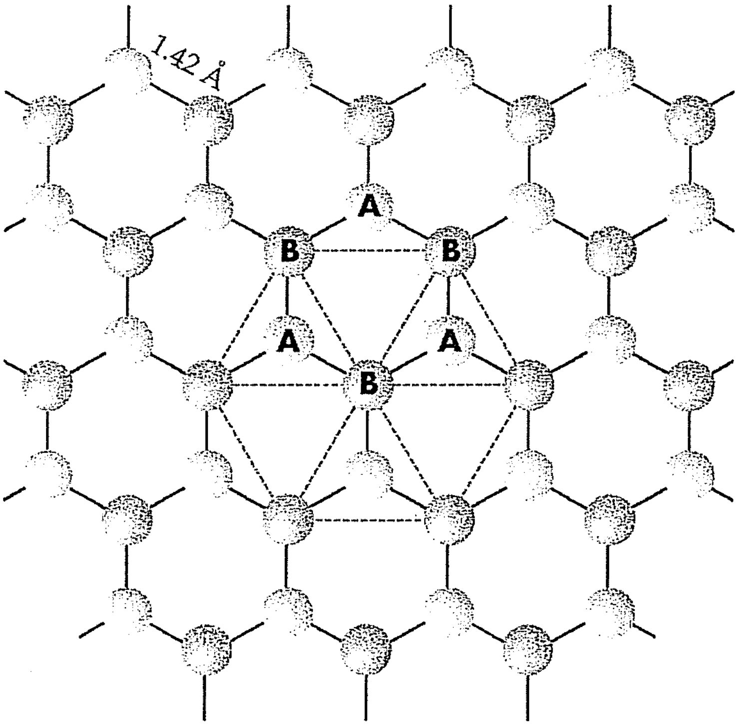
# Graphene: Band structure

From: Geim and MacDonald, Physics Today (August 2007), p. 35

## Box 1. Crystal and electronic structures of graphene

The honeycomb lattice of graphene, pictured below, consists of two interpenetrating triangular sublattices: The sites of one sublattice (green) are at the centers of triangles defined by the other (orange). The lattice thus has two carbon atoms, designated A and B, per unit cell, and is invariant under 120° rotations around any lattice site. Each atom has one *s* and three *p* orbitals. The *s* orbital and two in-plane *p* orbitals are tied up in graphene's strong covalent bonding and do not contribute to its conductivity. The remaining *p* orbital, oriented perpendicular to the molecular plane, is odd under inversion in the plane and hybridizes to form $\pi$ (valence) and $\pi^*$ (conduction) bands, as shown at right.



- 2 atoms per unit cell (at lattice pt. + at $\vec{\rho}$ relative to lattice pt.)
- $\sigma$ bonds in graphene plane

  → $sp^2$ hybridization

  [Each atom contributes $2s, 2p_x, 2p_y$]
- Each atom is left with a $2p_z$ atomic orbital
  - Form Bloch sum for $2p_z$ orbitals at A-sites

$$\phi^{(A)}_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} \chi^{(A)}_{2p_z}(\vec{r}-\vec{R})$$

  - Form Bloch sum for $2p_z$ orbitals at B-sites

$$\phi^{(B)}_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}} e^{i\vec{k}\cdot\vec{R}} e^{i\vec{k}\cdot\vec{\rho}} \chi^{(B)}_{2p_z}(\vec{r}-\vec{R}-\vec{\rho})$$

Want to solve:

$$\hat{H}_{\text{crystal}} \psi_{\vec{k}}(\vec{r}) = E(\vec{k}) \psi_{\vec{k}}(\vec{r})$$

Write: (LCAO) $\psi_{\vec{k}}(\vec{r}) = C_A \phi^{(A)}_{\vec{k}}(\vec{r}) + C_B \phi^{(B)}_{\vec{k}}(\vec{r})$

Substituting into Schrödinger Eq., the equation becomes

$$\begin{pmatrix} H_{AA} - E S_{AA} & H_{AB} - E S_{AB} \\ H_{BA} - E S_{BA} & H_{BB} - E S_{BB} \end{pmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0$$

where
$$\begin{cases} H_{\alpha\beta} = \int \phi^{*(\alpha)}_{\vec{k}}(\vec{r})\, \hat{H}_{crystal}\, \phi^{(\beta)}_{\vec{k}}(\vec{r})\, d^3r \\ S_{\alpha\beta} = \int \phi^{*(\alpha)}_{\vec{k}}(\vec{r})\, \phi^{(\beta)}_{\vec{k}}(\vec{r})\, d^3r \end{cases}$$

