Graphene I: Electronic band structure and Dirac fermions[1]

A suspended sheet of pure graphene – a plane layer of C atoms bonded together in a honeycomb lattice – is the "most two-dimensional" system imaginable. Such sheets have long been known to exist in disguised forms – in graphite (many graphene sheets stacked on top of one another), C nanotubes (a graphene sheet rolled into a cylinder) and fullerenes (buckyballs), which are small areas of a graphene sheet sewn together to form an approximately spherical surface. Moreover, it was appreciated that every time one writes on a sheet of paper with a "lead" (i.e. graphite) pencil one probably produces the odd flake of graphene, along with a whole lot of other by-products; however, until 2004, it was generally believed (a) that an extended graphene sheet would not be stable against the effects of thermal and other fluctuations, and (b) that even if they were stable, it would be impossible to isolate them so that their properties could be systematically studied. In that year, André Geim and his colleagues at the University of Manchester in the UK demonstrated that both these beliefs were false: they created single graphene sheets[2] by peeling them off a graphite substrate using scotch tape, and characterized them as indeed single-sheet by simple optical microscopy on top of a SiO_2 substrate. (This procedure, which turns out to be exquisitely sensitive to the details of the substrate, was an essential ingredient in the success of the whole operation. A more recent and faster selection technique is Raman spectroscopy). Subsequently it was found that small graphene sheets do not need to rest on substrates but can be freely suspended from a scaffolding; furthermore, bilayer and multilayer sheets can be prepared and characterized. As a result of these developments, the number of papers on graphene published in the last few years exceeds 3000.

It was realized more than 60 years ago that the electronic band structure of graphene, should it ever be possible to produce it, would be likely to be particularly interesting. Let us start by considering a perfectly flat and pure free-standing graphene sheet, with the standard periodic boundary conditions; subsequently we shall come back and consider how the corrections to this zeroth-order model which certainly occur in real life may affect the results. We start by setting up an appropriate notation. The electronic structure of an isolated C atom is $(1s)^2(2s)^2(2p)^4$; in a solid-state environment the $1s$ electrons remain more or less inert, but the $2s$ and $2p$ electrons hybridize. One possible result is four sp^3 orbitals, which naturally tend to establish a tetrahedral bonding pattern that soaks up all the valence electrons: this is precisely what happens in the best known solid form of C, namely diamond, which is a very good insulator (band gap $\sim 5\,\text{eV}$). However, an alternative possibility is to form three sp^2 orbitals, leaving over a more or less pure p-orbital. In that case the natural tendency is for the sp^2 orbitals to arrange themselves in a plane at $120°$ angles, and the lattice thus formed is the honeycomb lattice.

We note that there are two inequivalent sublattices, here labeled A and B, with the

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[1] A good general reference for this and the next two lectures is A. H. Castro Neto et al., Revs. Mod. Phys., **81**, 109 (2009). See also Geim et al., Nature Materials **6** 183 (2007).

[2] And also single-atom-thick sheets of a number of other materials such as BSCCO.

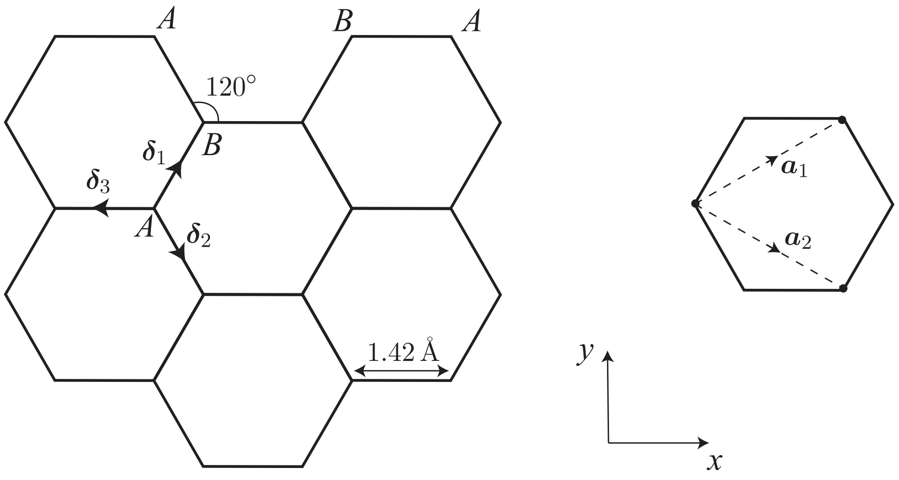


Figure 1:

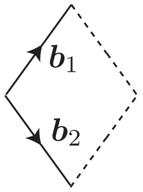
environments of the corresponding atoms being mirror images of one another. It is convenient to choose our Bravais lattice to have primitive lattice vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ given as shown by (the notation is (x, y))

$$\boldsymbol{a}_1 = \frac{a}{2}\left(3, \sqrt{3}\right), \qquad \boldsymbol{a}_2 = \frac{a}{2}\left(3, -\sqrt{3}\right) \tag{1}$$

where a is the nearest-neighbor C-C spacing (≈ 1.42 Å). The reciprocal lattice vectors $\boldsymbol{b}_1, \boldsymbol{b}_2$ defined by the condition $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}$ are then

$$\boldsymbol{b}_1 = \frac{2\pi}{3a}\left(1, \sqrt{3}\right), \qquad \boldsymbol{b}_2 = \frac{2\pi}{3a}\left(1, -\sqrt{3}\right) \tag{2}$$

We define the first Brillouian zone of the reciprocal lattice in the standard way, as bounded by the planes bisecting the vectors to the nearest reciprocal lattice points. This gives an FBZ of the same form as the original hexagons of the honeycomb lattice, but rotated with respect to them by $\pi/2$.



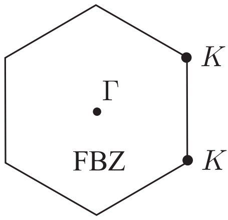
It is clear that the six points at the corners of the FBZ fall into two groups of three which are equivalent, so we need consider only two equivalent corners that we label K and K' as in the figure. Explicitly, their positions in momentum space are given by

$$\boldsymbol{K} = \frac{2\pi}{3a}\left(1, \frac{1}{\sqrt{3}}\right), \qquad \boldsymbol{K}' = \frac{2\pi}{3a}\left(1, -\frac{1}{\sqrt{3}}\right) \tag{3}$$

It is convenient to note at this point that for an A-sublattice atom the three nearest-neighbor vectors in real space are given by

$$\boldsymbol{\delta}_1 = \frac{a}{2}\left(1, \sqrt{3}\right), \qquad \boldsymbol{\delta}_2 = \frac{a}{2}\left(1, -\sqrt{3}\right), \qquad \boldsymbol{\delta}_3 = -a(1,0) \tag{4}$$

while those for the B-sublattice are the negatives of these.

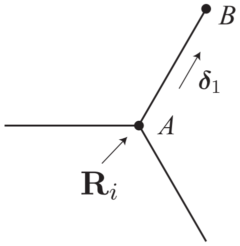


For a first approach to the electronic band structure, let's start by modeling it by a tight-binding model with nearest-neighbor hopping only: The relevant atomic orbital is the single $(p\sigma)$ (or more correctly π) C orbital which is left unfilled by the bonding electrons, and which is oriented *normal* to the plane of the lattice: as usual, this orbital can accommodate two electrons with spin projection ±1. If we denote the orbital on atom i with spin σ by (i, σ), and the corresponding creation operator by $a^\dagger_{i\sigma}(b^\dagger_{i\sigma})$ for an atom on the $A(B)$ sublattice, then the nearest-neighbor tight-binding Hamiltonian has the simple form

$$\hat{H}_{\mathrm{TB,\,n.n.}} = -t \sum_{\substack{ij=\mathrm{n.n.}\\ \sigma}} (a^\dagger_{i\sigma} b_{j\sigma} + \mathrm{H.c.}) \tag{5}$$

The numerical value of the nearest-neighbor hopping matrix element t, which sets the overall scale of the π-derived energy band, is believed to be about 2.8 eV; the exact value is unimportant for subsequent results. We shall first explore the band structure, and the nature of the electronic states, generated by the simple Hamiltonian (5), and later examine how these are affected by corrections to it.

