

Can graphene be used to teach quantum mechanics?

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Graphene is a wonder material of the future with remarkable attributes of immense technological significance. It is an allotrope of carbon (C) in the structure of a single layer of C atoms, each on the vertex of a hexagonal (honeycomb) lattice. Graphene displays extraordinary properties: (i) mechanical strength – it is one hundred times stronger than the strongest steel; (ii) unusual transport – it is a highly efficient conductor of both heat and electricity; (iii) magnetism – it has a large and nonlinear diamagnetism facilitating levitation; (iv) catalysis – a single layer of graphene is hundred times more chemically reactive than thicker sheets; (v) bio-materials – it is an extremely sensitive bio-sensor, just to name a few. It is not surprising then that graphene has captured the imagination and inquisition of today's internet-savvy high-school and undergraduate students. Yet, it is fascinating to note that all the material characteristics of graphene are the outcome of basic quantum mechanical principles – non-relativistic as well as relativistic. Quantum mechanics is generally considered to be an abstruse topic being far removed from the day-to-day reality of the 'classical' world. Given the curiosity that graphene has generated amongst the youth, is it possible to channelize this excitement to arouse heightened awareness of the subject of quantum mechanics? It is this aspect of 'science education' that we will explore in this note and offer a curriculum of bringing the rich laboratory of graphene to the realm of blackboard teaching of quantum mechanics. We will see that we can build up the story by starting from fundamental quantum chemistry that is taught to today's class XI students and construct, step-by-step, a pathway to modern ideas of quantum condensed matter.

A carbon (C) atom has six electrons which can be configured as $1S^2 2S^2 2P^2$. Here the first entry (1 or 2) stands for $n=1$ or $n=2$, n being the principal quantum number. S and P represent $l=0$ or 1 respectively, where l is the orbital quantum number. In writing this we have tacitly incorporated wave-particle duality (Appendix 1) – the electrons are not just point particles, they are in extended wave-function states. In addition, the superscript 2 implies that we can put two electrons of opposite spins in the same quantum state without violating the Pauli exclusion principle (Appendix 2). Now the two $1S^2$ electrons are closest to the C nucleus, and are therefore called the 'core electrons'. They do not participate in any solid-state phenomena, and hence can be ignored for all practical purposes. That leaves us with four of what are called 'valence electrons' in the $2S^2 2P^2$ orbitals. However, the two $2P^2$ electrons can lower their Coulomb repulsion energy by admitting themselves into separate magnetic quantum number m -states, such as in this case $2P_x^1 2P_y^1$, yielding the $2S^2 2P_x^1 2P_y^1$ configuration for the four valence electrons.

There is however a catch – the above configuration would imply divalency of C which in point of fact is tetravalent, as

evidenced by the existence of methane (CH_4).

The resolution of this dilemma derives from what is called 'promotion' – one of the electrons in the $2S$ orbital can be promoted to the still-available $2P_z$ orbital¹. It may appear at first sight that promotion would cost energy, but that is more than offset by the gain in Coulomb repulsion by physically separating the two electrons. Thus we arrive at the configuration: $2S^1 2P_x^1 2P_y^1 2P_z^1$, for the four valence electrons. Note that the choice of the X -, Y - and Z -axes is quite arbitrary, but once made, the X - and Y -axes constitute a plane with the Z -axis perpendicular to it. What is astonishing is that the chosen XY -plane will turn out to be the defining layer of graphene, due entirely to the quantum origin of bonding. A further point to note is that because the singly occupied orbitals $2S^1$, $2P_x^1$, $2P_y^1$ and $2P_z^1$ represent four distinct quantum states, there is no issue with the Pauli exclusion principle – the four electrons are to be assigned the same intrinsic spin (up or down). This empirical observation is called Hund's rule, which reflects spin correlation – electrons with parallel spins behave as though they have a tendency to stay apart causing less repulsion¹. Thus as far as the intrinsic spin is concerned it

is just a trivial label, merely for the purpose of book-keeping.

