

The Electronic Structure of Graphite

A Chemist's Introduction to Band Theory

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Solid-state theory now figures prominently in the chemist's agenda. Understanding it is a prerequisite for entering materials science, where chemists are being involved at a faster rate than ever before. Recent advances in materials science have been making the field more attractive to students, as is the case with high- T_c superconductors, intercalation compounds, conducting polymers, catalysts, etc. Slowly but relentlessly solid-state science has become quite standard chemical knowledge and is no longer regarded as the physicist's exclusive territory.

However, many basic topics in solid-state science courses are still considered difficult by chemistry students; one of these is the band theory of solids, which is regarded as altogether too formal or too abstract for chemistry courses. Recent efforts to bring the subject closer to the chemist are good evidence that what is needed is an enhanced connection between concepts of chemical bonding and those of band theory. Furthermore, there is still a dearth of examples in which calculations are clear and simple, with results that are easy to visualize and to interpret chemically.

In this paper I offer a simple example for calculation of band structures that was tested by graduates and advanced undergraduates at Facultad de Química, U. N. A. M. This calculation of the band structure of a single layer of carbon atoms in graphite, in the Hückel/tight-binding approximation, has proven to be easy-to-calculate and easy-to-understand. Relevant aspects of the electronic structure of graphite are described by this calculation, yet it is much simpler than the standard textbook example for tight-binding theory for diamond because only a single basis function is needed on each carbon atom.

The stated purposes of this paper were approached by Duke and O'Leary in *this Journal* (1) and by Endres (2). The subject matter itself was covered previously with a different approach and context by Burdett (3) and Kertesz (4). A recent, thorough review of the electronic properties of graphite can be found in Grasso's book (5). For convenience I assume that students approaching this example have a background in quantum chemistry at the level of textbooks by Hanna (6) or Lowe (7) and that they are being exposed to band theory in a standard textbook, such as those by Harrison (8) or Ashcroft and Mermin (9). Reference will be made to this last one, as it is widely used.

Excellent general introductions to the electronic structure of solids are found in books by Hoffmann (10) and by Cox (11). The material presented here should complement them.

Graphite is well-known to chemistry students from basic courses, which cover its peculiarities and use it in eye-catching demonstrations. As an example for electron delocalization and for sp^2 hybridization, its electronic structure is often described after benzene and polycyclic aromatic hydrocarbons in general chemistry and in atomic and molecular structure courses. The stability of graphite relative to diamond is commonly discussed in first-year thermodynamics and is related to delocalization and resonance. We use it to stress these connections in order to bring our first-year undergraduate courses closer to one another.

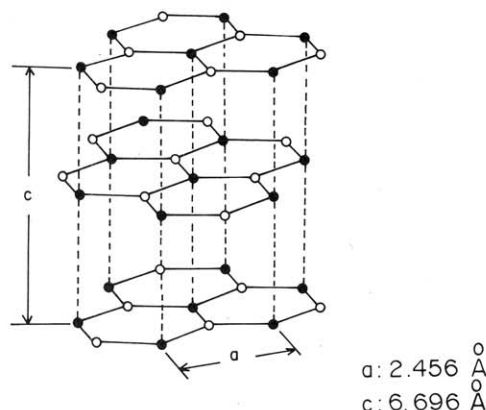


Figure 1. Three-dimensional crystal structure of graphite; the nearest-neighbor C—C distance is 1.42 Å.

In more advanced courses, on inorganic or solid-state chemistry, the student is likely to encounter graphite intercalation compounds and their fast-growing chemistry. Usually, chemistry students also learn that in-plane bonding in graphite is an excellent example of covalent bonding in solids, whereas the bonding between planes is usually described as "van der Waals".

The crystal structure of graphite (Fig. 1) in its most common form consists of planes of carbon atoms in a hexagonal arrangement, stacked alternately so that half of the carbon atoms are stacked directly upon one another and the other half are stacked between the centers of the hexagonal rings. In a single plane all atoms are equivalent. The distance between carbons is 1.42 Å in the plane, typical of resonant double-bond systems, and it is 3.35 Å between planes. Thus, the bond between planes is much weaker than those in the planes, and it is expected that the electronic structure will be dominated by the chemical bonds in the planes, with only minor effects derived from the interplanar bonding.

