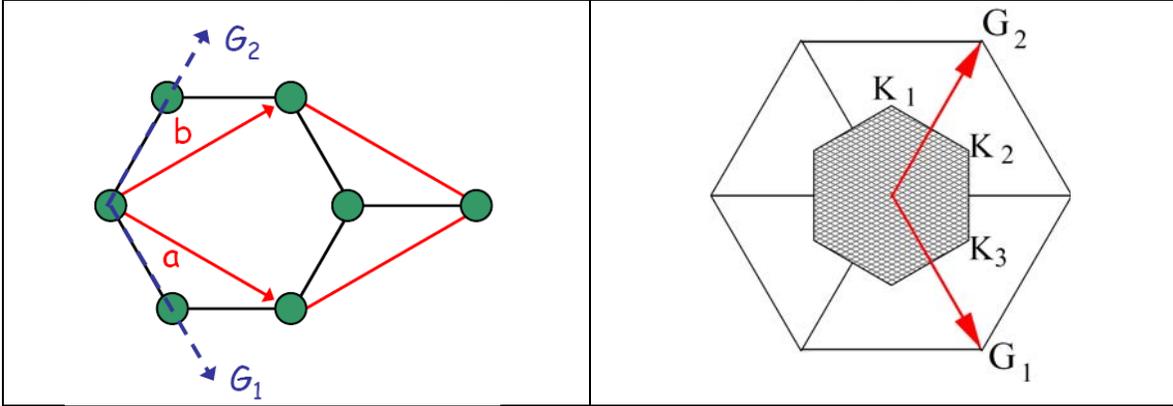


Electrons in graphene – massless Dirac electrons and Berry phase

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 \mathbf{a} and \mathbf{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 \mathbf{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.

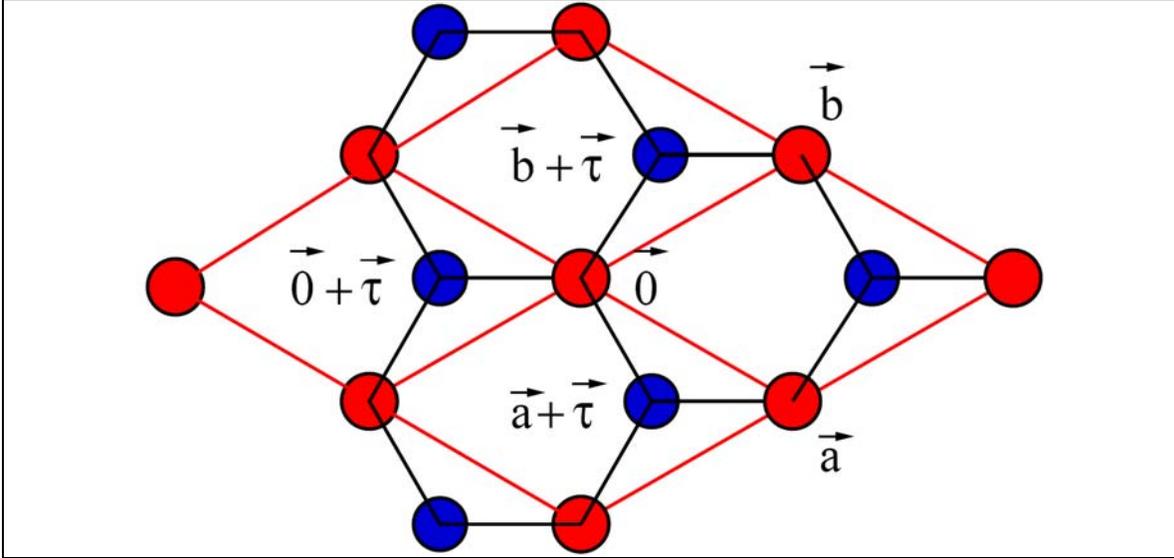
A useful picture of electron behavior can be derived by using Hückel theory to look at the π electrons (p_z orbital-derived states.) The two sublattices are shown below in different colors, with the “A” sublattice at vectors $\vec{R} = n_1\vec{a} + n_2\vec{b}$, and the “B” sublattice at vectors $\vec{R}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

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

where $|\vec{R}\rangle$ is a p_z (π) state on an A sublattice atom at site \vec{R} , $|\vec{R} + \vec{\tau}\rangle$ 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 abbreviation “ $h.c.$ ” means Hermitean conjugate. 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,

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

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



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

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

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

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

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 $e(\vec{k}) \rightarrow 0$ at the zone corners. Everywhere else in k -space,