Non-trivial solution $\Rightarrow$

$$\begin{vmatrix} H_{AA} - E S_{AA} & H_{AB} - E S_{AB} \\ H_{BA} - E S_{BA} & H_{BB} - E S_{BB} \end{vmatrix} = 0$$

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In the same spirit in the simplest TBM,

$S_{AA} = 1 = S_{BB}$, $S_{AB} = S_{BA} \approx 0$

$$\therefore \begin{vmatrix} H_{AA} - E & H_{AB} \\ H_{BA} & H_{BB} - E \end{vmatrix} = 0 \quad \text{for each } \vec{k} \text{ in } 1^{st} \text{ B.Z.}$$

$\hookrightarrow$ equivalent to saying $E(\vec{k})$ is given by the eigenvalues of
$$\begin{pmatrix} H_{AB}(\vec{k}) & H_{AB}(\vec{k}) \\ H_{BA}(\vec{k}) & H_{BB}(\vec{k}) \end{pmatrix}$$

Each $\vec{k} \Rightarrow 2$ eigenvalues $\Rightarrow 2$ bands ($\pi$ and $\pi^*$ bands)

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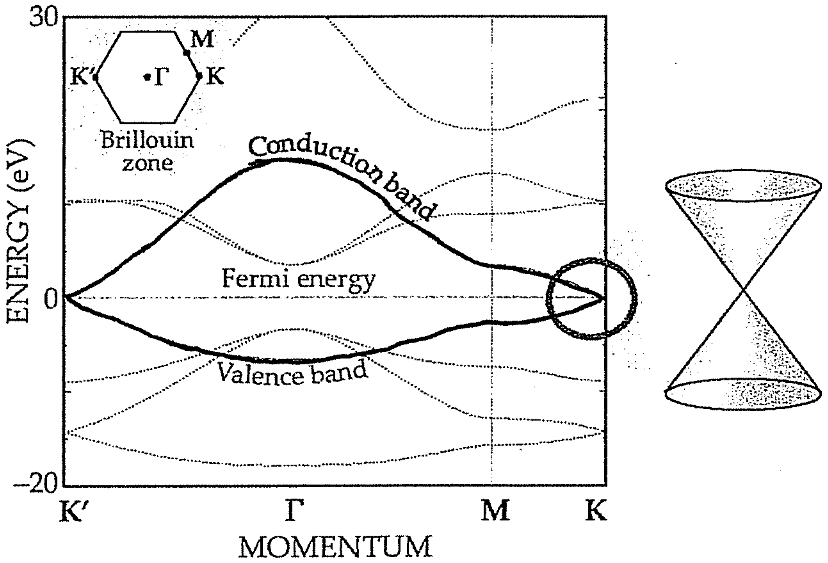
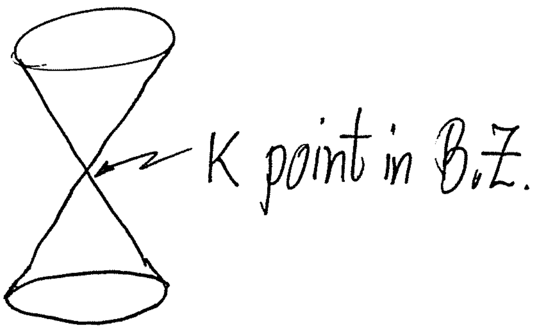


In the Bloch band description of graphene's electronic structure, orbital energies depend on the momentum of charge carriers in the crystal Brillouin zone (inset, right). The $\pi$ and $\pi^*$ bands (blue in the electronic structure plot) are decoupled from the $\sigma$ and $\sigma^*$ bands (red) because of inversion symmetry and are closer to the Fermi energy because they participate less in bonding. The Fermi energy separates occupied and empty states. In a neutral graphene sheet, this is the energy where valence and conduction bands meet (zero energy above, often referred to as the neutrality point). The bands form conical valleys that touch at two of the high-symmetry points, conventionally labeled **K** and **K′**, in the Brillouin zone. Near these points the energy varies linearly with the magnitude of momentum measured from the Brillouin-zone corners. The four other Brillouin-zone corners are related to **K** and **K′** by reciprocal lattice vectors and do not represent distinct electronic states.

Dark lines:
- 2 bands formed by LCAO of $2p_z$ orbitals
- electrons fill states up to Fermi energy (taken to be zero in figure)
- gapless – the empty (conduction) band and the full (valence) band touch at K and K′.

- Near K (and K'), the band structure is like a cone!



- This conical (thus linear when counted from K) form of the band structure leads to much interest in graphene, in addition to graphene's potential applications in electronics.

Why?