It is convenient to write the TB eigenfunctions in the form of a spinor, whose components correspond to the amplitudes on the A and B atoms respectively within the unit cell labeled by a reference point $\boldsymbol{R}^0_i$. It is a matter of convention how we choose the pair A and B and the point $\boldsymbol{R}^0_i$, but for definiteness, let us choose B to separated from A by $\boldsymbol{\delta}_1$ and $\boldsymbol{R}^0_i$ at the position of A_1 as shown. Then the TB eigenfunctions have the form (apart from the spin index)



$$\begin{pmatrix} \alpha_{\mathbf{k}} \\ \beta_{\mathbf{k}} \end{pmatrix} = \sum_i \exp i\mathbf{k}\cdot\boldsymbol{R}^0_i \begin{pmatrix} a^\dagger_i\, e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_1/2} \\ b^\dagger_i\, e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1/2} \end{pmatrix} \tag{6}$$

where $b^\dagger_i$ creates an electron on the B atom in cell i. The factor $e^{\pm i\mathbf{k}\cdot\boldsymbol{\delta}/2}$ in the spinor components is inserted in order to simplify subsequent expressions. The resulting Hamiltonian in the **k**-representation is purely off-diagonal in this representation:

$$\hat{H}_{\mathbf{k}} = \begin{pmatrix} 0 & \Delta_{\mathbf{k}} \\ \Delta^*_{\mathbf{k}} & 0, \end{pmatrix} \qquad \Delta_{\mathbf{k}} \equiv -t \sum_{l=1}^{3} \exp i\mathbf{k}\cdot\boldsymbol{\delta}_l \tag{7}$$

From the explicit expressions (4) for the nearest neighbor vectors $\boldsymbol{\delta}_l$ we obtain

$$\Delta_{\mathbf{k}} = -t \exp -ik_x a \left(1 + 2 \exp \left(i \cdot \frac{3k_x a}{2} \right) \cos \sqrt{\frac{3}{2}}\, k_y a \right) \tag{8}$$

Evidently the eigenvalues of $H, \epsilon_{\mathbf{k}}$ are given by

$$\epsilon_{\mathbf{k}} = \pm |\Delta_{\mathbf{k}}| = \pm t \left(1 + 4 \cos \frac{3k_x a}{2} \cos \sqrt{3}\, \frac{k_y a}{2} + 4 \cos^2 \sqrt{\frac{3}{2}}\, k_y a \right) \tag{9}$$

$\big($which some elementary algebra shows is identical to CN's eqn. (6)$\big)$. It is interesting to enquire whether there are any values of $\mathbf{k}$ for which $\Delta_{\mathbf{k}}$ (hence $\epsilon_{\mathbf{k}}$) is zero? Any such value must satisfy the conditions

$$\begin{aligned} & \frac{3k_x a}{2} = 2n\pi, \qquad \cos \frac{\sqrt{3}}{2} k_y a = -1/2 \qquad\qquad (n \text{ integral}) \qquad (10) \\ \text{or} \qquad & \frac{3k_x a}{2} = (2n+1)\pi, \qquad \cos \frac{\sqrt{3}}{2} k_y a = +1/2 \end{aligned}$$

The first choice takes k_y outside the FBZ, but the second (with $n = 0$) is satisfied exactly at the "corner" points $\boldsymbol{K}$ and $\boldsymbol{K'}$ which we previously identified; for a reason that will soon be clear, these points are called the "Dirac points".

The first significant feature of this result is that, since the energy band is exactly symmetric about the point $\epsilon_{\mathbf{k}} = 0$, and this condition is met *only* at the two Dirac points (not, as in a typical textbook metal, over a complete surface (in 2D line) of $\mathbf{k}$-values), it follows that for exactly half filling of the band *the DOS at the Fermi level is exactly zero.* But in the absence of doping graphene has exactly one electron per "spin" per atom (2 per unit cell), so taking spin into account the bond is indeed exactly half filled. Thus, *undoped graphene is a perfect semimetal!*[3] It is helpful to visualize what is going on at the Dirac points in terms of the amplitudes for the electron to be on the A or the B sublattice. Since the two sublattices are physically equivalent, it is clear that when the state is on energy eigenfunction then, apart possibly from trivial phase factors involved in the precise definition of the a_i and b_i, the behavior must be either symmetric or antisymmetric with respect to the exchange of A and B. For example, for $\mathbf{k} = 0$ there are two possibilities: either $a_i = b_i$, giving energy $-3t$, or $a_i = -b_i$, giving energy $+3t$. For $\mathbf{k} \neq 0$ the effective "lumped" matrix element for tunneling between the two sublattices is given precisely by $\Delta_{\mathbf{k}}$:

$$\Delta_{\mathbf{k}} \equiv -t \sum_{l=1}^{2} e^{i\mathbf{k}\cdot\boldsymbol{\delta}_l} \tag{11}$$