I shall review the basic equations of band theory, specifically the tight-binding approximation, and describe the necessary details of the unit cell and crystal structure of graphite, as well as of its reciprocal lattice and Brillouin zone. I will set up the secular determinant and solve for the energy eigenvalues, and then describe and interpret the band structure obtained. Emphasis will be placed on the algebraic simplicity of the theory and on understanding the results.

Review of Basic Theory

One of the main consequences of periodicity in crystal structures is that the electron wave function must obey Bloch's theorem. One statement of this theorem is

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r}) \quad (1)$$

where ψ is the one-electron wave function in the crystal, $u(\mathbf{r})$ is a function of the space coordinate \mathbf{r} with the same periodicity as the crystal lattice, and \mathbf{k} is a vector in reciprocal space, where \mathbf{k} is 2π times the inverse wavelength of the plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$. This statement is usually read as meaning that the wave function for an electron in a periodic potential is a periodic function ($u(\mathbf{r})$) modulated by a plane wave ($e^{i\mathbf{k}\cdot\mathbf{r}}$) whose wavelength

$$\lambda = \frac{2\pi}{|\mathbf{k}|}$$

Any approximation to the one-electron wave function in crystals must satisfy Bloch's theorem. One approximation which the chemist intuitively expects to work well, at least for covalently bonded systems, is the tight-binding approximation. This is just the usual LCAO approximation of molecular-orbital theory, modified to satisfy Bloch's theorem. Such a condition is fulfilled by a solution to the Schrödinger equation

$$H\psi = E\psi \quad (2)$$

which is proposed to be of the (unnormalized) form

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{r} - \mathbf{R}) \quad (3)$$

where the sum runs over all vector positions \mathbf{R} of lattice sites. (If there is more than one atom per unit cell, the sum further runs over all atom positions within the unit cell.) The functions (ϕ 's) are expanded as linear combinations of basis functions ($\psi_n(\mathbf{r})$'s)

$$\phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r}) \quad (4)$$

As in molecular LCAO theory, the basis set (the set of the ψ_n 's) is expected to be small; the sum in eq 1 is expected to converge rapidly. Also, the ψ_n 's are usually chosen to be atomic orbitals.

If a variational treatment is now applied to the wave function of eq 3, assuming that the Hamiltonian describes the periodic potential of the crystal, the results parallel those of molecular-orbital theory: the energy eigenvalues are obtained from the zeros of a secular determinant. The main difference is that now the energy eigenvalues depend on the reciprocal lattice vector \mathbf{k} . Thus, the secular determinant must be set up and solved for each \mathbf{k} of interest.

The secular equation is

$$|H_{ij}(\mathbf{k}) - ES_{ij}(\mathbf{k})| = 0 \quad (5)$$

where

$$H_{ij}(\mathbf{k}) = \sum_{\mathbf{R}} h_{ij}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} \quad (6)$$

$$S_{ij}(\mathbf{k}) = \sum_{\mathbf{R}} s_{ij}(\mathbf{R}) e^{i\mathbf{k}\cdot\mathbf{R}} \quad (7)$$

Summation indices are as in eq 3. The indices i and j number the basis functions in each unit cell. If only one basis function is taken on each atom, then the indices for the atom and the basis function coincide. For readers familiar with the work of Duke and O'Leary (1), these are the two- or three-dimensional generalizations of their eqs 2.12 and 2.13, with vector instead of scalar variables for the cell and atom positions. In eqs 6 and 7, h_{ij} and s_{ij} are the Hamiltonian and overlap matrix elements of conventional molecular-orbital theory. They become smaller as the magnitude of \mathbf{R} increases, so that the sums are expected to converge. However, they oscillate strongly as they decay, and in an exact calculation the convergence of these sums is a very delicate matter. The decay behavior of the matrix

elements and of the convergence and truncation of the sums still merit attention in the literature (13-15).