From a single carbon atom to graphene

As is already implicit, the wave nature of the electron makes it lose its identity – we cannot say for sure which electron belongs to which orbital. This loss of identity can be further appreciated by what is referred to as 'hybridization' – the three electrons in the $2S^1 2P_x^1 2P_y^1$ orbitals can go into three superposed states (Appendix 1) yielding sp^2 hybridization a , b and c (ref. 1)

$$\begin{aligned} |sp_a^2\rangle &= (|2S\rangle - \sqrt{2}|2P_y\rangle)/\sqrt{3}, \\ |sp_b^2\rangle &= (|2S\rangle + (\sqrt{3}|2P_x\rangle \\ &\quad + |2P_y\rangle)/\sqrt{2})/\sqrt{3}, \\ |sp_c^2\rangle &= (-|2S\rangle + (\sqrt{3}|2P_x\rangle \\ &\quad - |2P_y\rangle)/\sqrt{2})/\sqrt{3}. \end{aligned} \quad (1)$$

It may be emphasized that the notation sp^2 has nothing to do with our earlier employed notation for the orbitals, at the beginning of this section. Here sp^2 simply

implies hybridization of one S electron with two P electrons (Figure 1 a). The unhybridized P orbital is along the Z-axis, perpendicular to the plane in which the three hybrids lie (Figure 1 b)¹.

We now answer the question – what happens when two C atoms are brought together? Figure 2 shows the pattern of a C–C double bond. An sp² hybrid on one C-atom (*a*, *b* or *c*, in eq. (1)) overlaps with its neighbour to form a σ-bond, and the remaining sp² hybrids form bonds with neighbouring C-atoms, all at an angle of 120° with each other. It is interesting to delve into the nomenclature of the σ-bond – sigma is S in the Greek alphabet, implying that the underlying bond has cylindrical symmetry around the internuclear axis and it resembles a pair of electrons in an S orbital when viewed along the internuclear axis. The formation of the C–C σ-bond brings the two unhybridized 2P orbitals into a position where they can overlap to form a π-bond. Again, it is so called because, viewed along the internuclear axis, a π-bond

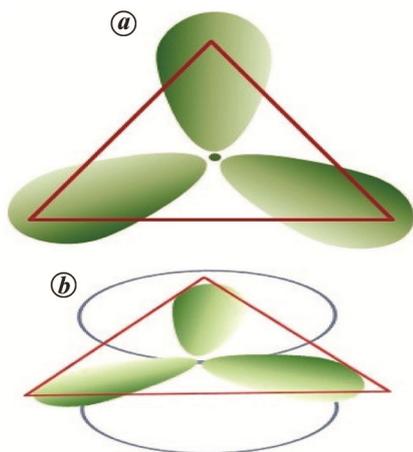


Figure 1. a, Three sp² orbitals depicted by eq. (1). b, Unhybridized p-orbital is normal to the XY-plane in which the three sp² hybrids lie.

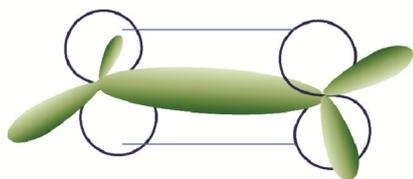


Figure 2. C–C double bond, in which an sp² hybrid of one carbon-atom overlaps with its partner in the neighbouring site to form a σ-bond. This facilitates the two unhybridized 2p orbitals to come together to form a π-bond.

resembles a pair of electrons in the P orbital, and π is the Greek equivalent of P (ref. 1).

It is indeed fascinating to realize that it is the 120° orientations of the three (strongly) σ-bonded pairs of neighbouring C-atoms which lead to the honeycomb structure of planar graphene in which each C-atom finds itself surrounded by three other nearest-neighbour C-atoms at the vertices, indicated by pink and green alternately in Figure 3, of an equilateral triangle². Once the structure is in place, it is the lone 2P_z electron of a C-atom that can π-bond with a similar 2P_z electron of a neighbouring C-atom. Again, Hund’s rule suggests that the two π-bonded electrons have the same spin¹. As it turns out, it is the weakest-bound π-electron that is responsible for all the spectacular properties of graphene³.