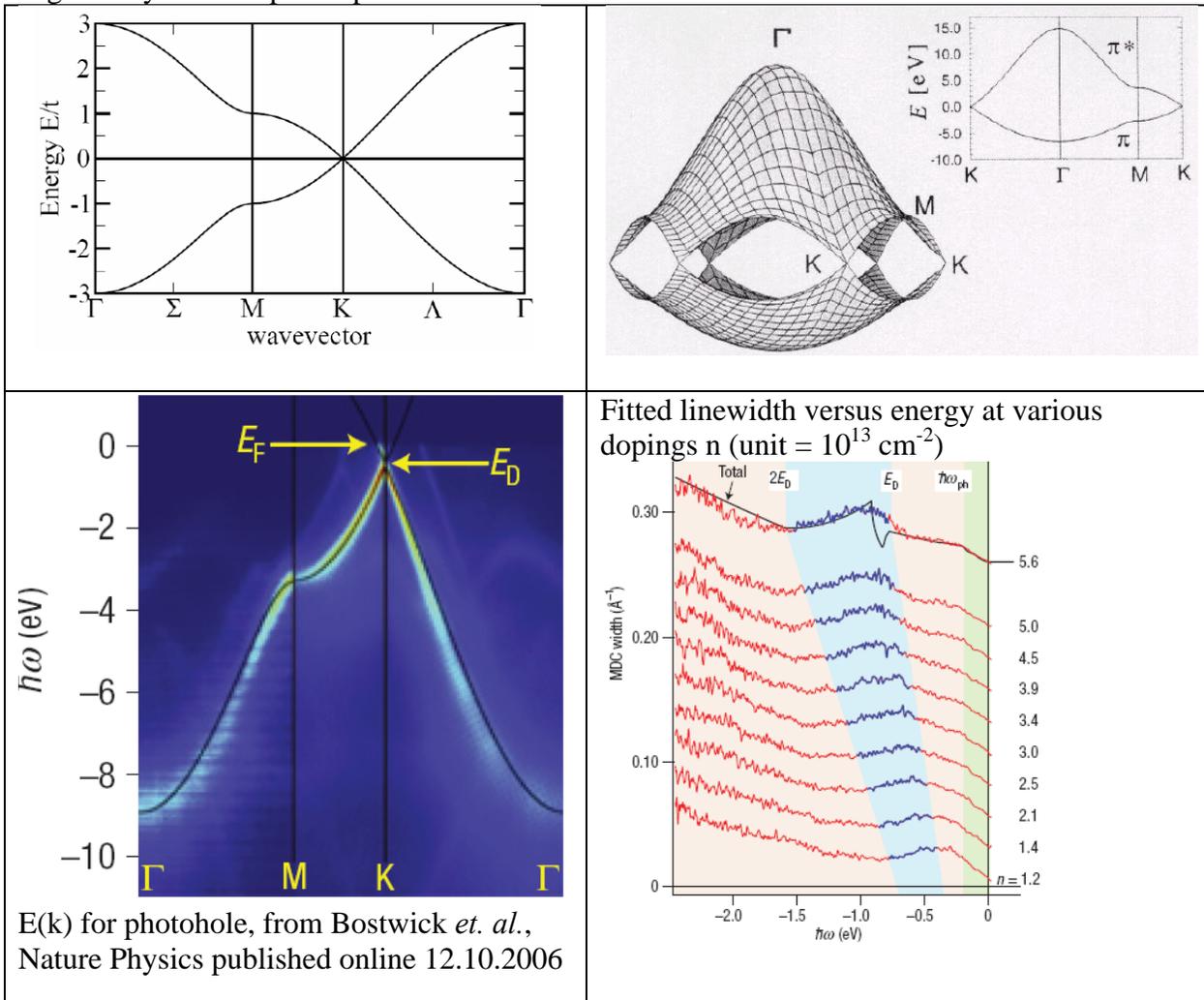
$e(\vec{k}) \neq 0$ and the splitting of the two graphene π -bands is $2|e(\vec{k})|$. The two bands (called

π and π^*) lie 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 beautiful photoemission experiment by Bostwick *et. al.* is also shown. The dispersion seen for the photohole fits amazingly well to the Hückel formula.