- $\vec{k} \sim \vec{p}$ (off by $\hbar$)
- linear $\Rightarrow$ $E \sim |\vec{p}|$
- Recall: $E = cp$ for light, which is a massless entity
- Thus, the behavior of electrons at K is that of a massless particle!

[Relatistic : Quantum Mechanics?]
Dirac's formulation.

Near K-point, the 2x2 Hamiltonian matrix has the form of

$$\hat{H} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}$$

$$= \hbar v_F \left[ \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} k_x + \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} k_y \right]$$

$$= \hbar v_F \left( \sigma_x k_x + \sigma_y k_y \right)$$

$\sigma_x, \sigma_y$ are Pauli matrices

$$= v_F \hbar \, \vec{\sigma} \cdot \vec{k}$$

$$= v_F \, \vec{\sigma} \cdot \vec{p}$$

It happens that this $\hat{H}$ has the form of the Hamiltonian for Dirac equation for massless fermion!

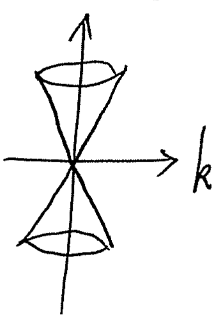
$\therefore$ A simple solid state system (graphene) happens to provide a testbed for QED!

Eigenvalues of $\hbar v_F \begin{pmatrix} 0 & k_x - i k_y \\ k_x + i k_y & 0 \end{pmatrix}$

[k is counted from K-point]

$$\begin{vmatrix} -\lambda & k_x - i k_y \\ k_x + i k_y & -\lambda \end{vmatrix} = 0 \Rightarrow \lambda^2 - \underbrace{\underbrace{|k_x + i k_y|^2}_{k_x^2 + k_y^2}}_{k^2} = 0$$

$$\Rightarrow \lambda = \pm k \Rightarrow$$



$$E = \pm \hbar v_F k$$

Remarks:

Are all these so "new"?

- Not quite!

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# The Band Theory of Graphite

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The structure of the electronic energy bands and Brillouin zones for graphite is developed using the "tight binding" approximation. Graphite is found to be a semi-conductor with zero activation energy, i.e., there are no free electrons at zero temperature, but they are created at higher temperatures by excitation to a band contiguous to the highest one which is normally filled. The electrical conductivity is treated with assumptions about the mean free path. It is found to be about 100 times as great parallel to as across crystal planes. A large and anisotropic diamagnetic susceptibility is predicted for the conduction electrons; this is greatest for fields across the layers. The volume optical absorption is accounted for.

TBM

$$H_{11}=\int\phi_1{}^*H\phi_1d\tau,\quad H_{12}=H_{21}{}^*=\int\phi_1{}^*H\phi_2d\tau,$$

$$H_{22}=\int\phi_2{}^*H\phi_2d\tau$$

and

$$S=\int\phi_1{}^*\phi_1d\tau=\int\phi_2{}^*\phi_2d\tau.$$

Eliminating $\lambda$ we obtain the secular equation

$$\begin{vmatrix} H_{11}-ES & H_{12} \\ H_{21} & H_{22}-ES \end{vmatrix}=0,$$

from which it is found that

$$E=\frac{1}{2S}\{H_{11}+H_{22}\pm((H_{11}-H_{22})^2+4|H_{12}|^2)^{\frac{1}{2}}\}. \quad (2.5)$$

DOS near Fermi energy

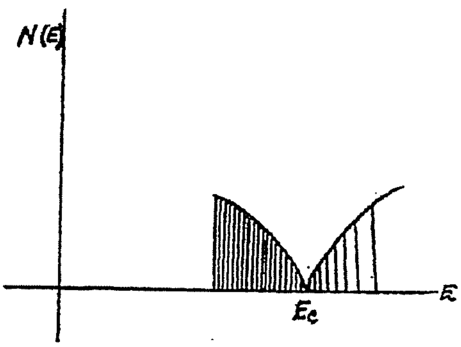

FIG. 6.

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# Electronic Band Structure and Optical Properties of Graphite from a Variational Approach*

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The electronic band structure of graphite has been calculated from an *ab initio* variational approach using a linear-combination of atomic-orbitals (LCAO) basis of Bloch states, including nonspherical terms in the one-electron crystal potential. Matrix elements of the Hamiltonian are evaluated directly without any tight-binding approximations. The optical transitions deduced from the energy bands calculated using a single-layer crystal model agree nicely with recent polarized-light reflectance measurements. Details of the band structure are calculated for the three-dimensional Brillouin zone and related to the results obtained using the single-layer crystal structure. The results are encouraging, not only from the standpoint that the method employed is an *ab initio* approach with no special *a priori* assumptions, but also because the band structure is quite insensitive to the particulars of the crystal potential function.