There are two usual choices for the sets of \mathbf{k} vectors for which the energy eigenvalues are to be determined. In the first, the \mathbf{k} vectors are chosen along high-symmetry directions in reciprocal space; these are usually the k_x or k_y axes, the k_z axis, and lines along which simple relations between the \mathbf{k} components hold, such as $k_x = k_y$ (with $k_z = 0$), $k_x = k_y = k_z$, etc., or in noncubic crystals, directions such as $k_x = \sqrt{3/2}k_y$ (with $k_z = 0$). This choice allows a plot of energy versus \mathbf{k} vector along selected directions, the most usual graphical representation of energy bands (fondly known to practitioners as "spaghetti").

The second frequent choice of \mathbf{k} vectors is simply a regular grid in the Brillouin zone, which is used for calculations of the density of states and related properties. This choice does not allow easy visualization of energy-band results themselves. However, the density of states, especially if resolved per atom and angular momentum component, or projected on the basis functions, is a very useful tool for discussing bonding properties, spectra, etc. Better representations of bonding and spectroscopic properties can be derived from quantities whose calculation is closely related to that of the density of states, such as joint densities of states, Hoffmann's COOP's, etc.

Crystal Structure, Reciprocal Lattice, and Brillouin Zone

The crystal structure of graphite is shown in Figure 1. The unit cell and the choice of lattice vectors used for the two-dimensional single layer are shown in Figure 2. These lattice vectors are not orthogonal, which is a good illustration of the use of crystal coordinates and their relation to Cartesian coordinates (16). Another important point is that the graphite structure must be described with more than one atom per unit cell (two in the single layer, and four in the full, three-dimensional structure). The value of the lattice constant is $a_0 = (3^{1/2})(d_{C-C}) = 4.6487$ au (where 1 au = 0.529 Å). The atom positions within the unit cell are (0, 0) and $(3^{1/2}/3, 1/2)$ in Cartesian coordinates, or (0, 0) and $(1/3, 2/3)$ in crystalline coordinates.

The positions of the nearest neighbors of the atom at the origin are $(1/2, 2/3)$, $(1/3, -1/3)$, and $(-2/3, -1/3)$ in crystalline coordinates or $(3^{1/2}/3, 1/2)$, $(3^{1/2}/3, -1/2)$, and $(-2/3^{1/2}, 0)$ in Cartesian coordinates.

The reciprocal lattice can be obtained in a simple manner. It is defined by basis vectors \mathbf{b}_1 and \mathbf{b}_2 which satisfy the conditions

$$\mathbf{a}_1 \cdot \mathbf{b}_1 = \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi \quad (8)$$

$$\mathbf{a}_1 \cdot \mathbf{b}_2 = \mathbf{a}_2 \cdot \mathbf{b}_1 = 0 \quad (9)$$

With the coordinates given for \mathbf{a}_1 and \mathbf{a}_2 in Figure 3, these conditions provide two systems of linear equations in two unknowns (the components of the \mathbf{b} vectors). By solving these equations, one obtains (in units of $2\pi/a_0$)

$$\mathbf{b}_1 = (-2/3^{1/2}, 0)$$

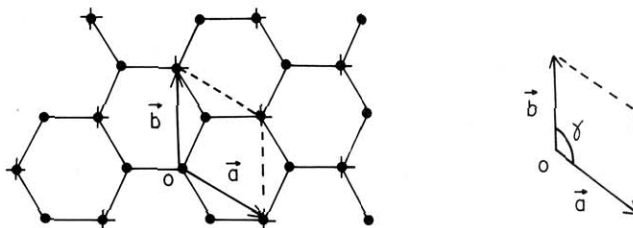


Figure 2. Two-dimensional lattice structure of a single layer of carbon in graphite.