Tight-binding approximation

Given this background we now focus on the hexagonal structure of graphene comprising two interpenetrating lattices of equilateral triangles (Figure 3). These two sublattices are denoted by *A* (say, pink) and *B* (say, green). An electron at an *A*-site can tunnel to a *B*-site (Appendix 4), with allowance for only nearest-neighbour hops. As discussed in Appendix 4, the phrase ‘hop’ is only loosely used here – in quantum mechanical terms there is overlap of the wave function of the electron between sites *A* and *B*. A delocalized electron is neither at an *A*-site nor at a *B*-site – it is in a mixed superposed state (Appendix 1)^{4,5}.

Referring to Appendix 3, if the electron is at the *i*th site of the *A*-sublattice, we designate the quantum state by the Dirac ket $|+\rangle_{i\{A\}}$. On the other hand, an

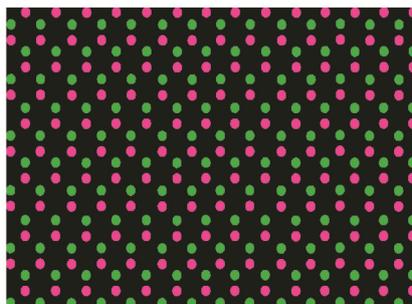


Figure 3. Honeycomb lattice formed by carbon atoms in graphene.

unoccupied state is denoted by $|-\rangle_{j\{A\}}$. The mixed states are the symmetric and anti-symmetric combinations akin to the ‘bonding’ and ‘anti-bonding’ states of Pauling⁶

$$\begin{aligned}
 |\text{Sym}\rangle &= (|+\rangle + |-\rangle)/\sqrt{2}, \\
 |A.\text{Sym}\rangle &= (|+\rangle - |-\rangle)/\sqrt{2}.
 \end{aligned}
 \tag{2}$$

Using the projection matrices of Appendix 4, we can now write down a Hamiltonian in the tight-binding approximation (TBA) as follows⁷

$$\begin{aligned}
 H = -t\sum_{\langle i\{A\}j\{B\}\rangle} &(|+\rangle_{i\{A\}}\langle -|_{j\{B\}} \\
 &+ |-\rangle_{j\{B\}}\langle +|_{i\{A\}}),
 \end{aligned}
 \tag{3}$$

where *t* is just an energy parameter depicting tunnelling. As stressed earlier, the intrinsic spin does not enter into *H* and is therefore not indicated here.

As shown in Appendix 5 (eq. (A9)), the translational periodicity of the two-dimensional layer of graphene can be exploited to obtain the eigenvalue of the Hamiltonian, for each value of the wave vector *k*, as

$$\epsilon_k = \sqrt{|t(k)|^2} \text{ or } -\sqrt{|t(k)|^2}.
 \tag{4}$$

The two energy branches reflect the particle–hole symmetry of graphene, akin to the particle–antiparticle symmetry in Dirac theory (Appendix 6). Explicit expressions for ϵ_k can be computed using eq. (A9) which, when plotted, gives Figure 4, in which the positive branch refers to the conduction band while the negative branch refers to the valence band. In correspondence with the fact that the π-electron belongs to the half-filled 2P_z orbital, the valence band is completely filled while the conduction band is completely empty. However, as will be

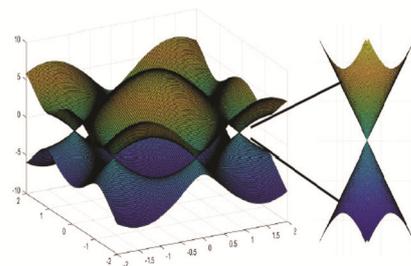


Figure 4. (Left) Electronic energy dispersion of honeycomb lattice in graphene. (Right) Zoom view of single Dirac point of energy band.

