Dirac and Weyl Fermions in
3D Hopf-linked Honeycomb Lattices: Hopfene

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Carbon allotropes such as diamond, nano-tube, Fullerene, and Graphene, have unique lattice symmetries of crystal lattice, but these are topologically trivial. We have proposed a topologically-nontrivial allotrope, named Hopfene, which has three-dimensional (3D) arrays of Hopf-links to bind 2D Graphene sheets both vertically and horizontally. Here, we describe the electronic structures of Hopfene by simple tight-binding calculations. We confirmed the original Dirac points of 2D Graphene were topologically protected upon the introduction of the Hopf links, and low-energy excitations are described by 1D, 2D, and 3D Dirac and Weyl Fermions.

FIG. 1. New 3D carbon allotrope, Hopfene. (a) Crystal structure. Graphene sheets are stacked both horizontally and vertically. Colours of carbon atoms are just guide to the eyes, representing AB- and CD-sublattices. (b) Hopf-links at the intersection. (c) Extended view inside Hopfene. (d) Horizontal and (e) vertical Graphene sheets, showing the penetration of bonds across the sheets perpendicular to each other.

Asymptotic low-energy dispersion of an elementary particle is correlated with the symmetries of the vacuum, and the emergence of the mass is a manifestation of a broken symmetry\[^1\]. In condensed-matter physics, we can design materials with certain symmetries, and carbon allotropes are especially useful, because there are huge varieties of families with different translational and rotational symmetries of the crystal lattices in a form of a cage\[^2\], a tube\[^3\]–\[^4\], and a sheet\[^5\]–\[^8\]. These materials are revolutionising the material science and technologies, leading to novel applications such as Micro-Electro-Mechanical-Systems (MEMS)\[^9\] and Field-Effect-Transistors (FETs)\[^6\], however, these materials are topologically trivial without having a link nor a knot. On the other hand, there are vast majorities of synthetic materials with non-trivial topological configurations, known in polymers\[^10\]–\[^12\], macromolecules\[^13\]–\[^16\], and proteins\[^17\]. Recently, we have applied the concept of topological materials to design a new carbon allotrope, Hopfene, based on a idea of using Hopf-links\[^18\].

The proposed crystal structure of Hopfene\[^18\] is shown in Fig. 1. Hopfene is made by stacking two-dimensional (2D) honeycomb lattices, Graphene\[^5\]–\[^7\] sheets, both vertically and horizontally (Fig. 1 (a)) with arrays of Hopf-links at intersections (Figs. 1 (b) and (c)). The Graphene sheets are aligned parallel to the direction along zig-zag edges and perpendicular to the arm-chair edges (Figs. 1 (d) and 1 (e)). In contrast to Carbon-Nano-Tubes (CNTs), for which the structures were categorised by the way to role-up a Graphene sheet, Hopfene is characterised by the way to insert Graphene sheets\[^18\]. In this example of Fig. 1, available slots for Graphene sheets are occupied every alternative slots, and it is called as (2,2)-Hopfene. The crystal is tetragonal with the lattice constants of \(a = b = 2a_0\) within the \(x - y\) plane and \(c = \sqrt{3}a_0\) along \(z\) (Figs. 1 (d) and 1 (e)) at the bond length of \(a_0\). The details of the Hopfene structures were described in Ref. \[^18\], and the purpose of this letter is to explore the impacts of Hopf-links on the electronic band diagrams.

Graphene\[^5\]–\[^7\] is attracting significant interests, because the low-energy linear excitations are described by massless Dirac Fermions, which are considered to be emerged from magnetic monopoles located at valleys of the band structure, called Dirac points\[^4\]–\[^19\]–\[^21\]. These
monopoles with certain geometrical Pancharatnam-Berry phase factors\cite{21,22} are topologically protected, so that the electronic structures are robust against the perturbation as far as space and time reversal symmetries are guaranteed\cite{19,20}. We have confirmed this feature and found the dimensional crossover of Dirac and Weyl fermions due to the inter-valley mixing between orthogonal Graphene sheets.