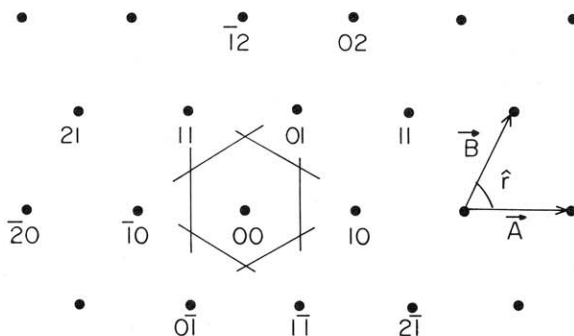


Figure 3. Reciprocal lattice of two-dimensional graphite. Points are labeled as vector multiples of the basis vectors. The hexagon surrounding 00 is the first Brillouin zone.

or equivalently,

$$\mathbf{b}_1 = (2/3^{1/2}, 0) \quad (10)$$

$$\mathbf{b}_2 = (1/3^{1/2}, 1) \quad (11)$$

Figure 4 shows that the reciprocal lattice thus generated is hexagonal. Figure 4 also shows the Brillouin zone with the coordinates and conventional names of high-symmetry points and lines, and for completeness, the three-dimensional Brillouin zone appropriate for the full crystal structure. The two-dimensional Brillouin zone is the $k_z = 0$ plane of the three-dimensional zone.

This completes our description of the crystal structure, and we can now build our tight-binding calculation.

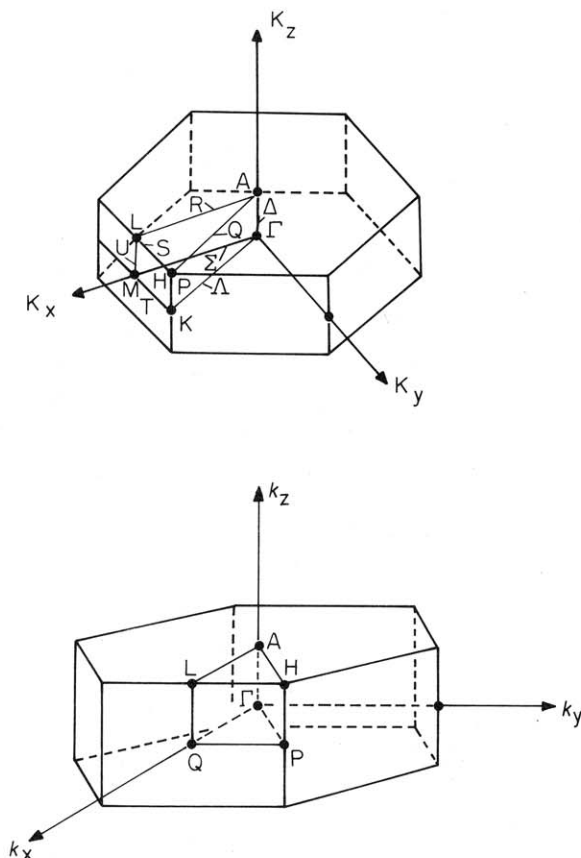


Figure 4. First Brillouin zone of graphite, showing two conventional systems of labeling.

Secular Determinant in the Hueckel Approximation

Next we evaluate eqs 6 and 7 specifically for graphite, which is fairly difficult in an exact calculation. Since our goal is to present a simple calculation in which the math does not obscure the underlying principles, we will introduce some severe simplifications.

To begin, we choose a basis set that includes only one $2p_z$ atomic orbital on each atom, thus using only two basis functions per unit cell. The indices i and j in eqs 5–7 take on only the values 1 and 2, for the atom at the origin and the atom inside the cell, respectively.

With this basis set, our results describe the π states only, i.e., the one-electron states with wave functions that are antisymmetric to reflection through the xy plane. The entire electron distribution of these states is off the plane, as are the π states of organic molecules with conjugated double bonds (e.g., ethylene, butadiene, benzene). This choice of states is frequent in the study of organic molecules, where the Hueckel approximation was first applied successfully. Now we shall introduce some drastic approximations in order to evaluate the matrix elements themselves.

First, we shall make the strict tight-binding approximation, and assume that all chemical bonding occurs between first-neighbor atoms, implying that only s_{11} and s_{22} are nonzero and equal to 1 because we assume our basis functions to be normalized. Overlap between functions on different atoms is set to zero, which is compensated in the parametrization of H .

Second, we will not attempt to explicitly evaluate the matrix elements h_{ij} . We assume a value of 0 for Hamiltonian matrix elements between the central atom and second or higher-order neighbors. Hamiltonian matrix elements between the central atom and its first neighbors are given the value β , and the diagonal elements h_{11} and h_{22} are given the value α .

