Dirac Loops in Carbon Allotropes

Kieran Mullen,1 Bruno Uchoa,1 and Daniel T. Glatzhofer2

1Department of Physics and Astronomy, University of Oklahoma, Norman, Oklahoma 73069, USA
2Department of Chemistry and Biochemistry, University of Oklahoma, Norman, Oklahoma 73069, USA

We propose a family of structures that have “Dirac loops”: closed lines in momentum space with Dirac-like quasiparticles, on which the density of states vanishes linearly with energy. The structures all possess the planar trigonal connectivity present in graphene, but are three dimensional. We present a simplified tight-binding calculation of their band structure, and discuss the consequences of their multiply-connected Fermi surface for transport. We conclude with a discussion of the feasibility of realizing the structures as an allotrope of carbon.

Introduction. Dirac semi-metals have been defined as three dimensional (3D) materials where the conduction and valence bands linearly cross at a discrete set of degenerate points [1]. Those materials have both inversion and time reversal symmetry, unlike their Weyl counterparts, where either symmetry is broken, and the cones split in two non-degenerate copies with non-zero Chern number which are connected by symmetry protected Fermi arcs [2]. Less well known are Dirac loops, 3D closed lines in momentum space on which the energy vanishes linearly with the perpendicular components of momentum [3]. Semiclassical paths encircling those lines produce a π Berry phase, as in graphene. To date there are no experimental observations of Dirac loops, and they were predicted to exist only in systems with superlattices in which the parameters such as interactions and magnetic field are finely tuned [3].

In graphene, the existence of the Dirac point results from the planar trigonal connectivity of the honeycomb lattice and its sub-lattice symmetry. The planar structure of the trigonal sp² bonds is generically more stable than the sp³ structure of diamond, which opens a large spin-orbit gap due to the hybridization of σ and π orbitals [3, 4]. However, graphene is not the only planar trigonally connected allotrope of carbon. Crossed lattices of polyacetylene were theoretically proposed as a metallic allotrope of carbon [5]. Several other trigonally connected structures have been also considered in the chemical literature [6, 7]. It is therefore natural to ask if there are variations on this geometry that might produce exotic Fermi surfaces with Dirac-like excitations.

In this Letter we propose a family of 3D carbon structures that have Dirac-like quasiparticle excitations along a Dirac loop, without requiring any tuning. Some of these structures lie in the family of harmonic honeycomb lattices, which have been recently studied in the context of the Kitaev model [10, 11, 12], and experimentally realized in honeycomb iridates [14]. The simplest example is the hyper-honeycomb lattice, whose unit cell is shown in Fig. 1a. Due to the trigonal connectivity of the carbon bonds, the lattice is generated by a multicompontent basis formed by the several carbon atoms contained in the unit cell. When the system is doped away from half filling, the Fermi surface is toroidal, and highly anisotropic. Although the system is a 3D metal, we show that the application of a uniform magnetic field creates a discrete spectrum of Landau levels (LLs), where the zero LL is present whenever the corresponding cyclotronic semi-classical paths encircle the Dirac line. We investigate the charge and magneto-transport of this system, and discuss the experimental feasibility of these new carbon allotropes and their chemical stability.

FIG. 1. (Color online) Simple carbon allotropes that produce a Dirac loop. a) The hyper-honeycomb lattice, with a four atom unit cell: atoms 1, 2 and 3 are in the XY plane, while atoms 2, 3 and 4 are in the YZ plane. Atoms 1 and 2 form a vertical chain with black links; atoms 3 and 4 form horizontal chain with blue links. The chains are connected by links (red ) in the z-direction. b) An eight atom unit cell : atoms 1-4 create a vertical chain with black links; atoms 3 and 4 form horizontal chain with blue links. The chains are connected by links (red) in the z-direction. b) An eight atom unit cell : atoms 1-4 create a vertical chain of hexagons along the x-direction, while atoms 5-7 create a horizontal chain when repeated in the y-direction. All atoms are connected by three co-planar sp² bonds spaced by 120°.
Projected Hamiltonian. Our discussion starts with the simplest structure shown in Fig. 1b, the hyper-honeycomb lattice, which has four carbon atoms in the unit cell. The tight binding basis is of the form \( \psi_{\alpha,k}(\vec{r}) = \phi_\alpha(\vec{k}) e^{i\vec{k}\cdot\vec{r}} \), with \( \alpha = 1, 2, 3, 4 \) labeling the components of a four vector \( \Phi_k \), which describes the amplitudes of the electronic wavefunction on the four atoms in the unit cell.

