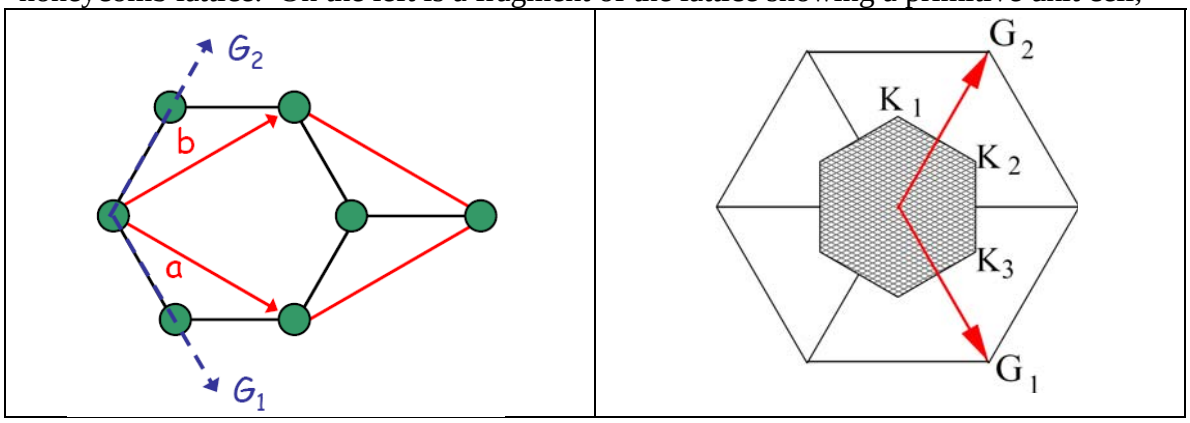
Electrons in graphene – massless Dirac electrons and Berry phase

Graphene is a single (infinite, 2d) sheet of carbon atoms in the graphitic honeycomb lattice. On the left is a fragment of the lattice showing a primitive unit cell,



with primitive translation vectors **a** and **b**, and corresponding primitive vectors $\mathbf{G_1}$, $\mathbf{G_2}$ of the reciprocal lattice. On the right is the central part of the reciprocal lattice and the first Brillouin zone. The corners of the Brillouin zone are the points K_i given by $\vec{K}_1 = (\vec{G}_2 - \vec{G}_1)/3, \vec{K}_2 = (2\vec{G}_2 + \vec{G}_1)/3, \vec{K}_3 = (2\vec{G}_1 + \vec{G}_2)/3$, etc. Only two are inequivalent. Notice for example that $\vec{K}_3 = \vec{K}_1 + \vec{G}_1$.

Because the lattice is 2-dimensional, all translations commute with reflection in the plane of the lattice, so all electron (or vibrational) eigenstates can be chosen to be either even or odd under this reflection. For this reason, the single-particle electron states are rigorously separated into two classes, called "σ" and "π," the even σ states being derived from carbon *s* and p_x, p_y orbitals, and the odd π states being derived from carbon p_z orbitals. These latter are cylindrically symmetric in the *x*-*y* plane, lie near the Fermi level (half-filled) and are the electrically active states of interest in low energy physics.