Of course, this is the Hueckel approximation, which is used often in chemistry. From elementary quantum chemistry, the student knows that α and β are parameters whose numerical values are assigned semiempirically.

Given the values in the previous paragraphs for the overlap and Hamiltonian matrix elements, we evaluate the sums in eqs 6 and 7. In the overlap sums for S_{11} and S_{22} , contributions in each sum come only from a single atom, and the values of the contributions are 1. Thus,

$$S_{11} = S_{22} = 1 \quad (12)$$

The nondiagonal contributions to overlap are zero because they involve basis functions on different atoms.

The sums for the Hamiltonian matrix elements involve only four summands each: one for h_{11} ($\mathbf{R} = 0$), whose value is α , and three for the first neighbors, for which

$$h_{12} = \beta \quad (13)$$

All other contributions to H are zero because they come from higher-order neighbors.

To construct the H matrix elements, the summation (eq 7) must be performed, including the phase factors $e^{i\mathbf{k}\cdot\mathbf{R}}$. These are easily evaluated when one substitutes the \mathbf{R} coordinates given above for the three first neighbors. As a result, the secular determinant is

$$\begin{vmatrix} \alpha - E & \beta \left(e^{i\mathbf{k}\cdot(1/3, 2/3)} + e^{i\mathbf{k}\cdot(1/3, -2/3)} + e^{i\mathbf{k}\cdot(-2/3, -1/3)} \right) \\ H_{12}^* & \alpha - E \end{vmatrix} = 0 \quad (14)$$

Crystalline coordinates have been used here. If one prefers to use Cartesian coordinates, the vector positions inside the exponential must be changed to the corresponding expressions. Now we have a 2×2 determinant that equals zero. To obtain an explicit expression for the eigenvalues E (E_1 and E_2), one evaluates the determinant using Cramer's rule, which involves using algebra with complex exponen-

tials. Finally we get a rather simple second-degree equation in E whose roots are

$$E_{1,2} = \alpha \pm A^{1/2} \beta \quad (15)$$

with

$$A = 3 + 2 \cos [\mathbf{k} \cdot (\mathbf{a}_1 + \mathbf{a}_2)] + 2 \cos (\mathbf{k} \cdot \mathbf{a}_2) + 2 \cos (\mathbf{k} \cdot \mathbf{a}_1) \quad (16)$$

By eq 15, for each \mathbf{k} we get two energy eigenvalues, i.e., our calculation yields two energy bands. One of them lies below the value α and the other one lies above it. (β is negative; thus, E_1 is the lower value.) Since in Hueckel theory α represents roughly the energy of a single $2p_z$ function in an isolated carbon atom, the lower band is "bonding", and the higher is "antibonding".

Energy Bands

It is difficult to represent the energy eigenvalues as a function of \mathbf{k} in general. To understand the energy bands, we first evaluate them at points of high symmetry, with the following results:

$$\Gamma, E = \alpha \pm 3\beta \quad (17)$$

$$M, E = \alpha \pm \beta \quad (18)$$

$$K, E = \alpha \quad (19)$$

The band splitting, that is, the energy difference between the bonding and the antibonding bands, is maximal at Γ and equals 6β . This allows a parametrization of β since this splitting can be evaluated experimentally. Its value is roughly 18 eV, so that β is estimated to be -3 eV. This is larger (in absolute value) than the usual β for hydrocarbons, reflecting the higher degree of electron delocalization which appears in an infinite system.

Equation 19 shows that the bonding and the antibonding bands are degenerate at the K point. Experimentally, this degeneracy does not appear because it is raised by the interaction between neighboring planes. However, the band splitting at the K point remains small, and consequently graphite has a very small band gap. Thus, graphite is a semimetal with high conductivity. Furthermore, any doping of graphite will largely increase the number of charge carriers. Consequently graphite intercalation compounds (GIC's) can achieve extremely high electrical conductivities, with values comparable to those of metals.