We have employed a tight-binding Hamiltonian for (2,2)-Hopfene\cite{18} (Fig. 1) as

$$\hat{H} = \sum_{\mathbf{k}\sigma} \hat{\psi}^\dagger_{\mathbf{k}\sigma} \left( \begin{array}{c} \mathcal{H}(h_{AB}) \\ \mathcal{H}_H \\ \mathcal{H}(h_{CD}) \end{array} \right) \hat{\psi}_{\mathbf{k}\sigma},$$

where $\hat{\psi}_{\mathbf{k}\sigma} = (a_{\mathbf{k}\sigma}, b_{\mathbf{k}\sigma}, c_{\mathbf{k}\sigma}, d_{\mathbf{k}\sigma})$ and $\hat{\psi}^\dagger_{\mathbf{k}\sigma}$ are annihilation and creation operators for electrons with the momentum $\mathbf{k}$ (in the units of $2\pi(a^{-1}, a^{-1}, c^{-1})$) and the spin $\sigma$ in A-D sublattices. The matrix components in Graphene sheets are

$$\mathcal{H}_G(h) = \left( \begin{array}{ccc} 0 & h & 0 \\ h^* & 0 & 0 \\ 0 & 0 & 0 \end{array} \right)$$

with $h_{AB} = -t_G(e^{i\mathbf{k}\cdot\mathbf{a}/2} + 2e^{-i\mathbf{k}\cdot\mathbf{a}/4}\cos(k_z c/2))$ and $h_{CD} = -t_G(e^{i\mathbf{k}\cdot\mathbf{a}/2} + 2e^{-i\mathbf{k}\cdot\mathbf{a}/4}\cos(k_z c/2))$. The components for Hopf-links are described by a $2 \times 2$ matrix

$$\mathcal{H}_H = -t_H \left( \begin{array}{cc} \phi_k & \phi_k \\ \phi_k & -\phi_k \end{array} \right)$$

with $\phi_k = (e^{ika}, e^{-ika})$. The nearest neighbour transfer energies for Graphene and Hopf-links are $t_G = 2.8$ eV\cite{4,23} and $t_H \approx 1.5\pm0.5$ eV, which was roughly estimated in comparison with the first principle calculation\cite{21,22}. $\hat{H}$ is a $4 \times 4$ matrix with the $SU(2) \otimes SU(2)$ symmetry to describe electron transfers within and between Graphene sheets. By diagonalising $\hat{H}$ at each $\mathbf{k}$, we can easily obtain the band diagram with 4 energy dispersions, $E_1(\mathbf{k})$-$E_4(\mathbf{k})$, measured from the bottom (Fig. 2).

In Graphene, Dirac points are located at $K = (0,-2/3)$ and $K' = (0,-2/3)$, and there are 4 equivalent points at $(\pm 1/2, \pm \sqrt{3}/2)$ due to the symmetry of the 2D honeycomb lattice\cite{3}. In Hopfene, on the other hand, these 6 Dirac points for horizontal and vertical Graphene sheets are not equivalent any more, because these are located within the first Brillouin zone and not at the edge of the zone. Consequently, 10 Dirac points in Hopfene with $t_H = 0$ are located at $(\pm 1/2, 0, \pm \sqrt{3}/2), (0, \pm 1/2, \pm \sqrt{3}/2)$, and $(0, 0, \pm 2/3)$. In particular, the last points of $(0,0,\pm 2/3)$ are degenerate, because these are originated from both horizontal and vertical Graphene sheets. In the presence of $t_H \neq 0$, the Dirac points will be shifted in $\mathbf{k}$-space, and the slope of the dispersion will be changed, but the essential topological feature will be kept unchanged.

The other interesting feature of the band diagram in Hopfene is the emergence of the flat-bands. At $t_H = 0$, bands will not be dispersive along the direction perpendicular to the Graphene sheets (Fig. 2 (a)), and therefore, the Dirac points will become nodal lines\cite{20}. Both Dirac points and nodal lines are topologically protected, so that they cannot disappear by adiabatic turn-on of $t_H$ (Fig. 2 (b)), unless Dirac points or nodal lines with opposite geometrical winding numbers would be merged, simultaneously, leading to the destruction of apparent monopoles with opposite magnetic charge.

It was not possible to obtain analytic solution of $\hat{H}$ in general, regardless of its simplicity. Therefore, we have checked the weak coupling limit, $t_H \to 0$ at $(0,0,2/3)$, where we obtain

$$\mathcal{H}_G(h_{AB}) \approx \hbar v_G(\sigma_1 k_z + \sigma_2 k_x)$$

$$\mathcal{H}_G(h_{CD}) \approx \hbar v_G(\sigma_1 k_z + \sigma_2 k_y)$$

$$\mathcal{H}_H \approx -(t_H + \hbar \tilde{v}_H) 1 + \frac{2}{\hbar} \hbar v_H (i \sigma_3 (k_x - k_y) - \sigma_2 (k_x + k_y))$$