\[
\mathcal{H}_{\alpha,\beta} = \begin{pmatrix}
0 & 2e^{i\phi_x} \cos \left( \frac{\sqrt{3}}{2} k_x a \right) & 0 & e^{-ik_z a} \\
2e^{-i\phi_x} \cos \left( \frac{\sqrt{3}}{2} k_x a \right) & 0 & e^{ik_z a} & 0 \\
0 & e^{ik_z a} & 0 & 2e^{i\phi_y} \cos \left( \frac{\sqrt{3}}{2} k_y a \right) \\
e^{i\phi_x} & 0 & 2e^{-i\phi_y} \cos \left( \frac{\sqrt{3}}{2} k_y a \right) & 0
\end{pmatrix},
\]

with \( a \) the interatomic distance. This Hamiltonian has a zero energy eigenvalue along the curve defined by \( k_z = 0 \) and

\[
4 \cos \left( \frac{\sqrt{3} k_x a}{2} \right) \cos \left( \frac{\sqrt{3} k_y a}{2} \right) = 1.
\]

Eq. (2) defines a zero energy line \( \vec{k}_0 = (k_x(\phi), k_y(\phi), 0) \) shown in the solid white lines in Fig. 2b, where \( \phi \) is the cylindrical polar angle with respect to the center of the Brillouin zone (BZ) at the \( \Gamma \) point. The energy spectrum of the Hamiltonian has four bands, shown in Fig. 2a, where the two lowest energy bands are particle hole-symmetric and cross along the nodal lines, in the \( k_z = 0 \) plane. The bands displayed in Fig 2a follow the path shown in the triangular line of panel b, with the point \( R \) located in the middle of the flattened corners of the BZ. Both \( \Gamma \) and \( R \) are high symmetry points, whereas the \( M \) point is a projection of a high symmetry point into the \( k_z = 0 \) plane. The energy bands are periodic under momentum displacements commensurate with the reciprocal lattice vectors \( \vec{b}_1 = (2\pi/\sqrt{3}a, 0, \pi/3a) \), \( \vec{b}_2 = (0, 2\pi/\sqrt{3}a, -\pi/3a) \) and \( \vec{b}_3 = (0, 0, 2\pi/3a) \).

Expanding the \( \Phi \) eigenvectors around the nodal line and projecting the Hamiltonian (1) in the two dimensional subspace that accounts for the lowest energy bands, the projected Hamiltonian can be written as

\[
\mathcal{H}_P(\vec{q}) = [v_x(\phi)q_x + v_y(\phi)q_y] \sigma_x + [v_z(\phi)q_z] \sigma_z,
\]

where \( \vec{q} \equiv \vec{k}(\phi) - \vec{k}_0(\phi) \) is the momentum measured away from the nodal line, \( \sigma_x, \sigma_z \) are \( 2 \times 2 \) Pauli matrices (we set \( \hbar \rightarrow 1 \))

\[
\pm E_k = \pm \sqrt{[v_x(\phi)q_x + v_y(\phi)q_y]^2 + [v_z(\phi)q_z]^2}
\]

is the low energy spectrum. The Fermi velocities \( v_i(\phi) \) \((i = x, y, z)\) are plotted in Fig. 2d, and can be approximated by simple trigonometric functions. The quasiparticles of Hamiltonian (3) are chiral in that there is a Berry phase \( i \oint \vec{A}_k \cdot d\vec{k} = \pi \) associated with paths in momentum space that encircle the loop, which can be viewed as a continuum of Dirac cones along a closed line in the BZ. This state of affairs of closed nodal lines with a chiral quasiparticle excitations is what we have in mind.
define as Dirac loops. Away from half-filling, the Fermi surfaces are toroids containing the nodal line $k_0(\phi)$, as shown in Fig. 3.

