidth of 40 meV along the HK spine. But the presence of such terms is crucial toward understanding the properties of graphite. At \( B = 0 \), they result in semimetallic behavior, whereas the toy model incorrectly predicts a zero gap semiconductor. For weak fields, they lead to overlap of the LLs and destruction of the QHE. However, as we shall show, the principal gaps surrounding the central \( n = 0 \) LLs survive for \( B > 7.0 \) T (holes) and \( B > 15.4 \) T (particles). Lightly doped graphite, then, will exhibit a 3DQHE at these fields. We next describe our solution of the JD model in a magnetic field on a torus and a Laughlin cylinder, finding the LLs and the surface states, and determining the critical fields \( B_c \) at which energy gaps open across the entire Brillouin zone \([23]\).

The JD model \([3, 10]\) is a tight-binding Hamiltonian derived from the \( k \cdot p \) theory of SWMC. Its nine parameters are given in Tab. \ref{tab:table1}. In addition to nearest neighbor hoppings, there are also further neighbor hoppings, both in-plane (extending to third and fourth neighbor) and between planes. There is also an energy asymmetry \( \Delta = \varepsilon_{A(C)} - \varepsilon_{B(D)} \). We then introduce a magnetic field through Peierls phases along the links, consistent with all rotational (and screw axis) symmetries of the underlying lattice, as depicted in Fig. \ref{fig:fig3}.

We solve the model through a combination of exact diagonalization, Lanczos method (for \( q > 1000 \), where the flux per hexagonal plaquette is \( 1/q \) Dirac quanta \( \phi_0 = hc/e \)), and low field expansion. For the bulk band structure, we impose doubly periodic (i.e. toroidal) boundary conditions in the \((x, y)\) plane, while to study edge (surface) states we impose singly periodic (i.e. cylindrical) boundary conditions. The latter case may also be solved via a transfer matrix formalism \([24]\). Due to the algebraic complexity of the problem, we postpone the explicit details of the \( B \)-field Hamiltonian and transfer matrix for a future publication. For \( q > 20 \) the Hofstadter broadening becomes negligible and the band energies as a function of \( k_x \) become non-dispersive, corresponding to the real situation in which the magnetic field splitting is small.

### Table I: Tight-binding parameters

| Parameter | \( t_{AB} \) | \( t_{CD} \) | \( t_{BC} \) | \( t_{BD} \) | \( t_{AD} \) |
|-----------|---|---|---|---|---|
| \( t_{AB} \) | 4200 | 44 | 10 |
| \( t_{CD} \) | 512.5 | | |
| \( t_{BC} \) | | | 390 |
| \( t_{BD} \) | | | | 315 |
| \( t_{AD} \) | | | | 44 |

### Figure 3: Definition of JD hopping matrix elements and flux assignment

Sites \( A \) and \( B \) belong to different graphene layers than sites \( C \) and \( D \), and Bernal stacking corresponds to sites \( A \) and \( C \) differing by a \( c \)-axis translation. Not shown are the further-neighbor in-plane hopping \( t_{AB}^{1,1} \) and \( t_{AB}^{1,2} \). The magnetic flux per hexagon is \( \phi = 2\pi p/q \) is the magnetic flux per hexagon in units of \( hc/e \), and \( n \) runs from 1 to \( q \), the number of hexagons in a magnetic unit cell.
FIG. 4: Clockwise from upper left: (a) $B = 5$ T, no gap present in the full spectrum. (b) $B = 12$ T, clear gap in the hole LL spectrum. (c) $B = 20$ T clear gaps for both hole and electron LL. Spin-up (blue) and spin-down (red) bands are shown. (d) Principal energy gaps surrounding $n = 0$ LLs, including effects due to Zeeman splitting. The particle gap collapses at $B^c_e = 15.4$ T and the hole gap at $B^c_h = 7.0$ T. All energies have been shifted upward by 100 meV.

FIG. 5: Zero mode, first electron Landau level and surface states spectrum over the full Brillouin zone for one spin species at $B = 40$ T. (a) Surface states spectrum (b) Zero mode and first electron Landau level spectrum (c) Surface states and bulk Landau levels together. The $n = 1$ ($n = 0$) levels are shifted by $+0.1$ eV ($-0.1$ eV) for clarity. There are two surface states per spin species crossing the bulk gap.

compared to the in-plane hopping amplitude.

We observe the following characteristics of the spectrum. The zero mode has a dispersion of 40 meV in the low field limit. The first LL, however, disperses strongly as a function of $k_z$ and for each value of $q$ we scan the energy $E(k_z)$ spectrum to look for the smallest gap. Fig. 4 shows the bulk Landau Level spectrum for $B = 5$, 12, and 20 Tesla, as well as the field-dependence of the principal gaps surrounding the central, weakly dispersive $n = 0$ LLs. We find that both gaps are indirect for $B < 30$ T. In Fig. 5 we plot the bulk band and surface state spectrum as a function of $k_x$ and $k_z$, which proves the existence of gaps and surface states over the entire Brillouin zone. On the Laughlin cylinder, for each value of $k_z$, we obtain 2 edge states on each of the upper/lower edge of the cylinder. Unlike the low-field bulk LLs, the edge states disperse as a function of $k_z$ and cross the bulk gap to give $2e^2/hc_0$ per spin. We have checked that our numerical results match the theoretical analysis of the continuum $k$ approximation of the JD model.

At low fields, each LL accommodates $\frac{\sqrt{3}}{2}a^2 B/4\phi_0 = 3.16 \times 10^{-6} B$ [T] states per carbon atom. Accounting for the quadruple degeneracy of the LLs (two $K$ points and two spin polarizations), the central $n = 0$ levels will be filled for fields below 20 T at a doping of only 0.025%. For the lowest field for which we predict the effect, the doping is a modest 0.01%. Unlike in a many-body gap, the Fermi level is not pinned and the width of the LL will be given by the width of the mobility single-particle gap in disordered graphite. Strong disorder leads to wide Hall plateaus, and weak disorder to narrow ones.

Besides the prediction of a quantized response, the chiral surface sheet should exhibit ballistic in-plane longitudinal response $\rho_{xx} \to 0$ as $T \to 0$. Remarkable transport properties are also present along the direction parallel to the magnetic field. In this direction the system is a stable metal with a temperature independent resistivity $\rho_{xx}$, with a value which can be much larger than $h/e^2$, although, unlike previously predicted, we do expect the metallic phase to be unstable to very strong disorder and impurity concentration which levitates the bulk extended states above the Fermi level.

In conclusion, we predict the appearance of one plateau of 3D quantized Hall transport in doped bulk graphite under strong magnetic fields parallel to its $c$-axis. We analyzed the Hofstadter problem in graphite and estimate the minimum field to be approximately 7.0 T (for holes) and 15.4 T (for electrons). While our general conclusions are robust, differences among material parameters reported in the literature can shift the critical fields by several Tesla. The recent advances and interest in graphene and graphite make our prediction testable with current experimental techniques.

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