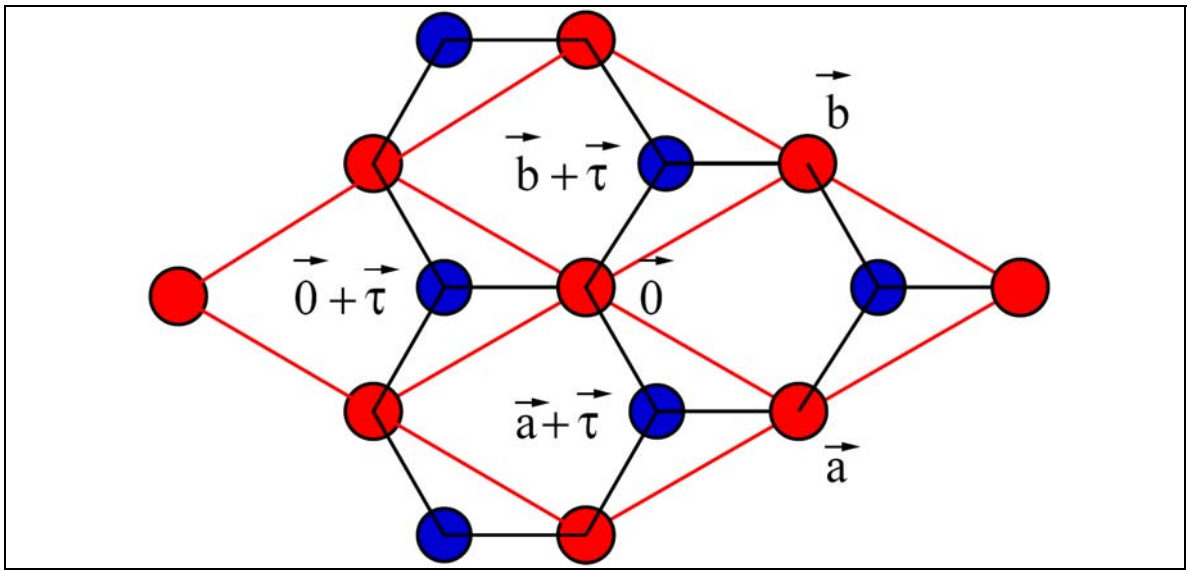
A useful picture of electron behavior can be derived by using Hückel theory to look at the π electrons (p_z orbital-derived states.) The two sublattices are shown below in different colors, with the "A" sublattice at vectors $\vec{R} = n_1\vec{a} + n_2\vec{b}$, and the "B" sublattice at vectors $\vec{R} + \vec{\tau}$, with $\vec{\tau} = -(\vec{a} + \vec{b})/3$. The Hamiltonian in nearest neighbor Hückel theory is

$$H = -t\sum_{\vec{R}} \left\{ \left|\vec{R}\right\rangle\left\langle \vec{R} + \vec{\tau}\right| + \left|\vec{R}\right\rangle\left\langle \vec{R} + \vec{a} + \vec{\tau}\right| + \left|\vec{R}\right\rangle\left\langle \vec{R} + \vec{b} + \vec{\tau}\right| + h.c. \right\}$$

where $\left|\vec{R}\right\rangle$ is a p_z (π) state on an A sublattice atom at site $\vec{R}$, $\left|\vec{R} + \vec{\tau}\right\rangle$ is a similar state on a B sublattice atom, and *t* is the "hopping integral" (positive) from a state to an adjacent similar state. The graphite lattice is "bipartite." The hopping matrix element couples states on the A sublattice only to states on the B sublattice, and vice versa. We now transform to the basis of Bloch waves,

$$\left|\vec{k}A\right\rangle = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\left|\vec{R}\right\rangle$$

$$\left|\vec{k}B\right\rangle = \frac{1}{\sqrt{N}}\sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}}\left|\vec{R} + \vec{\tau}\right\rangle.$$



This transformation block-diagonalizes the 1-electron Hamiltonian into 2 x 2 sub-blocks, with diagonal elements $\langle \vec{k}A|H|\vec{k}A\rangle$ and $\langle \vec{k}B|H|\vec{k}B\rangle$ both zero, and off-diagonal elements

$$\langle \vec{k}A|H|\vec{k}B\rangle = \frac{1}{N}\sum_{\vec{R}\vec{R}'} e^{i\vec{k}\cdot(\vec{R}'-\vec{R})}\langle \vec{R}|H|\vec{R}+\vec{\tau}\rangle = -t\left(1+e^{i\vec{k}\cdot\vec{a}}+e^{i\vec{k}\cdot\vec{b}}\right) = e(\vec{k}).$$