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[3] A semimetal is defined as having zero DOS for $\epsilon = 0$ (where ϵ is the energy measured with respect to the Fermi energy) but a nonzero DOS for $\epsilon > 0$.

so the two energies are $\pm|\Delta_{\mathbf{k}}|$ as we have seen. However, at a Dirac point $\Delta_{\mathbf{k}}$ tends to zero, so the relative signs (phases) on the two sublattices are completely arbitrary; in particular we can if we wish choose the energy eigenstate to be localized completely on sublattice A or sublattice B, with the other sublattice totally unoccupied. Note also that at the Dirac points, the phase shift on going from one unit cell to the next is $\pm\pi/3$.

We now discuss the nature of the energy spectrum and eigenfunctions for $\mathbf{k}$ close to a Dirac point (let us say for definiteness the point $\boldsymbol{K}$). It is convenient to define the (2D) vector $\mathbf{k}-\boldsymbol{K}$ as $\mathbf{q}$. Then, expanding the expression for $\Delta_{\mathbf{k}}$ around $\mathbf{q}=0$, we find

$$\Delta(\mathbf{q}) = 2e^{-iK_xa}\mathbf{q}\cdot\boldsymbol{\nabla}_{\mathbf{k}}\left(e^{3ik_xa/2}\cos\sqrt{\frac{3}{2}}k_ya\right)_{\mathbf{k}=\boldsymbol{K}} = -\frac{3t}{2a}(\exp -iK_xa)(iq_x-q_y). \tag{12}$$

It is convenient to extract an overall constant factor $-i\exp -iK_xa$ (which clearly does not affect any physical results) and thus write

$$\Delta(\mathbf{q}) = \hbar v_{\mathrm{F}}(q_x+iq_y)\big(+\mathcal{O}(q/K)^2\big), \qquad v_{\mathrm{F}} \equiv 3t/2\hbar a \cong 10^6 \text{ m/sec.} \tag{13}$$

Note that if we had expanded around $\boldsymbol{K}'$ (for which $K'_x \equiv K_x, K'_y \equiv -K_y$) we would have obtained

$$\Delta_{K'}(\mathbf{q}) = \hbar v_{\mathrm{F}}(q_x-iq_y) = \Delta^*_{(K)}(\mathbf{q}) \tag{14}$$

i.e. with the same convention for $\mathbf{q}$, the "helicity" is reversed.

It is very suggestive to write the Hamiltonian in the form

$$\hat{H} \equiv \hbar v_{\mathrm{F}}\begin{pmatrix} 0 & q_x+iq_y \\ q_x-iq_y & 0 \end{pmatrix} \equiv \hbar v_{\mathrm{F}}\ \hat{\boldsymbol{\sigma}}\cdot\mathbf{q}, \qquad \epsilon(q) = \pm v_{\mathrm{F}}|q| \tag{15}$$

where the components of the operator $\hat{\boldsymbol{\sigma}}$ are the usual[4] Pauli matrices. It is clear that the eigenvalues are a function only of the *magnitude* of $\mathbf{q}$, not its direction in the 2D space:

$$\epsilon(q) = \pm\hbar v_{\mathrm{F}}|q|. \tag{16}$$

The Hamiltonian (15) is, from a formal point of view, exactly that of an ultra-relativistic (or massless) particle of spin 1/2 (such as the neutrino), with the velocity of light c replaced by the Fermi velocity v_{F}, which is a factor ~ 300 smaller. Moreover, the "left-handed neutrino" given by (13) is not equivalent to the "right-handed antineutrino" that lives near K' rather than K. Thus there arises the prospect, which excites a lot of people, of finding analogs to many phenomena predicted to occur (but often not yet seen experimentally) in a solid-state context. However, it should be remembered that the Dirac excitations near $\boldsymbol{K}$ are not the antiparticles of those near $\boldsymbol{K}'$; rather it is the two possible combinations of

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[4] But strictly speaking, to make it equivalent for the Dirac point at $\boldsymbol{K}$ we would need to adopt an unconventional definition of "handedness."

the excitations near *one* Dirac point on the A and B sublattices, with energies $\pm\hbar v_{\mathrm{F}}|q|$ respectively, which are one another's "antiparticles." The eigenfunctions are, for the vicinity of the point $\boldsymbol{K}$.