with the velocities of $v_G = 3t_G a_0/(2\hbar)$ and $v_H = 3t_H a_0/(2\hbar)$ for Graphene and Hopf-links, Dirac constant of $h$, $k_z = k_z - 2/3$, the identity matrix $1$, and Pauli matrices of $\sigma_1$, $\sigma_2$, and $\sigma_3$. The constant energy of $-t_H$ barely shifts the bands by forming bonding and anti-bonding states between horizontal and vertical Graphene sheets by Hopf-links, and will not change the linearity. The reset of the Hamiltonian can be diagonalised and we obtained the effective Hamiltonian at $(0,0,2/3)$ as

$$\hat{H}_{eff} = \sum_{\mathbf{k}\sigma} \tilde{\Psi}^\dagger_{\mathbf{k}\sigma} (v_x k_z \sigma_1 + v_y k_y \sigma_2 + v_z k_z \sigma_3) \hat{\psi}_{\mathbf{k}\sigma},$$

where $\tilde{\psi}_{\mathbf{k}\sigma} = (a_{\mathbf{k}\sigma}, \gamma_{\mathbf{k}\sigma})$ and $\tilde{\psi}^\dagger_{\mathbf{k}\sigma}$ are annihilation and creation operators of quasi-particles for the Dirac valley and the velocity along $z$ was renormalised to be $v_z = (3t_G + t_H) a_0/\hbar$, while $v_x = v_y = v_G$. Therefore, the 3D Weyl Fermions will be obtained by the mixing of 2D Dirac Fermions at the degenerate Dirac point. We also obtained the flat-band, which penetrates the Dirac point.

For a stronger Hopf-link of $t_H = 1.5$ eV, we have calculated band structures by solving $\hat{H}$ numerically (Figs. 3-5 and Supplementary Video \cite{26,27}). We confirmed
3D Weyl Fermions, which have linear dispersions along all directions (Figs. 3 (a)-(c)), appeared near the degenerate Dirac points with the energy of $E_D = -1.0$ eV (Fig. 3). We found the 3D Fermi surfaces, which should be spheroids, found at the Fermi energy $E_F$ of -1.2 eV (Fig. 3 (d)) for lower valleys, and they disappeared at $E_D$ as we increased $E_F$, while they appeared again at $E_F$ of -0.8 eV (Fig. 3 (e)) in the same locations of $k$-space for higher valleys. We also checked the linearity of the band at the Dirac point by plotting in both $k_x$-$k_y$ (Figs. 3 (f) and 3 (g)) and $k_x$-$k_z$ (Fig. 2 (b)) planes, so that the Weyl bands were formed between $E_3(k)$ and $E_1(k)$. It was also identified that the flat-band $E_2(k)$ is penetrating between $E_3(k)$ and $E_1(k)$, along $k_z$ and $k_y$ directions, while $E_2(k)$ is degenerate with $E_3(k)$ along $k_x$ (Fig. 3 (c)). These features are topologically equivalent to those expected at the weak coupling limit.

At the higher energy of $E_D = 3.2$ eV, we found 2D Dirac Fermions at $k = (0, 0, 0.48)$ (Fig. 4). Near this point, the dispersions were linear along $k_x$ (Fig. 4 (a)) and $k_y$ (Fig. 4 (b)), but it was almost flat along $k_z$ (Fig. 4 (c)). This means that the confinement along $k_z$-direction was weak, so that the Fermi surfaces was spreading significantly along $k_z$ (Figs. 4 (d) and (e)). Consequently, the cross sections of the Fermi surfaces along the $k_x$-$k_y$ plane were circular, leading to the 2D electronic characters. These 2D Dirac Fermions are similar to those in a single Graphene sheet with regard to the 2D topological shape of the Fermi surface. However, they also have dispersion along $k_z$ in Hopfene, so that they should be described as quasi-2D, strictly speaking, similar to correlated electronic materials such as cuprates [28], in contrast to the monolayer of Graphene, where the perfect 2D confinement was achieved.

We also found the quasi-1D Dirac Fermions, which were made of flat-band along the $k_x$-$k_y$ plane (Figs. 5 (a) and (b)), while they have linear dispersions along $k_z$ (Fig. 5 (c)). In this case, the highest energy states in $k$-space will become Fermi points along $k_z$ (Figs. 5 (d) and (e)). The electronic properties of these states will be quasi-1D. We have 8 different 1D Dirac points in the plot of the Fermi surface of Figs. 5 (d) and (e). Generations of these points would be linked to the original Dirac points and flat-bands. If we had the Dirac points coming from Graphene or Hopf links, these points will survive upon the introduction of the adiabatic turn-on of $t_H$, if $t_H$ is sufficiently small. Suppose we extend this linear dispersion from Dirac points to meet the flat-band, another Dirac points will be generated at the crossing points.
These generations should accompany both positive and negative topological charges with opposite chiralities, and thus the number of generated Dirac points would be even. In our Hopfene, we found huge amounts of Dirac points, characterised by different dimensionality.