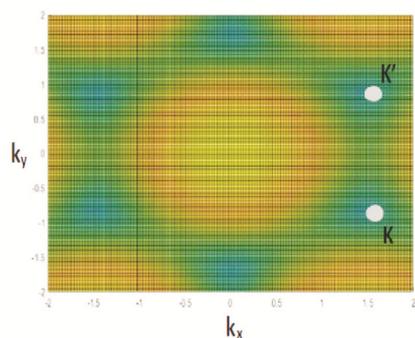


Figure 5. Top view of electronic energy dispersion of graphene as shown in Figure 4 (left).

discussed in the next section, the valence and conduction bands touch at two distinct points in the wave-vector space called the K and K' points, where the band gap goes to zero (Figure 5). For this reason, graphene behaves like a semi-metal.

Graphene as a Dirac solid

For all solid-state properties such as heat capacity, electrical conductivity, resistivity, etc. electrons have to be promoted to the conduction band⁷. The process is evidently facilitated near the K and K' points (Figure 5). In addition, the low-temperature properties of graphene would be dictated by low-wave vector excitations. Hence, it makes sense to expand the energy $t(k)$ near K and K' . In order to carry out this exercise we write down below the lattice vectors with reference to Figure 3, and in terms of the basic lattice parameter a (~ 0.14 nm)^{3,5}

$$a = a/2 (3, \sqrt{3}), a = a/2 (3, -\sqrt{3}). \quad (5)$$

The corresponding reciprocal lattice vectors are

$$\begin{aligned} b_1 &= 2\pi/3a (1, \sqrt{3}), \\ b_2 &= 2\pi/3a (1, -\sqrt{3}). \end{aligned} \quad (6)$$

It is easy to check that

$$a_m \cdot b_n = 2\pi \delta_{mn}, \quad (7)$$

where δ_{mn} is a Kronecker delta.

The three nearest-neighbour vectors are

$$\delta_1 = a/2 (1, \sqrt{3}), \delta_2 = a/2 (1, -\sqrt{3}),$$

$$\delta_3 = a (-1, 0). \quad (8)$$

Finally, the two special points K and K' are given by

$$\begin{aligned} K &= 2\pi/3a (1, 1/\sqrt{3}), \\ K' &= 2\pi/3a (1, -1/\sqrt{3}). \end{aligned} \quad (9)$$

With this machinery at hand and by writing $k = K + q$, and expanding to the lowest order in q , we arrive at

$$\begin{aligned} t_K(q) &= v(q_x - iq_y), v = 3\pi ta, \\ H_K(q) &= v(\sigma \cdot q). \end{aligned} \quad (10)$$

A similar exercise around the K' point yields

$$H_{K'}(q) = v(\sigma^* \cdot q). \quad (11)$$

Here v , which has the dimension of velocity, is estimated to be one-third hundredth of the speed of light.

Conclusion

The focus in this note has been purely a pedagogical one, in order to reach out to students on an apparently abstract subject of quantum mechanics through the exotic material of graphene. Most of the quantum-mechanical concepts employed here are available in high-school plus-two syllabus, albeit scattered. For instance, ideas on orbitals, bonding, Schrödinger equation, electron spin, etc. find places in chemistry, rudimentary notions of special relativity in physics, while matrices appear in mathematics. Bringing all these themes together in the context of graphene also exemplifies the importance of interdisciplinary research in materials science. Finally, it ought to be stressed again, that calling graphene a Dirac solid is metaphorical – the actual electrons in graphene neither have zero mass nor do they travel with the speed of light. It is just that the so-called dispersion relation of energy and momentum, which has its origin in the special honeycomb structure of graphene, that itself owes its existence to hybridized orbitals in a carbon atom, makes the analogy with massless Dirac theory a fascinating reality. What is amazing is that certain predictions of relativistic quantum mechanics which have so far eluded experimental verification can now find justification in the down-to-earth laboratory of graphene.