The single particle Bloch energies are thus $\varepsilon(\vec{k}) = \pm|e(\vec{k})|$, where

$$|e(k)|/t = \sqrt{1+4\cos\left(\frac{\sqrt{3}k_x a}{2}\right)\cos\left(\frac{k_y a}{2}\right)+4\cos^2\left(\frac{k_y a}{2}\right)}.$$

Let us write $e(\vec{k}) = |e(\vec{k})|e^{i\phi(\vec{k})}$. The Schrödinger equation is then $H(\vec{k})|\psi_k\rangle = \varepsilon(\vec{k})|\psi_k\rangle$, with the Hamiltonian matrix being

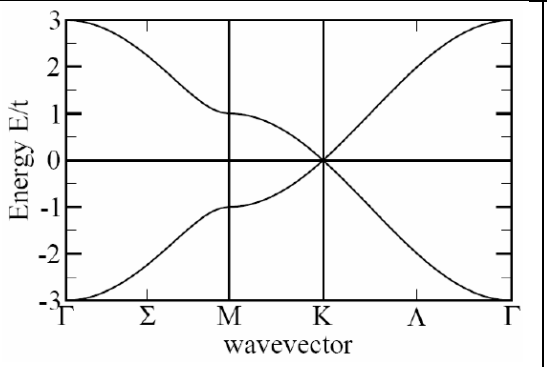
$$\hat{H}(\vec{k}) = \begin{pmatrix} 0 & |e(\vec{k})|e^{+i\phi(\vec{k})} \\ |e(\vec{k})|e^{-i\phi(\vec{k})} & 0 \end{pmatrix}$$

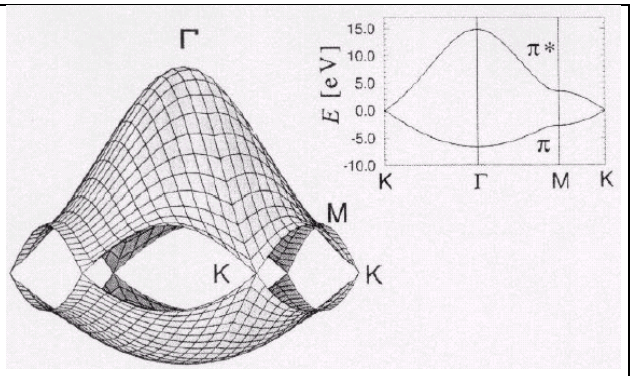
Then the eigenvectors ψ_k are

$$|k-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{+i\phi/2} \\ -e^{-i\phi/2} \end{pmatrix} \text{ and } |k+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{+i\phi/2} \\ e^{-i\phi/2} \end{pmatrix}.$$

Note that the phase factors $1+e^{i\vec{k}\cdot\vec{a}}+e^{i\vec{k}\cdot\vec{b}}$ become the 1/3rd roots of unity, $1+e^{+i2\pi/3}+e^{-i2\pi/3}=0$, when $\vec{k}$ lies on a corner point of the Brillouin zone, K_1, K_2. Therefore, the energy $e(\vec{k})\to 0$ at the zone corners. Everywhere else in *k*-space, $e(\vec{k})\neq 0$ and the splitting of the two graphene π-bands is $2|e(\vec{k})|$, the two bands (called π and π*) lying symmetrically above and below the Fermi energy, E=0. The bands are plotted below to the left. A more elegant two-dimensional presentation, from Saito and Kataura (Dresselhaus, Dresselhaus, and Avouris, eds., Carbon Nanotubes, Springer, 2001) is shown below to the right. A perfect graphene sheet has one electron per carbon

in the π-levels. Therefore, the Fermi level is between the two symmetrical bands, with zero excitation energy needed to excite an electron from just below the Fermi energy to just above at the k-point. The (ππ*) degeneracy at isolated points K at the Fermi energy is general to the one electron description of graphene. It follows from symmetry, and is not just an accidental result of the model. For example, the figure below from Saito and Kataura shows that even though a more accurate theory does not have exact particle-hole symmetry, the degeneracy at the *K* points persists.