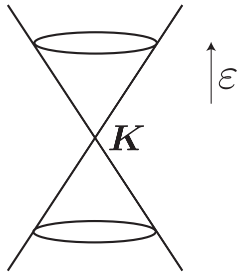
$$\psi^{\pm}_{(K)}(\mathbf{q}) = \frac{1}{\sqrt{2}}\begin{pmatrix} \exp i\theta_{\mathbf{q}}/2 \\ \pm\exp -i\theta_{\mathbf{q}}/2 \end{pmatrix}, \qquad \theta_{\mathbf{q}} \equiv \tan^{-1}(q_x/q_y) \tag{17}$$

Note that when $\mathbf{q}$ rotates once around the Dirac point, the phase of $\psi^{(\pm)}_{K}(\mathbf{q})$ changes by π, not by 2π, as is characteristic for "spin-1/2" particles.

It is now straightforward to obtain quantities such as the DOS and cyclotron mass. It is clear that for nonzero ϵ the DOS will be proportional to the number of states that have $|\mathbf{q}| = |\epsilon|/\hbar v_{\mathrm{F}}$; specifically, since the number of states with q-values less than q close to a specific Dirac point is $q^2/2\pi$, the DOS associated with this point is

$$n_{\mathbf{K}}(\epsilon) = \frac{1}{\hbar v_{\mathrm{F}}}\frac{dn_{\mathbf{K}}}{dq} = \frac{1}{(\hbar v_{\mathrm{F}})^2}\,\epsilon \tag{18}$$

Since there are two Dirac points, the total DOS is twice this.



These results have an interesting consequence for the effect of doping. At zero doping, as we have seen, the lower half of the band is filled exactly up to the Dirac points. If by applying a suitable "gate" voltage to the graphene relative to the substrate (or suspension) we induce a nonzero charge, this is equivalent to injecting (depending on the sign of the voltage) a number of electrons in the upper half of the Dirac cones or holes in the lower half; for definiteness let's consider the former. If the temperature is low enough, the electrons will form a degenerate Fermi sea and we can define a "Fermi surface" (in 2D a line) and the corresponding Fermi wave vector q_{F}. Taking into account the spin and "valley" degeneracies, we find (cf. above)

$$q_{\mathrm{F}} = (\pi n_s)^{1/2} \qquad n_s \equiv \text{no. of (extra) electrons/unit area} \tag{19}$$

We can define an "effective mass" m^* in the usual way by $m^* \equiv \hbar q_{\mathrm{F}}/v_{\mathrm{F}}$, and then find that

$$m^* = \frac{\pi^{1/2}\hbar}{v_{\mathrm{F}}}\,n_s^{1/2} \tag{20}$$

In a textbook 3D solid, the most direct way of measuring the effective mass m^* is through the specific heat. In a 2D system such as graphene such a measurement is not usually practical, but one can alternatively use the fact that for an isotropic system the mass measured in a cyclotron resonance experiment ("cyclotron mass") is identical to the m^* defined above. (This is because the cyclotron mass m_c^* is quite generally given, in the semiclassical limit, by the expression $m_c^* = (1/2\pi)(\partial A/\partial\epsilon)$, where A is the $\mathbf{k}$-space area enclosed by an orbit of energy ϵ; for our case this expression is just $\frac{\hbar}{v_{\mathrm{F}}} q_{\mathrm{F}}$. i.e.equal to m^*). Cyclotron resonance experiments on graphene verify that m^* is indeed proportional to $n_s^{1/2}$ as predicted (see CN fig. 4).

We now turn to the question of corrections to the simple results derived above. The most obvious correction comes from second-nearest-neighbor hopping, with some matrix element t' (clearly, in the honeycomb lattice all second-nearest neighbors are on the same sublattice as the original atom and are equivalent). This gives rise to a term[5]

$$H_{\text{n.n.n.}} = -\frac{t'}{2} \sum_{i,j=\text{n.n.n.},\sigma} (a_{i\sigma}^\dagger a_{j\sigma} + b_{i\sigma}^\dagger b_{j\sigma} + \text{H.c.}) \tag{21}$$

The most salient feature of this term is that it is exactly symmetric between the A and B sublattices; hence, it gives a contribution $-t'f(\mathbf{k})$, which is proportional, in the "spinor" representation, to the unit matrix. Such a term destroys the perfect symmetry of the band around $\epsilon = 0$ (since the term $-t'f(\mathbf{k})$ is added to both the upper and the lower branches); however, it cannot spoil the degeneracy of the two solutions at the Dirac points $\boldsymbol{K}$ and $\boldsymbol{K}'$ (which, however, no longer in general correspond to $\epsilon = 0$ but to some shifted value $\epsilon_0 = -t'f(\boldsymbol{K})$; we may as well shift the zero of energy to this point).