A similar analysis can be done for the unit cell shown in Fig. 1b, which has 8 carbon atoms in the unit cell. In that case, the tight binding Hamiltonian is an $8 \times 8$ matrix with 8 different bands. This Hamiltonian can be projected into the low energy states, resulting in a Hamiltonian with the same form as Eq. (3).

The above structures are merely two in a hierarchy of possible lattices that can be made with perpendicular zigzag chains of trigonally connected carbon atoms. We denote these structures with two integers $(n_x, n_y)$, where $n_x$ ($n_y$) is the number of vertical (horizontal) complete honeycomb hexagons contained in the unit cell. In this notation, the hyper-honeycomb lattice shown in Fig. 1a describes a $(0, 0)$ lattice, while Fig. 1b has one complete honeycomb hexagon along both the vertical and horizontal zigzag chains in the unit cell, and hence is a $(1, 1)$ structure. The symmetric higher order structures $(n, n)$ belong to the family of harmonic honeycomb lattices, denoted as $H_n$, with $n \in \mathbb{N}$ [14]. In this family, the screw axis symmetry is preserved and they all display Dirac loops at zero energy around the $\Gamma$ point, with the $H_0$ case shown in Fig. 1a being the simplest polyalkene chain arrangement. Asymmetric structures where $n_x \neq n_y$ have a very anisotropic unit cell and their nodal lines are displaced in the BZ (see supplementary materials).

Minimal model. The simplest Hamiltonian that captures the physics described in Hamiltonian (3) is a minimal model where we approximate the nodal line (2) by a zigzag chains of trigonally connected carbon atoms. We of possible lattices that can be made with perpendicular zigzag chains of trigonally connected carbon atoms. We

$$H_0(\mathbf{q}) = -v_0 q_x \sigma_x + v_z q_z \sigma_z,$$

where $q_p = k_p - k_0$, is the small change in the cylindrical radial momentum $k_p \equiv (k_{p_x}^2 + k_{p_z}^2)^{1/2}$ away from the radius of the nodal line, and $v_0$, $v_z > 0$ are the corresponding velocities in the $\hat{\rho}$ and $\hat{z}$ directions. Hamiltonian (5) disperses linearly along the two normal directions, $\hat{\rho}$ and $\hat{z}$. The density of states per volume varies linearly with the energy $D(E) = k_0 E/(2\pi v_0 v_z)$, including a factor of two for the spin degeneracy.

Charge transport. We now consider the consequences of the nodal loop for transport. In the minimal model (5), the velocity in the $\hat{\phi}$ direction is always zero. Hence, it is impossible to create solenoidal currents in the $\hat{\phi}$ direction by the application of a time changing magnetic field along the $z$ direction. While this is no longer precisely true for the nodal line of Eq. (2) shown in Fig. 2b, which is only nearly circular, we expect the current response to a solenoidal driving force to be greatly suppressed.

For short range impurities, the DC conductivity can be calculated self-consistently at zero temperature [20]. Going back to the projected Hamiltonian (9), we define the Green’s function $\hat{G}_k(\omega) = [\omega - \hat{H}_0(k) - \hat{\Sigma}(\omega) + i\delta]^{-1}$, where the $2 \times 2$ matrix $\hat{\Sigma}(\omega) = V_0 \sum_k \hat{G}_k(\omega)$ is the self-energy due to a local quenched disorder potential $(V(x)V(x')) = V_0^2 \delta(x - x')$ [21]. At zero frequency, the self consistent solution of the self-energy $\hat{\Sigma}(0) = i\Omega$ is diagonal and purely imaginary, where $\Omega = \lambda \exp[-2\pi v_0 v_z/(k_0 V_0^2)]$ is the scattering rate defined by an ultraviolet energy cut-off $\Lambda \sim \tau$. The DC conductivity in the direction $\hat{\rho}$ is $\sigma_{\rho}(0) = e^2 \lim_{\omega \to 0} tr \sum_k \hat{\rho}_n A(k, \omega) \hat{\nu}_n A(k, \omega)$ where $A(k, \omega) = -2i\text{Im} \hat{G}_k(\omega) = \Gamma/(E_k^2 + \Gamma^2)$ is the spectral function, $e$ is the electron charge and $\hat{\nu}_n = \hat{\rho} \cdot \nabla_n \hat{H}_0$ is the velocity operator projected along the $\hat{\rho}$ direction. In 3D, the conductivity has units of $e^2/h$ divided by length (restoring $h$). When $\Gamma \ll \Lambda$, the conductivity is, as expected, independent of the scattering rate [17], and gives