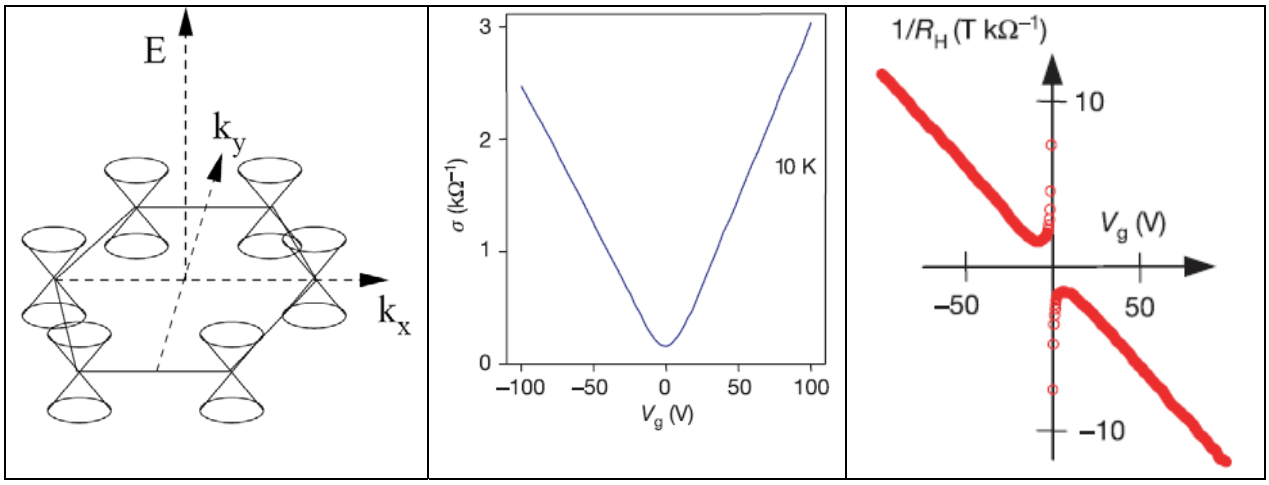


The wavefunctions of graphene have attracted a lot of interest. Let us consider a circular path in *k*-space around the point K_1 or equivalently, K_2. The energy is a linear function of $\delta\vec{k} = \vec{k} - \vec{K}_1$. If you move adiabatically in k-space around the K point, the wavefunctions acquire a "Berry phase" $e^{i\pi}$=*-1* when completing a circuit. This can be seen by expanding the wavefunctions to first order in $\delta\vec{k}$.