It might, however, be wondered whether by affecting the *absolute* energies of the states close to the Dirac point the term (21) spoils the simple results we have obtained e.g. for the cyclotron resonance frequency. Fortunately this is not the case: the Dirac points are actually *extremes* of the quantity $f(\mathbf{k})$! To see this, note that the explicit expression for this quantity is

$$f(\mathbf{k}) = -t^{1/2} \sum_{ij=\text{n.n.n.}} (\exp i\mathbf{k}\cdot\boldsymbol{K}_{ij} + \text{H.c.}) \equiv -t' \sum_{ij=\text{n.n.n.}} \cos \mathbf{k}\cdot\boldsymbol{R}_{ij} \tag{22}$$

Now the next-nearest-neighbor values of $\boldsymbol{R}_{ij}$ are the primitive lattice vectors $\boldsymbol{a}_i, \boldsymbol{a}_j, \boldsymbol{a}_i - \boldsymbol{a}_j$ and their negatives, so we have

$$f(\mathbf{k}) = -\left\{ 2\cos\left(\sqrt{3}\, k_y a\right) + 4\cos\left(\frac{\sqrt{3}}{2}\, k_y a\right)\cos\left(\frac{3}{2}\, k_x a\right)\right\} t' \tag{23}$$

It may be verified that the value of $f(\mathbf{k})$ at the Dirac points is $+3t'$ and its gradients there zero. Thus, even in the presence of next-nearest-neighbor hopping the form of the Hamiltonian near a Dirac point is given, up to the uninteresting constant $3t'$, by eqn. (15). When one goes up to terms of order q^2, one finds that while the t' term is isotropic around $\boldsymbol{K}$ (as one might perhaps anticipate from its sixfold symmetry) the original t term introduces a "trigonal" dependence ($\sim \sin 3\theta_{\mathbf{q}}$, where $\theta_{\mathbf{q}} \equiv \tan^{-1} q/q_x$). However, the order

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[5] The factor 1/2 is to avoid overcounting. If the prefactor is t' then the sum should be only over "positive" next nearest neighbors.

of magnitude of this term is $\sim q/K$ relative to the "Dirac" one, and it is usually neglected in analysis of experiments.

While the simple Dirac-like form of the Hamiltonian (15) is very pleasing, one might ask how generic it is? So far we have considered only nearest- and next-nearest neighbor hopping; would (for example) further-neighbor hopping spoil the results? And on exactly which properties of the honeycomb lattice do they depend? Here are some (fairly undigested) thoughts.[6]

First, it seems virtually certain that provided it does not become ferromagnetic (something for which there is no experimental evidence nor, as far as I am aware, theoretical support), undoped graphene must be either a semimetal or a semiconductor. This follows simply from the fact that there are two atoms per unit cell, and thus for each $\mathbf{k}$ within the FBZ there must be two energy eigenstates, which in general are nondegenerate. Whether they repel to give a standard band gap as in a textbook semiconductor, or touch as in the simple model explored above, there is room in the lower band (including spin) for exactly the 2 valence electrons per unit cell that are available in graphene.[7] The only escape from this conclusion would appear to be if the energy of the "upper" band for some $\mathbf{k}$ wave to term set to be lower than that of the "lower" band for a *different* $\mathbf{k}$; this is forbidden in 1D, but as far as I know there is no general principle that forbids it in 2 (or 3) D. However, there seems no reason, theoretical or experimental, to believe that this situation occurs in real-life graphene. Note that the conclusion does not depend on symmetry between the A and B sublattices.

Secondly, I strongly suspect that given the symmetry of the Hamiltonian under $A \to B$, the existence of a couple of "Dirac points," that in points where the energy bands touch, is generic. This will be the case if we can always find two points within (or on the edge of) the FBZ such that for this $\mathbf{k}$ the *total* coupling between the A and B sublattices vanishes, since then we have two completely equivalent excitations localized on one sublattice or the other.