$$\sigma_{\rho}(0) = (e^2/h)C_{\rho}/a,$$

where $C_{\rho}$ is a non-universal dimensionless geometrical factor. In the $H_0$ allotrope, $C_{\rho} = 0.142$ in the $z$ direction and $C_x = C_y = 0.0599$ along the $x$ and $y$ directions. In the minimal model (5), $C_z = 3k_0 v_0/(4v_z)$ for transport along any direction in the plane of the Dirac loop. Those values contrast with the theoretical conductivity of Dirac fermions in 2D for unitary disorder, $\sigma(0) = 4e^2/(\pi h)$ [17,18].

Quantum Hall effect. Due to the multiply connected nature of the Fermi surface, unusual effects can be expected when a magnetic field is applied. At low fields the Fermi surface can be observed in the Shubnikov-de Haas and de Haas-van Alphen effects [19]. At larger fields one expects to find remnants of the quantum Hall effect.

In the presence of a magnetic field, the minimal model (5) becomes $H_0(\rho, z) = -v_0 \sigma_x(\partial_\rho - A_\rho) + v_z \sigma_z(\partial_z - A_z)$,
where $\mathbf{A} = A_x \hat{z} + A_y \hat{y} + A_z \hat{\phi}$ is the vector potential. In this model, the application of a magnetic field along the $z$ axis, which can be described in the symmetric gauge by $\mathbf{A} = \frac{1}{2} B_z \hat{\phi}$, has no effect in the Hamiltonian, and hence does not produce cyclotronic orbits and LL quantization. Small deformations of the circular Dirac loop create large cyclotronic orbits, which can restore LL quantization at strong enough fields.

Conversely, a toroidal magnetic field pointing along the $\hat{\phi}$ direction can be produced with time dependent electric fields applied along the $\hat{z}$ direction. This magnetic field corresponds in the symmetric gauge to a vector potential $\mathbf{A} = -B_\phi \hat{z}$. Taking the square of the Hamiltonian $\mathbf{H}_0^2(\xi)$, $\mathbf{H}_0^2(\xi) = \frac{1}{2} \xi^2 [ (\xi^2 - \partial_z^2) \sigma_0 + \sigma_y ]$, where $\sigma_0$ is the identity matrix, $\xi \equiv \sqrt{v_z/\nu_0 (\rho/\ell_B - k_z \ell_B)}$ is a dimensionless variable with guiding center $X = -k_z \ell_B$, and $v_z = \sqrt{2m\nu_0 \ell_B}$ is defined by the magnetic length $\ell_B = 1/\sqrt{\phi_0}$. Rewriting the Hamiltonian in terms of ladder operators of the 1D Harmonic oscillator, $a = (\xi + \partial_x)/\sqrt{2}$ and $a^\dagger = (\xi - \partial_x)/\sqrt{2}$, the energy spectrum has a zero energy LL and is the same as in conventional 2D Dirac fermions in a magnetic field, $E = \pm \omega_c \sqrt{n}$, where $n$ is the LL index. In a perfectly circular Dirac loop, this produces the remarkable result that one can observe sharply well defined LLs in a 3D metallic system without any broadening from the transverse degree of freedom, regardless of the strength of the magnetic field.

In Fig. 4a, we consider the tight-binding Hamiltonian and show the LLs for a uniform magnetic field applied in the $x$ direction. In momentum space, the semiclassical paths that correspond to the cyclotronic orbits encircle the Dirac loop, producing a zeroth LL. Because of the 3D nature of the crystal, for a given field, each LL can correspond by a different section of the toroidal Fermi surface along the $k_x$ direction. In Fig. 4a, the zeroth LL has different semiclassical trajectories for $B_z = \phi_0/60\pi a^2$, with $\phi_0 = h/2e$ the magnetic flux quantum, which produce a finite bandwidth with a beating pattern. At this field, the other two higher LLs shown in Fig. 4a are each associated with a single semiclassical trajectory on the Fermi surface, and remain sharp. In Fig. 4b, we show the LL structure for a magnetic field applied along the $\hat{z}$ direction, with $B_z = \phi_0/60\pi a^2$. Because of the nodal loop in the projected Hamiltonian is not a perfect circle, the electrons can disperse along the $\hat{\phi}$ direction with a small Fermi velocity. The semiclassical paths due to the real space cyclotronic motion in this case do not encircle the Dirac loop, and hence do not produce a zeroth LL.