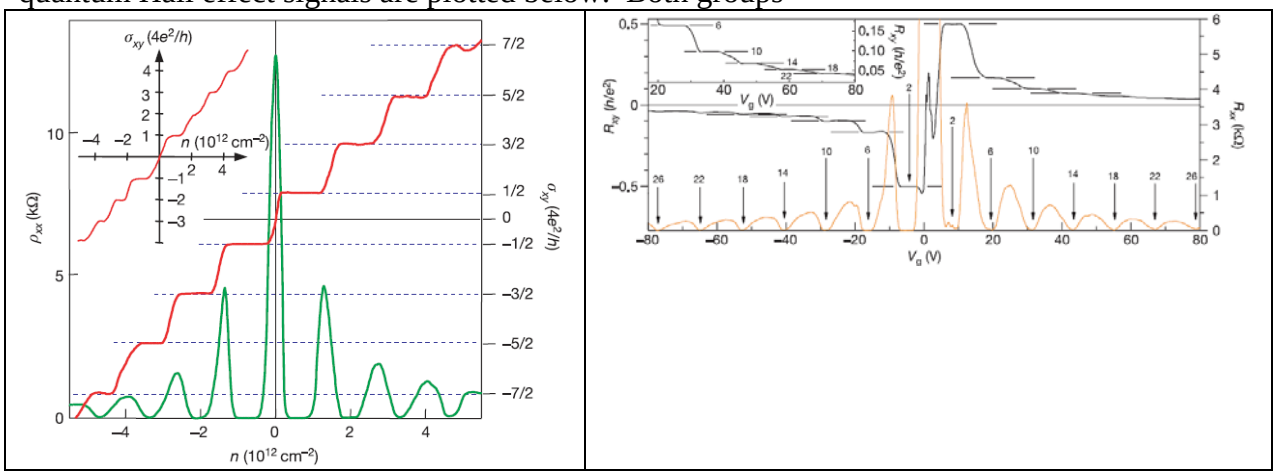
$$-\frac{e(\vec{k})}{t} = 1 + e^{i(\vec{K}+\delta\vec{k})\vec{a}} + e^{i(\vec{K}+\delta\vec{k})\vec{b}} \approx 1 + \left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right)\left(1 + i\delta\vec{k}\cdot\vec{a}\right) + \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)\left(1 + i\delta\vec{k}\cdot\vec{b}\right)$$

$$\approx -\frac{1}{2}i\delta\vec{k}\cdot\left(\vec{a}+\vec{b}\right) + \frac{\sqrt{3}}{2}i\delta\vec{k}\cdot\left(\vec{a}-\vec{b}\right) = \frac{\sqrt{3}}{2}\left|\delta\vec{k}\right| a e^{-i\pi/2} e^{-i\theta}$$

where θ is the angle from the *x*-axis in the k_x,k_y plane. Here the formulas $\vec{a}+\vec{b} = \sqrt{3}a\hat{x}$ and $\vec{a}-\vec{b} = -a\hat{y}$ were used. Thus $\left|e(\vec{k})\right|$ equals $\sqrt{3}\left|\delta\vec{k}\right| at$, and $e(\vec{k})$ has phase ϕ=*-*θ*-*π*/2*. Since the wavefunctions have phases $\pm\phi$*/2*, they change phase by π when θ increases by 2π, that is, when the $\vec{k}$ -vector goes once around a loop surrounding a K point. The code words "massless Dirac spectrum" are used to refer to the linear ε *versus k* relation, and the special points K_i are called the "Dirac points," shown below on the left. If a perfect graphene sheet is given an extra electron or hole, it will lie near a *K* point, and under a dc magnetic field $B\hat{z}$, will form a cyclotron orbit, orbiting around *K*. The Berry phase of π has the consequence that the quantized cyclotron orbits (Landau levels) will require half-integral numbers of wavelengths to give single-valued wavefunctions, to the energy will be quantized as $(n+1/2)\hbar\omega_c$ where *n* is an integer.



In **Nature** vol. **438**, 10 Nov. 2005, there were back-to-back papers from the Manchester-Chernogolovka-Nijmegen group (Geim *et al.*) and the Columbia group (P. Kim *et al.*) reporting the quantum Hall effect in graphene. The samples were monolayers of carbon lying on a thin silicon oxide layer on top of a doped silicon substrate which served as a gate electrode. The middle and right figures above are from the Geim paper showing how gate voltage dopes graphene *p*-type (as shown by the positive Hall coefficient R_H, through zero, to *n*-type. Both R_H and electrical conductivity σ extrapolate to zero when the Fermi level passes through the Dirac points. Interestingly, σ is actually pinned at a minimum value near $4e^2/h$, and seems not to actually go to zero. The quantum Hall effect signals are plotted below. Both groups



unambiguously see **half-integer** quantization, exactly as predicted by two theoretical groups shortly before the measurements.

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Notes prepared for Physics 556