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 $(\pi\pi^*)$ 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 Hückel 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

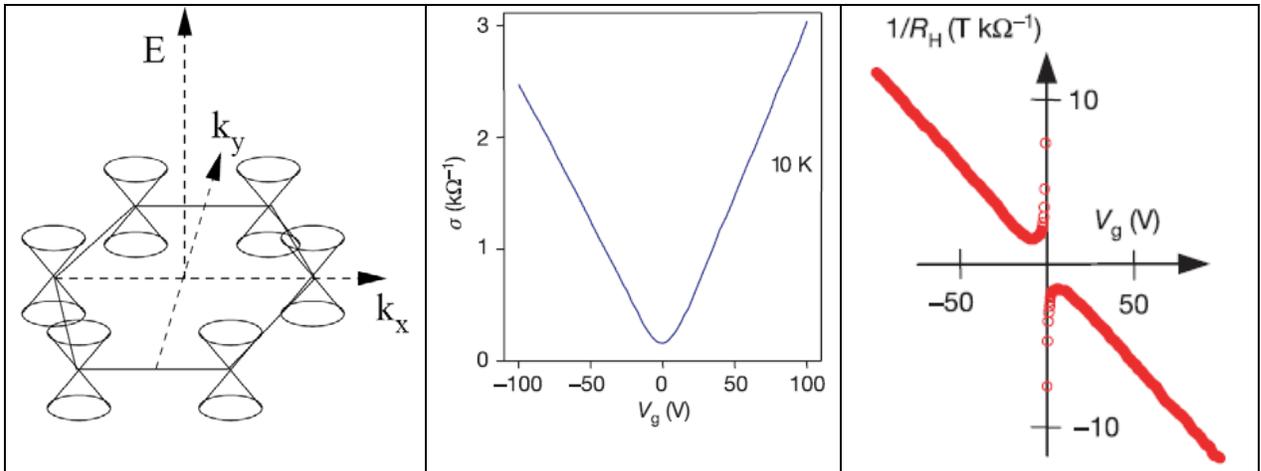
wavefunctions acquire a “Berry phase” $e^{i\pi} = -1$ when completing a circuit. This can be seen by expanding the Hamiltonian matrix to first order in $\delta\vec{k}$.

$$\begin{aligned} -\frac{e(\vec{k})}{t} &= 1 + e^{i(\vec{k}+\delta\vec{k})\cdot\vec{a}} + e^{i(\vec{k}+\delta\vec{k})\cdot\vec{b}} \approx 1 + \left(-\frac{1}{2} - i\frac{\sqrt{3}}{2}\right)(1 + i\delta\vec{k}\cdot\vec{a}) + \left(-\frac{1}{2} + i\frac{\sqrt{3}}{2}\right)(1 + i\delta\vec{k}\cdot\vec{b}) \\ &\approx -\frac{1}{2}i\delta\vec{k}\cdot(\vec{a}+\vec{b}) + \frac{\sqrt{3}}{2}\delta\vec{k}\cdot(\vec{a}-\vec{b}) = \frac{\sqrt{3}}{2}|\delta\vec{k}|ae^{-i\pi/2}e^{-i\theta} \\ &\approx -\frac{\sqrt{3}a}{2}i[\delta k_x - i\delta k_y] = \frac{\sqrt{3}}{2}|\delta\vec{k}|ae^{-i\pi/2}e^{-i\theta} \end{aligned}$$

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 $|e(\vec{k})|$ equals $\sqrt{3}|\delta\vec{k}|at$, and $e(\vec{k})$ has phase $\phi = -\theta - \pi/2$.

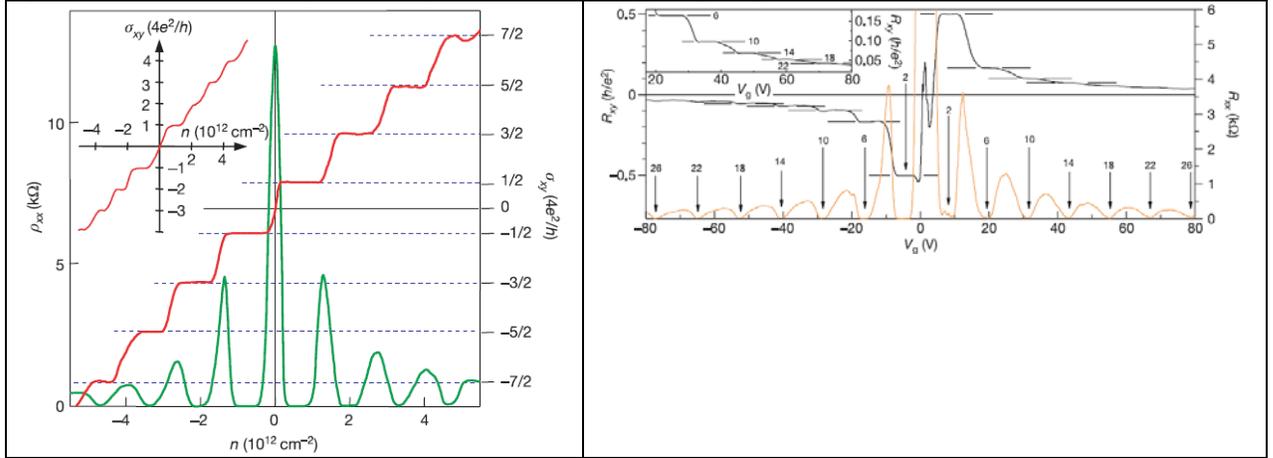
Since the wavefunctions have phases $\pm\phi/2$, they change phase by π when θ increases by 2π , that is, when the \vec{k} -vector goes once around a loop surrounding a K point.