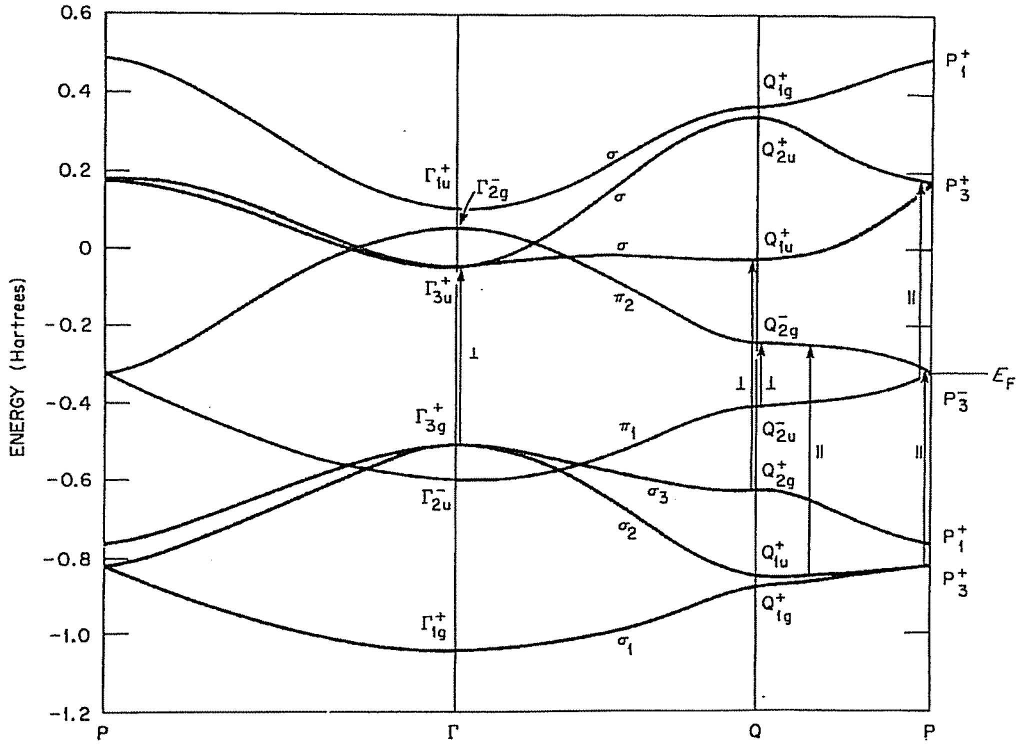

FIG. 3. Energy band structure for graphite in the single-layer crystal model. Allowed transitions which contribute structure to the reflectance are indicated for polarization parallel (∥) and perpendicular (⊥) to the *c* axis.

# Why is Graphene so hot now?

- Great potential in applications!
  [Replace Silicon, cheap]
- Learned much about 2D physics in 1980's-1990's, e.g., quantum Hall effect (already observed in graphene), thus could use graphene as an experimental system to explore low-dimensional physics (e.g. localization).
- Unusual band structure near K
  - relation to Dirac massless particle, QED

# Electronic Structure and the Properties of Solids

## THE PHYSICS OF THE CHEMICAL BOND

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(1980)

(1976) for the vibrational properties of chalcogenides. It is interesting to notice that the coiling of the chains makes the matrix elements between $\pi$ orbitals on adjacent atoms small (they would be zero with the 90° coiling of Fig. 3-12), and therefore narrows the corresponding nonbonding $\pi$ bands. If these were half full, as in graphite, this would cost significant energy and favor a flat configuration. However, since these bands are full in the chalcogenides, the change is of little consequence.

Planar and filamentary structures are of interest in their own right, but understanding their electronic structure and properties seems to depend upon a combination of concepts applicable also to other, more general systems rather than upon a unique set of concepts. We will not undertake a special study of them, therefore, but will carry them along as illustrative examples at the end of each chapter.

### PROBLEM 3-1 *Tetrahedral crystal structure*

Sketch the diamond structure as viewed along a [110] direction, analogous to Fig. 3-1,b. Shade atoms not in the plane of the figure and draw lines connecting nearest neighbors.

If spheres are packed in a face-centered cubic structure, what fraction of the space lies within a sphere? This is called the "packing fraction."

What is the packing fraction for the diamond structure?