**Chemical synthesis.** Although synthesis of such carbon allotropes can be challenging, the $\mathcal{H}$-0 allotrope could be synthesized in a layer by layer fashion using a monofunctionalized alkyn was supported by NSF grant DMR-1310407. B. U. acknowledges University of Oklahoma and NSF grant DMR-1352604 for partial support.  

![FIG. 4. (Color online) a) Energy of the LLs in units of $t$ for a magnetic field applied along the $x$ direction ($B = \phi_0/60\pi a^2$). The zeroth LL has a finite band width, while the higher LLs shown remain sharply defined (see text). b) LLs for a magnetic field $B = \phi_0/60\pi a^2$ applied along the $z$ direction. The semiclassical paths do not encircle the Dirac line, and the zeroth LL is absent. All momenta in units of $\pi/a$](image-url)
[6] A. H. Castro Neto and F. Guinea, Phys. Rev. Lett. 103, 026804 (2009).
[7] R. Hoffmann, T. Hughbanks, M. Kertesz, J. Am. Chem. Soc. 105, 4831 (1983).
[8] A. F. Wells, R. R. Sharpe, Acta. Cryst. 16, 857 (1963).
[9] M. V. Nikerov, D. A. Bochvar and I. V. Stankevich, Zhurnal Strukturoi Khimii, 23, 13 (1982).
[10] A. Kitaev, Annals of Physics 321, 2 (2006).
[11] I. Kimchi, J. G. Analytis, and A. Vishwanath, arXiv:1309.1171v2.
[12] S. Mandal, and N. Surendran, Phys. Rev. B 79, 024426 (2009).
[13] E. K-H Lee, R. Schaffer, S. Bhattacharjee, and Y. B. Kim Phys. Rev. B 89 045117 (2014).
[14] K A Modic et al., Nat. Comm. 5, 1 (2014).
[15] M. V. Berry, Proc. of the Royal Society of London, A 392, 451 (1984).
[16] J. Zak, Phys. Rev. Lett. 62, 2746, (1989).
[17] E. Fradkin, Phys. Rev. B, 33, 32633268 (1986).
[18] N. M. R. Peres, Rev. Mod. Phys., 82(3), 2673 (2009).
[19] N. W. Ashcroft and N. D. Mermin, Solid State Physics, Philadelphia PA: Holt, Rinehart and Winston, (1976) Print.

[20] Time reversed paths that encircle the Dirac line pick up a relative phase of $\pi$ and therefore cancel. However, backscattering between opposite sides of the BZ across the nodal line is not suppressed, as they can be described by paths that pick an overall Berry phase of $2\pi$.
[21] P. Lee, Phys. Rev. Lett., 71 (12), 1887 (1993).
[22] G. Pal, W. Apel, and L. Schweitzer, Phys. Rev. B 85, 235457 (2012).
[23] Q. Li, J. R. Owens, C. Han, B. G. Sumpter, W. Lu, J. Bernholc, V. Meunier, P. Maksymovych, M. Fuentes-Cabrera, M. Pan, Sci. Rep. 3, 2102 (2013).
[24] Jianzhao Liu, Jacky W. Y. Lam, and Ben Zhong Tang, Chem. Rev.,109, 5799 (2009).
[25] L. Bialy, and H. Waldmann, Chem. Eur. J., 10, 2759 (2004).
[26] T. R. Hoye, B. Baire, D. Niu, P. H. Willoughby, B. P. Woods; Nature 490, 208 (2012).
[27] P. R. Khoury, J. D. Goddard and W. Tam, Tetrahedron 60, 8103 (2004).
[28] R. H. Boyd, Tetrahedron 22, 119(1966).
[29] R. Stofer, H. Mussoy, Anqew. Chem. 89, 430 (1977).