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, so 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.

Nearly free electron method

As an alternative model for graphene, suppose we had a two dimensional electron gas (2-deg) with a weak periodic potential applied. The applied potential has honeycomb symmetry. As a more faithful realization, we could imagine a GaAs/(Ga,Al)As inversion layer with a patterned top electrode in honeycomb morphology. The Hamiltonian is

$$H = \frac{p^2}{2m} + \sum_{\vec{R}} [V(\vec{r} - \vec{R} - \vec{\tau}) + V(\vec{r} - \vec{R} + \vec{\tau})]$$

The geometry was shown in the first figure. The origin is now taken in the center of a hexagon, not on a ‘‘atom’’ site, and the ‘‘atoms’’ are then at $\pm \vec{\tau} = \pm(\vec{a} + \vec{b})/3$. I am assuming that the applied potential is the sum of localized cylindrical terms, depending only on $r = |\vec{r}| = \sqrt{x^2 + y^2}$. Then the single-particle states can be expanded in plane waves $|\vec{k}\rangle = (1/\sqrt{V})\exp(i\vec{k} \cdot \vec{r})$. Bloch’s theorem applies, and the Hamiltonian matrix has disconnected sub-blocks $H(\vec{k})$ of the form

$$[H(\vec{k})]_{\vec{G}, \vec{G}'} = \frac{\hbar^2(\vec{k} + \vec{G})^2}{2m} \delta(\vec{G}, \vec{G}') + V_{tot}(\vec{G} - \vec{G}')$$

where the off-diagonal terms V_{tot} are products of single-site pseudo-potential form factors $V(|\vec{G}|)$ times structure factors $S(\vec{G}) = \cos(\vec{G} \cdot \vec{\tau})$. The band structure is in zeroth

approximation just $E \equiv \varepsilon_0 = \varepsilon(\vec{k} + \vec{G}) = \hbar^2(\vec{k} + \vec{G})^2 / 2m$. The weak potential shifts energy only to second order, except at symmetric places in the Brillouin zone (e.g. boundaries) where $\vec{k} + \vec{G} = \vec{k} + \vec{G}'$ for some pair of reciprocal lattice vectors \vec{G} and \vec{G}' . The K points in the Brillouin zone are special. Consider the plane wave at the point K_I shown in the first figure, $|1\rangle = |\vec{K}_I\rangle$. This has a kinetic energy $\varepsilon = \varepsilon(K_I)$ degenerate with the kinetic

energy of $|2\rangle = |\vec{K}_1 + \vec{G}_1\rangle$ which lies at the special point K_3 in the first figure, and with $|3\rangle = |\vec{K}_1 - \vec{G}_2\rangle$ which lies at the special point K_5 . The dominant part of the matrix $H(\vec{k})$ is

$$H(\vec{k}) = \begin{pmatrix} \varepsilon_0 & -V/2 & -V/2 \\ -V/2 & \varepsilon_0 & -V/2 \\ -V/2 & -V/2 & \varepsilon_0 \end{pmatrix}.$$