\[ \begin{align*}
E_D = 2.8 \text{ eV} & \quad \text{(a)} \\
E_D = 2.8 \text{ eV} & \quad \text{(b)} \\
E_D \neq 2.8 \text{ eV} & \quad \text{(c)} \\
E_F = 2.5 \text{ eV} & \quad \text{(d)} \\
E_F = 3.1 \text{ eV} & \quad \text{(e)}
\end{align*} \]

FIG. 5. 1D Dirac Fermions of (2,2)-Hopfene. Band structures at Dirac point \( k = (2/3, 0, 1/2) \) at \( E_D = 2.8 \text{ eV} \) along (a) \( x \), (b) \( y \), and (c) \( z \) directions. Fermi points of (d) lower and (e) upper valleys.

In the present letter, we have assumed that we can control Fermi level at our disposal. In the real experiments, the Fermi level must be determined to ensure the charge neutrality. In our calculation, \( E_F \) in non-doped (2,2)-Hopfene was 0.85 eV. Due to the semi-metal structure of the electronic bands, it will not be possible to change the Fermi level by the application of the gate voltage in a metal-oxide-semiconductor structure. However, the metal intercalation such as doping of alkali-metal would be possible, because of the huge available space along \( z \) (c-axis) surrounded by Graphene sheets (Figs. 1 (a) and (c)). The flat-bands found in this letter would be favourable to possible observations of superconductivity and/or ferromagnetism, because of the increase in the density-of-states.

In conclusion, electronic structures of the 3D Hopf-linked honeycomb lattices, named Hopfene, shows the distinctive topological features characterised by 3D, 2D, and 1D Weyl and Dirac Fermions. The Fermi surfaces show the dimensional crossover upon changes of the Fermi level. The impacts of topological structures on electrical properties are significant and the materials will be useful as platforms to examine various concepts of physics including magnetic monopoles, geometrical phases, and topological superconductors.

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C. Schönenberger, Light-controlled conductance switching of ordered metal-molecule-metal devices, *Nano Lett.* **9**, 76 (2009).

[16] J. P. Sauvage, From chemical topology to molecular machines (Nobel lecture), *Angew. Chem. Int. Ed.* **56**, 11080 (2017).

[17] P. Dabrowski-Tumanski and J. I. Sulkowska, Topological knots and links in proteins, *PNAS* **114**, 3415 (2017).

[18] S. Saito and I. Tomita, Topological carbon allotropes: a proposal for materials innovation, arXiv:1904.08107 [cond-mat.mes-hall] (2019).

[19] M. Koshino and T. Ando, Transport in bilayer graphene: Calculations within a self-consistent Born approximation, *Phys. Rev. B* **73**, 10.1103/PhysRevB.73.245403 (2006).

[20] N. P. Armitage, E. J. Mele, and A. Vishwanath, Weyl and Dirac semimetals in three-dimensional solids, *Rev. Mod. Phys.* **90**, 10.1103/RevModPhys.90.015001 (2018).

[21] S. Pancharatnam, Generalized theory of interference, and its applications, *Proc. Indian Acad. Sci., Sect. A* **44**, 247 (1956).

[22] M. V. Berry, Quantal phase factors accompanying adiabatic changes, *Proc. R. Sco. Lond. A* **392**, 10.1098/rspa.1984.0023 (1984).

[23] A. H. CastroNeto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, The electronic properties of graphene, *Rev. Mod. Phys.* **81**, 109 (2009).

[24] D. A. Evans, History of the Harvard ChemDraw project, *Angew. Chem. Int. Ed.* **53**, 11140 (2014).

[25] I. Tomita and S. Saito, in preparation (2019).

[26] S. Saito and I. Tomita, See Supplemental Material at [URL will be inserted by publisher] for Supplementary Video. (2019).

[27] S. Saito and I. Tomita, The data from the paper can be obtained from the University of Southampton ePrint research repository: http://dx.doi.org/10.5258/SOTON/D0904 (2019).

[28] J. G. Bednorz and K. A. Müller, Possible highTc superconductivity in the Ba-La-Cu-O system, *Z. Physik B - Condensed Matter* **64**, 189 (1986).

[29] A. F. Hebard, M. J. Rosseinsky, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, Superconductivity at 18 K in potassium-doped C60, *Nature* **350**, 600 (1991).

[30] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Theory of superconductivity, *Phys. Rev.* **108**, 1175 (1957).

[31] A. Auerbach, *Interacting Electrons and Quantum Magnetism* (Springer, 1994).