It should be noted that the introduction of any kind of asymmetry in the Hamiltonian between the A and B sublattices, such as might occur for example on certain corrugated substrates, is liable to lift the degeneracy at the Dirac points, since the Hamiltonian can then be written in the form, up to a constant

$$\hat{H} = \begin{pmatrix} \Delta\epsilon/2 & v_{\mathrm{F}}(q_x + iq_y) \\ v_{\mathrm{F}}(q_x - iq_y) & -\Delta\epsilon/2 \end{pmatrix} \tag{24}$$

with eigenvalues

$$E_{+,-} = \left((\Delta\epsilon)^2 + {v_{\mathrm{F}}}^2|\mathbf{q}|^2\right)^{1/2} \tag{25}$$

introducing an energy gap $\Delta\epsilon$ at the Dirac point $q = 0$.

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[6] I may try to amplify these remarks in the lecture.

[7] This argument is of course just a special case of the familiar textbook argument that crystalline systems with an even number of electrons per unit cell must be insulators (or semiconductors).

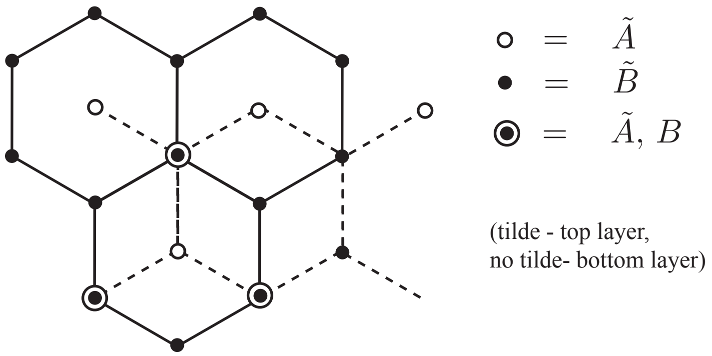

Figure 2:

Thirdly, provided the residual terms in the Hamiltonian may be treated as perturbations on the ones we have explicitly considered, one feature of the spectrum near the Dirac point should be very stable, namely the topological property that contours in **q**-space surrounding it have a winding number of 1; that is, the phase of the off diagonal term in the Hamiltonian changes by 2π (not 0 or 4π) when we consider the Dirac point in q-space. This property of the spectrum is crucial to the explanation of the anomalous QHE seen in graphene (next lecture).

We now turn to bilayer graphene. This system has been stabilized experimentally, and has some very interesting properties, so it is worthwhile to study its energy spectrum. Unfortunately the problem is complicated by the fact that the stacking is not of the simple form where each $A(B)$ atom in the top layer lies directly above one $A(B)$ atom in the bottom layer; rather, it is of the "Bernal" type, in which one A atom in the top layer (denoted $\tilde{A}$) lies above a B atom (denoted B) in the bottom layer, so that $\tilde{B}$ cannot lie directly above A. In fact the positioning is as drawn in Fig. 2.

We would expect a substantial hopping between $\tilde{A}$ and B atoms (recall that the C valence electrons are in π orbitals that "stick out" of the plane) and a weaker possible hopping between A and $\tilde{B}$ atoms (also $A \rightleftarrows \tilde{A}$, $B \rightleftarrows \tilde{B}$). For simplicity let us keep only $\tilde{A} \rightleftarrows B$ hopping and denote the relevant matrix element by γ. In the simplest model of the in-plane hopping the Hamiltonian is then

$$H_{\text{bil}} = -t \sum_{ij=\text{n.n.}} \Big\{ (a_i^\dagger b_j + \text{H.c.}) + (\tilde{a}_i^\dagger \tilde{b}_j + \text{H.c.}) \Big\} - \gamma_1 \sum_i (\tilde{a}_i^\dagger b_i + \text{H.c.}) \tag{26}$$

where $\tilde{a}_i^\dagger (a_i^\dagger)$ creates an electron on site $\tilde{A}(A)$, etc., When we now define a Fourier transforms in the standard way, the last term in (26) picks up no **k**-dependence, as $\tilde{a}_i$ and $b_i^\dagger$

operate at the same point in the xy-plane. Thus if we define a 4-dimensional spinor, in an obvious notation