Appendix. Supplementary reading on quantum mechanics

We enumerate below the basic tenets of quantum mechanics that a student has to grapple with. Each item can be read in conjunction with the electronic configuration of a C atom and then, a two-dimensional sheet of graphene, in Sec. II, the TBA and its momentum-representation, in Sec. III, and finally, graphene as a two-dimensional Dirac solid, in Sec. IV, of the text.

(1) **Wave-particle duality and superposition principle:** A particle such as an electron, positron, proton, neutron, ..., unlike their classical counterparts, cannot be localized. That is, the quantum particle does not have a definite position coordinate. Any attempt to localize the particle leads to a finite momentum – hence delocalization, in consonance with the uncertainty principle. Thus an electron is not just a particle – it is also a wave; the ‘density’ of the particle can be assessed by the probability amplitude of the wave. This duality aspect of a quantum entity is borne out by numerous experimental evidences of light-like interference, diffraction, phenomena⁸.

Once a quantum particle is believed to be a wave described by a linear equation for what is called the wave function any linear combination of the allowed wave functions is also a possible wave function of the particle. The concomitant superposition principle is at the heart of non-relativistic quantum mechanics described by the Schrödinger equation (1925–26)⁹.

(2) **Spin and Pauli Matrices:** A fundamental particle is endowed with an intrinsic attribute called spin that has all the transformation properties (under rotation) as the orbital angular momentum. For an electron, which is the centre of our attention, the spin is a half-integer multiple of the Planck constant as determined in the famous Stern–Gerlach (1922) experiment¹⁰. Because of this, an electron is a Fermion¹¹ that satisfies the Pauli Exclusion Principle such that no two fermions can occupy the same quantum state¹.

The three Cartesian components (along x , y and z -axes) of the spin vector can be represented by matrices which do not commute with each other, i.e. $AB \neq BA$. The non-commutativity of the spin-components directly arises from the fact that the position and the momentum

cannot be measured simultaneously, in conformity with the uncertainty principle. Indeed, all observables can be represented as matrices as in the Heisenberg formulation of quantum mechanics¹². For an electron which has a half-integer spin the aforesaid matrices have dimension of 2×2 (reflecting the fact that there are two possible oppositely oriented spin-values) given in dimension-less units (of Planck constant equal to unity) by

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (A1)$$

It is easy to check the non-commutativity of the matrices in eq. (1), referred to as Pauli matrices¹³.

(3) Dirac bra and ket and pseudo-spins: It is easy to verify by matrix multiplication that the two columns $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$, called the state-vectors, are the eigen states of σ_z with eigen values +1 and -1 respectively, corresponding to the two values of the oppositely oriented spin. It is Dirac who introduced compact notations for the state vectors and their conjugates as follows¹⁴

$$|+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, |-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \\ \langle +| = (1 \ 0), \langle -| = (0 \ 1), \quad (A2)$$

and called $|\dots\rangle$ and $\langle \dots|$ ket and bra respectively.

While the above ket and bra vectors are the spin-states of a real spin-half object such as an electron, it is easy to let our imagination run and equally view them as the state vectors of any two-state system¹⁵. Such two-state systems abound in nature, the common instances being the energy-states of a two-level atom or a qubit in quantum computation or the minima of a double-well (in which a quantum particle is constrained to move). The point is, the Hilbert space of such a two-state system is discrete and is of dimension 2×2 , and the Pauli matrices form a convenient tool to represent such 'fake' or pseudo spins.

(4) Projection matrix and tunneling: Consider the matrix

$$P_{+-} = |+\rangle\langle -| = \begin{pmatrix} 1 \\ 0 \end{pmatrix} (0 \ 1) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \quad (A3)$$

which evidently has matrix elements

$$\langle +|P_{+-}|+\rangle = \langle -|P_{+-}|-\rangle = \langle -|P_{+-}|+\rangle = 0,$$

but

$$\langle +|P_{+-}|-\rangle = 1. \quad (A4)$$

Thus, the only non-vanishing 'operation' P_{+-} can induce is to 'project' the state $|-\rangle$ into the state $|+\rangle$. Similarly, the matrix $P_{-+} = |-\rangle\langle +|$ projects the state $|+\rangle$ into the state $|-\rangle$. If $|+\rangle$ and $|-\rangle$ are employed to represent the left minimum and the right minimum respectively, of a double-well – a prototype two-state system – in which a quantum particle is envisaged to move, P_{+-} (P_{-+}) transfers the particle from the left (right) to the right (left) minimum. This phenomenon is called 'tunnelling'¹⁶.