The notation V is the form factor $V(\vec{G})$ for the relevant vector difference $\vec{K}_i - \vec{K}_j$, and the factor $-1/2$ is the corresponding structure factor S . Let us use a little group theory. The point group of graphene is D_{6h} . The three basis functions $|1\rangle, |2\rangle, |3\rangle$ do not close under the operations of D_{6h} because the rotation by $2\pi/6$ takes K_i into the inequivalent point K_2 . But these three functions do close under, and thus generate a representation of, the subgroup D_{3h} (known as the ‘‘little group’’ of the wavevector K .) It is easy to see that the vector $|0\rangle = (|1\rangle + |2\rangle + |3\rangle)/\sqrt{3}$ has A_1' symmetry and is an eigenvector with eigenvalue $E_0 = \varepsilon_0 - V$. Using ϕ to denote the angle $2\pi/3$, the vectors $|\phi\rangle = (|1\rangle + e^{i\phi}|2\rangle + e^{-i\phi}|3\rangle)/\sqrt{3}$ and $|-\phi\rangle$, the complex conjugate of $|\phi\rangle$, are basis vectors for an E' doublet of eigenvalue $E_l = \varepsilon + V/2$. This doublet lies lower in energy if V is negative, and is a Dirac point. To see that, we have to make a Taylor expansion for $H(\vec{K} + \delta\vec{k})$. The matrix becomes

$$H(\vec{k}) = \begin{pmatrix} \varepsilon_1 & -V/2 & -V/2 \\ -V/2 & \varepsilon_2 & -V/2 \\ -V/2 & -V/2 & \varepsilon_3 \end{pmatrix}$$

where ε_l is $\hbar^2(\vec{K}_l + \delta\vec{k})^2/2m$, and similar for ε_2 and ε_3 . To solve this, first transform to the basis of eigenvectors with $\delta\vec{k} = 0$, namely $|0\rangle, |\phi\rangle$, and $|-\phi\rangle$. The new matrix is

$$H(\vec{k}) = \begin{pmatrix} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)/3 - V & \text{small} & \text{small} \\ \text{small} & (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)/3 + V/2 & (\varepsilon_1 + \varepsilon_2 e^{i\phi} + \varepsilon_3 e^{-i\phi})/3 \\ \text{small} & (\varepsilon_1 + \varepsilon_2 e^{-i\phi} + \varepsilon_3 e^{i\phi})/3 & (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)/3 + V/2 \end{pmatrix}$$

where ‘‘small’’ means that the energy shift will be second order in $\delta\vec{k}$. Our concern now is with the eigenvalues and eigenvectors that evolve from the E' doublet (the second and third rows and columns of the matrix.) We need only solve this 2×2 submatrix, since the influence of the other state is second order. The elements of this matrix are

$$\begin{aligned} (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)/3 &= \varepsilon_0 + \hbar^2 |\delta\vec{k}|^2 / 2m \\ (\varepsilon_1 + \varepsilon_2 e^{i\phi} + \varepsilon_3 e^{-i\phi})/3 &= (\hbar^2 / m)(2\pi/3a)(i\delta k_x + \delta k_y) \end{aligned}$$

Therefore the relevant 2×2 submatrix is

$$H(\vec{k}) = \left(\varepsilon + \frac{\hbar^2 |\vec{\delta k}|^2}{2m} + \frac{V}{2} \right) \hat{1} + \frac{\hbar^2}{m} \frac{2\pi}{3a} |\vec{\delta k}| \begin{pmatrix} 0 & e^{-i(\theta-\pi/2)} \\ e^{i(\theta-\pi/2)} & 0 \end{pmatrix}.$$

The energy eigenvalues are massless Dirac spectra,

$$\varepsilon + \hbar^2 |\vec{\delta k}|^2 / 2m + V / 2 \pm (\hbar^2 / m) (2\pi / 3a) |\vec{\delta k}|,$$

and the eigenvectors contain $\exp(\pm i\theta/2)$, that is, they change sign when the angle $\theta = \tan^{-1}(\delta k_y / \delta k_x)$ goes once around the Dirac point. It is interesting that the conical dispersion around the Dirac points does not depend on the size of the applied potential. This can only be true when the conical energy increments $\pm (\hbar^2 / m) (2\pi / 3a) |\vec{\delta k}|$ are less than the increments $\pm V/2$ caused by the external potential. At larger separations $|\vec{\delta k}|$, the bands have to evolve back to free electron form.

The underlying Hamiltonian is real, but the matrix representations we looked at so far were complex Hermitean. This is a consequence of the choice of basis functions. A different basis could have given a real-symmetric Hamiltonian.

The question arises whether similar effects should show up in graphite. There is a nice recent paper “Phase analysis of quantum oscillations in graphite,” by I. A. Luk’yanchuk and Y. Kopelevich (Phys. Rev. Lett. **93**, 166402 (2004)) which comes close to addressing this issue. I am not sure the matter is yet laid to rest.