### PROBLEM 3-2 *Hybrid and bond orbitals in graphite*

The graphite structure was discussed in Section 3-F and illustrated in Fig. 3-10. If we take the $p_z$ orbitals to be oriented perpendicular to the plane of the graphite (these become the $\pi$ energy levels), we may proceed to construct the $\sigma$ bands from the $s$, $p_x$, and $p_y$ orbitals in close analogy to the construction of the bands in the diamond structure.

(a) Construct $sp^2$ hybrid states in analogy with the diamond-structure states of Eq. (3-1), choosing coefficients such that the hybrid wave functions are orthogonal to each other and normalized, and oriented in the direction of each of the three neighbors in the plane.

(b) Obtain the hybrid energy in terms of atomic $s$ and $p$ energies. Obtain also $-V_1$, the matrix element of the Hamiltonian between hybrids on the same atom, in analogy with Eq. (3-5). Values may all be obtained from the Solid State Table.

(c) The matrix elements between two hybrids in the same bond, $V_2^h$, can also be obtained from the Solid State Table in terms of the $V_{ss\sigma}$, the $V_{sp\sigma}$, and the $V_{pp\sigma}$ for $d = 1.42$ Å. Sketch the energy levels as far as the formation of bands, as on the upper left of Fig. 3-3. Think of the $\pi$-band energy as being the same as the $p$-orbital energy, neglecting the broadening into bands.

### PROBLEM 3-3 *Band energies in graphite*

~~The LCAO~~ Bloch states at $\Gamma$ ($\mathbf{k} = 0$) in graphite, as in diamond, can be written as pure sums of each orbital type; for example, there is one state given by $(2N_p)^{-1/2}$ times a sum of $p$ states oriented in the $x$-direction chosen in the plane of graphite; another is given by a similar sum but with each $p$ state from the second atom in each primitive cell multiplied by $-1$. (You will find this a bonding, low-energy state.) Find the energies of the eight bands of graphite at $\Gamma$, in analogy with Eq. (3-27). Label them $\sigma$ valence, $s$ valence, $\pi$ conduction, and so on.

The bands obtained by Painter and Ellis (1970) are shown in Fig. 3-13 for comparison. We have chosen the zero of energy to make comparison easy. The comparison would suggest that we may have overestimated $V_{pp\sigma}$ by a factor of two for this case, a difficulty that may be associated with carbon's being a first-row element.

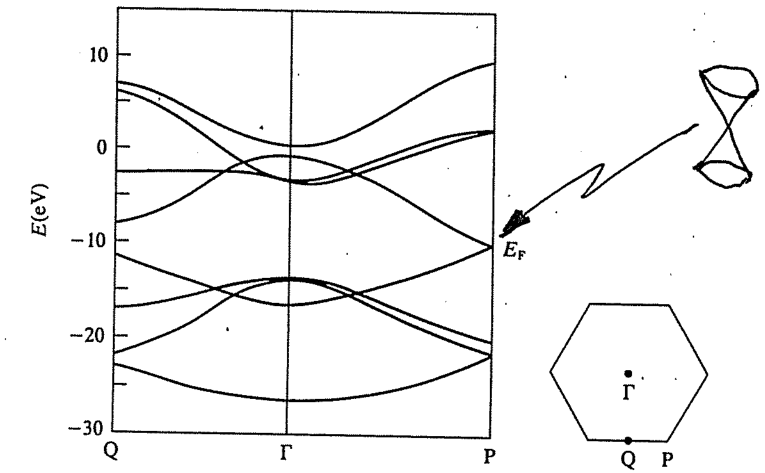

FIGURE 3-13
The energy bands of graphite given by Painter and Ellis (1970), corresponding to a separated graphite plane. The zero of energy has been selected to correspond roughly to an $\varepsilon_p$ taken from the Solid State Table. Symmetry points in the Brillouin Zone are shown to the right.

### PROBLEM 3-4 *Hybrid polarity in hexagonal* BN

Consider hexagonal boron nitride, shown in Fig. 3-10. Define a hybrid covalent and hybrid polar energy for this structure, in analogy with the corresponding definitions for tetrahedral solids in Eqs. (3-4) and (3-6). Compare the polarity obtained from these values with that of tetrahedral BN, listed in Table 7-2. Take $d = 1.42$ Å as in graphite. Notice that many values are modified by having $sp^2$ hybrids rather than $sp^3$ hybrids.

- A closed form was given in another book of W. A. Harrison "Elementary Electronic Structure" (1998), page 771.

$$\varepsilon(\vec{k}) = \text{constant} \pm t\sqrt{1+4\cos^2\left(\frac{\sqrt{3}}{2}k_x a_0\right)+4\cos\left(\frac{\sqrt{3}}{2}k_x a_0\right)\cos\left(\frac{3}{2}k_y a_0\right)}$$