(5) TBA in the momentum representation: Quantum mechanics naturally admits two distinct representations in the position and the momentum space, in view of the uncertainty principle. While the position space is the 'real space' the momentum constitutes the 'reciprocal space', which coincidentally is the natural space for diffraction/scattering experiments, employing, e.g. electrons or X-rays or neutrons. This point can be aptly illustrated in the case of graphene by expanding the Dirac kets in eq. (III. 2) in terms of their momentum counterparts as⁷

$$|+\rangle_{i(A)} = \sum_k |+, k\rangle \exp(ik.R_i), \\ \langle -|_{j(B)} = \sum_{k'} \langle -, k'| \exp(-ik'.R_j), \quad (A5)$$

where we have tacitly assigned the i th site in the A -sublattice as the occupied site and the j th site in the B -sublattice as the unoccupied/'hole' site. Equation (A5) represents the discrete version of the Fourier transform. The two position vectors R_i and R_j appropriate to the i th and j th sites are connected by the nearest-neighbour vector δ defined by (Figure 3)

$$R_j = R_i + \delta. \quad (A6)$$

The Fourier transforms in eq. (A5) are governed by the orthonormality relation

$$\sum_i \exp[i(k - k').R_i] = 2\pi\delta(k - k'), \quad (A7)$$

where the right hand side is a Dirac delta-function¹⁴. Using eq. (A7) the tight-binding Hamiltonian of eq. (III. 2) can be diagonalized in the momentum space as³⁻⁵

$$H = \sum_k (t(k)|+, k\rangle\langle -, k| + t^*(k)|-, k\rangle\langle +, k|), \quad (A8)$$

where

$$t(k) = 2\pi \sum_{\delta} \exp(-ik.\delta). \quad (A9)$$

The Hamiltonian however is still off-diagonal in the pseudo-spin space of Pauli matrices (cf. eq. (A1)), which can be explicitly expressed as, for each k -vector as

$$H_k = -\text{Re}[t(k)] \sigma_x + \text{Im}[t(k)] \sigma_y. \quad (A10)$$

The 2×2 matrix form in eq. (A10), upon employing eq. (A1), can be easily diagonalized to yield the two eigen values quoted in eq. (III. 3) of the text.

(6) Dirac equation for relativistic electrons and helicity: The energy (E)–momentum (p) relation in special theory of relativity can be written as

$$E^2 = m^2c^4 + p^2c^2, \quad (A11)$$

where m is the rest mass of the electron and c is the speed of light. In the non-relativistic limit,

$$E^2 \sim m^2c^4, \text{ or } E = +mc^2 \text{ or } -mc^2, \quad (A12)$$

implying that there are two energy branches – one for the particle (electron), the other for the anti-particle (positron).

On the other hand, in the extreme relativistic limit, the rest energy can be ignored, and

$$E \sim |p|c \text{ or } E \sim -|p|c, \quad (A13)$$

again suggesting two energy branches but a linear relation between E and p , unlike in the non-relativistic case wherein the relation is quadratic. Recall that it is the quadratic relation that led to the Schrödinger equation, adorned by a first order time-derivative but a second-order space-derivative.