$$\psi \equiv \begin{pmatrix} \psi_A \\ \psi_B \\ \psi_{\tilde{A}} \\ \psi_{\tilde{B}} \end{pmatrix} (\mathbf{k}) \tag{27}$$

the corresponding Hamiltonian $\hat{H}_{\mathbf{k}}$ has the form

$$\hat{H}_{\mathbf{k}} = \begin{pmatrix} 0 & v_{\mathrm{F}}(q_x + iq_y) & 0 & 0 \\ v_{\mathrm{F}}(q_x - iq_y) & 0 & \gamma_1 & 0 \\ 0 & \gamma_1 & 0 & v_{\mathrm{F}}(q_x + iq_y) \\ 0 & 0 & v_{\mathrm{F}}(q_x - iq_y) & 0 \end{pmatrix} \tag{28}$$

The crucial point, now, is that for $|\mathbf{q}| \to 0$, i.e. as we approach the Dirac point, we automatically have $\gamma_1 \gg v_{\mathrm{F}}|q|$, and thus the primary concern is to properly "dimerize" the $\tilde{A} - B$ band. Let's examine what happens exactly at the Dirac point. There is one symmetric combination ($\psi_{\tilde{A}} = +\psi_B$, $\psi_A = \psi_{\tilde{B}} = 0$) with low energy $-\gamma_1$, one high-energy combination ($\psi_{\tilde{A}} = -\psi_B$, $\psi_A = \psi_{\tilde{B}} = 0$) and two zero-energy states, which we may for example take as localized on the A and $\tilde{B}$ sublattices respectively. More generally, for arbitrary values of $\mathbf{k}$ in the FBZ we expect a low-energy (symmetric $\tilde{A} - B$) band, which will certainly be filled, a high-energy (antisymmetric $\tilde{A} - B$) band, which will certainly be unfilled, and two states which, at least for $v_F q \lesssim \gamma_1$, are mainly linear combinations of the A and $\tilde{B}$ sites. The interesting point is that for undoped bilayer graphene, by simple counting of the states, exactly one of the two "$A - \tilde{B}$" bands will be filled. So it becomes essential to work out the effective Hamiltonian within this 2D space.

The most intuitive way to do this is the following: Consider a process in which an electron hops from A on to the "B part of" this (unoccupied) antisymmetric $\tilde{A} - B$ band, then from $\tilde{A}$ on to $\tilde{B}$ (all the time keeping its $\mathbf{k}$-vector close to (say) the Dirac point $\boldsymbol{K}$). The effective matrix element for this 2-step process is, since the sign of the probability amplitude in the unoccupied (antisymmetric) $\tilde{A} - B$ state is opposite on $\tilde{A}$ and B,

$$V_{\mathrm{eff}}(A \to \tilde{B}) = -\frac{V_{A \to (\tilde{A}-B)} V_{(\tilde{A}-B) \to \tilde{B}}}{E_{(\tilde{A}-B)}} \tag{29}$$

Since the matrix element to hop from A to B is the *same* as that for $\tilde{A} \to \tilde{B}$, (not its complex conjugate!), and the energy denominator is just γ_1, this gives

$$V_{\mathrm{eff}(A \to \tilde{B})} = \frac{(V_F(q_x + iq_y))^2}{\gamma_1} \tag{30}$$

i.e. the effective Hamiltonian in the $A - \tilde{B}$ subspace is

$$\hat{H}_{A-\tilde{B}} = (v_F^2/\gamma_1) \begin{pmatrix} 0 & (q_x + iq_y)^2 \\ (q_x - iq_y)^2 & 0 \end{pmatrix} \tag{31}$$

so that (in the absence of an interlayer bias) the spectrum is *parabolic* around the Dirac point, and moreover the winding number is 2 rather than 1. This is of importance for the analysis of the behavior of the system in a magnetic field, in particular of the QHE.

However, it should be noted that in contrast to the single-layer case, where it is rather difficult to bias one sublattice relative to another, in the bilayer case described by (28) the two "basis" states A and $\tilde{B}$ lie in different layers, so it is relatively easy to bias them relative to one another. In that case it is easy to see that a band gap is introduced at the Dirac point, in fact mainly

$$E(q) = (E_0 + {v_{\mathrm{F}}}^4 q^4/\gamma_1^2)^{1/2}. \tag{32}$$

In real life the situation is rather more complicated because, inter alia, of the effects of the $A \rightleftarrows \tilde{B}$ hopping: see CN.