However, relativity requires space-time symmetry which implies that E and p must appear on the same footing. Cognizant of this, Dirac suggested the following generalization of the Schrödinger equation¹⁷

$$i \frac{\partial}{\partial t} [\psi(r, t)] = [-ic \alpha \cdot \partial + mc^2 \beta] \psi(r, t), \quad (A14)$$

where we have used the fact that in quantum mechanics E transforms as $i\partial/\partial t$ and p transforms as $-i\partial$. Further, Dirac was mindful of the ubiquitous intrinsic spin as well as the charge conjugation, parity and time-reversal (CPT) symmetry. Thus he introduced α and β as two 4×4 matrices, defined by

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (\text{A15})$$

where 1 is the unit 2×2 matrix and the σ -matrix has been already introduced in eq. (A1).

With eqs (A1) and (A2) at hand the Dirac equation fans into a set of four-component equations that can be written as

$$\begin{aligned} i\partial/\partial t |e\uparrow(r, t)\rangle &= mc^2 |e\uparrow(r, t)\rangle \\ &+ cp_z |\pi\uparrow(r, t)\rangle + c(p_x - ip_y) |\pi\downarrow(r, t)\rangle, \\ i\partial/\partial t |e\downarrow(r, t)\rangle &= mc^2 |e\downarrow(r, t)\rangle \\ &- cp_z |\pi\downarrow(r, t)\rangle + c(p_x + ip_y) |\pi\uparrow(r, t)\rangle, \\ i\partial/\partial t |\pi\uparrow(r, t)\rangle &= -mc^2 |\pi\uparrow(r, t)\rangle \\ &+ cp_z |e\uparrow(r, t)\rangle + c(p_x - ip_y) |e\downarrow(r, t)\rangle, \\ i\partial/\partial t |\pi\downarrow(r, t)\rangle &= -mc^2 |\pi\downarrow(r, t)\rangle \\ &- cp_z |e\downarrow(r, t)\rangle + c(p_x + ip_y) |e\uparrow(r, t)\rangle. \end{aligned} \quad (\text{A16})$$

Here the arrows (up and down) designate the intrinsic spin, and π represents the charge-conjugated positron, which was interestingly discovered four years later¹⁸.

Equations (A15) and (A16) suggest that the Dirac Hamiltonian can be rewritten as

$$H = \Sigma + mc^2 \beta, \quad (\text{A17})$$

where Σ is a 4×4 matrix, called ‘helicity’ and defined by³⁻⁵

$$\Sigma = c(\sigma \cdot p). \quad (\text{A18})$$

Given that σ transforms like the orbital angular momentum Σ is odd under parity transformation and hence, relates to ‘chirality’.

(7) **Ultra relativistic limit and the two-dimensional case:** Particles that move with near the speed of light, the extreme example of what are neutrinos, are called mass less Weyl fermions⁴. For them the rest energy term in eq. (A17) can be neglected. In addition, if one considers $2 + 1$, i.e., two-space and one-time dimensions, the z -motion can also be ignored. We then rearrange the four equations in (A16) by grouping the first and the fourth in one set, and the second and the third in another, and arrive at

$$\begin{aligned} i \frac{\partial}{\partial t} |e\uparrow(r, t)\rangle &= c(p_x - ip_y) |\pi\downarrow(r, t)\rangle, \\ i \frac{\partial}{\partial t} |\pi\downarrow(r, t)\rangle &= c(p_x + ip_y) |e\uparrow(r, t)\rangle, \end{aligned} \quad (\text{A19a})$$

and

$$\begin{aligned} i \frac{\partial}{\partial t} |e\downarrow(r, t)\rangle &= c(p_x + ip_y) |\pi\uparrow(r, t)\rangle, \\ i \frac{\partial}{\partial t} |\pi\uparrow(r, t)\rangle &= c(p_x - ip_y) |e\downarrow(r, t)\rangle. \end{aligned} \quad (\text{A19b})$$

This division becomes meaningful in the context of the two Dirac points K and K' discussed in the text. Indeed if we rewrite eqs (A19a) and (A19b) in the Fourier-transformed space and express the momentum components as derivatives with respect to the corresponding spatial components, we arrive at eqs (10) and (11) respectively, of the text. Interestingly however, while the pre-factor above is the speed of light, in Dirac theory, it turns out to be of the order of Fermi velocity, in graphene.

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