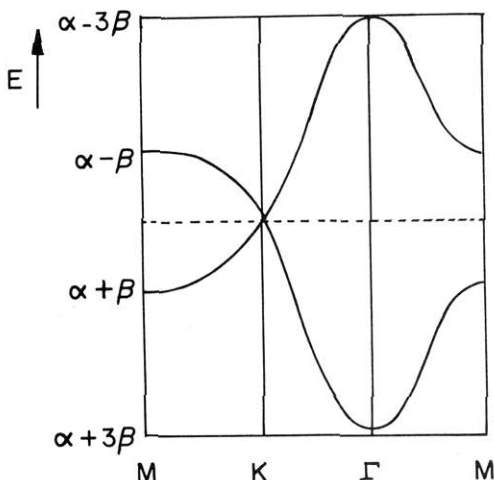


Figure 5. Energy bands of two-dimensional graphite from the simple calculation described in the text. Energy is shown as a function of \mathbf{k} along high-symmetry directions in the first Brillouin zone, using the labeling convention of Fig. 4 in the xy plane.

A more complete representation of the energy bands can be made graphically. A few \mathbf{k} points are chosen along high-symmetry lines. (The first choice explained in the review of basic theory above.) The plots of E versus \mathbf{k} are shown in Figure 5, which clearly shows the maximal band splitting at Γ and the degeneracy at K . Although the bands are symmetric with respect to α in this calculation, they are not so in more realistic calculations that include electron-electron interactions.

A simple extension of the present work allows us to calculate the density of states. It turns out to be formed by two peaks, one for the bonding and one for the antibonding states. By integrating the density of states, the Fermi level is found to lie at α . At this level of approximation, the density of states at the Fermi level is exactly zero. In a more refined calculation this is not true, but the value remains very small. Rigorously, this fact and the above-mentioned zero bandgap explain the semimetallic character of graphite.

Interpretation of the Band Structure Results

The band structure results can be correlated with a chemical point of view. First, the lowest energy is found for the point Γ in reciprocal space, where $\mathbf{k} = 0$ and the phase factors $e^{i\mathbf{k}\cdot\mathbf{r}}$ are all 1. Therefore, all $2p_z$ orbitals on carbon atoms enter the Bloch functions in phase. (All "+" lobes are on the same side of the plane.) This means they all contribute to bonding between neighboring atoms, thus explaining the low energy attained by this crystal orbital.

At the point K , $E = \alpha$ (eq 19). Evaluation of the phase factors leads to the conclusion that the relation between nearest neighbor basis functions is nonbonding. That is why the energy for this crystal orbital equals that of infinitely separated, that is, nonbonded, carbon atoms.

The Fermi level lies at α because the bonding band can hold only one electron per atom, which is true for all bands. The chemist has already encountered this in molecules: Each molecular orbital can hold only one electron of each spin, even if it is extended over the whole molecule. The novel feature in band theory is that a band covers an extended range of energies, instead of having a single well-defined discrete value like a molecular-orbital. However, a band is actually a collection of crystal orbitals with the same basis functions but with varying phase factors and thus varying bonding character.

In molecular orbitals, the phase relations between neighboring basis functions are restricted to a few possible variations. In band theory, these relations are described by the phase factors $e^{i\mathbf{k}\cdot\mathbf{r}}$ in the form of a plane wave, so that varying the wave vector \mathbf{k} allows for continuous variation of the phase relations. Therefore, in crystal orbitals, one has a smooth transition from bonding to nonbonding to antibonding character, instead of the stepwise change in bonding character seen in molecular orbitals.

Furthermore, one can realize that the zero value for the band gap in graphite (or a very small one for the full three-dimensional crystal) enables thermal excitation, even at low temperatures, to bring electrons into the conduction (antibonding) band. This can also be achieved by application of low voltage, which causes electric conduction.

Another way to modify the conductivity of graphite is intercalation. Due to the rather loose bonding between carbon atom planes, it is easy for atoms or even whole molecules to enter the interplanar spaces and diffuse within them. These GIC's have ordered structures. Their effect on the electrical conductivity is similar to that of dopants in semiconductors, that is, donation of electrons or holes in otherwise unaffected bands of the graphite host. This increases enormously the number of charge carriers

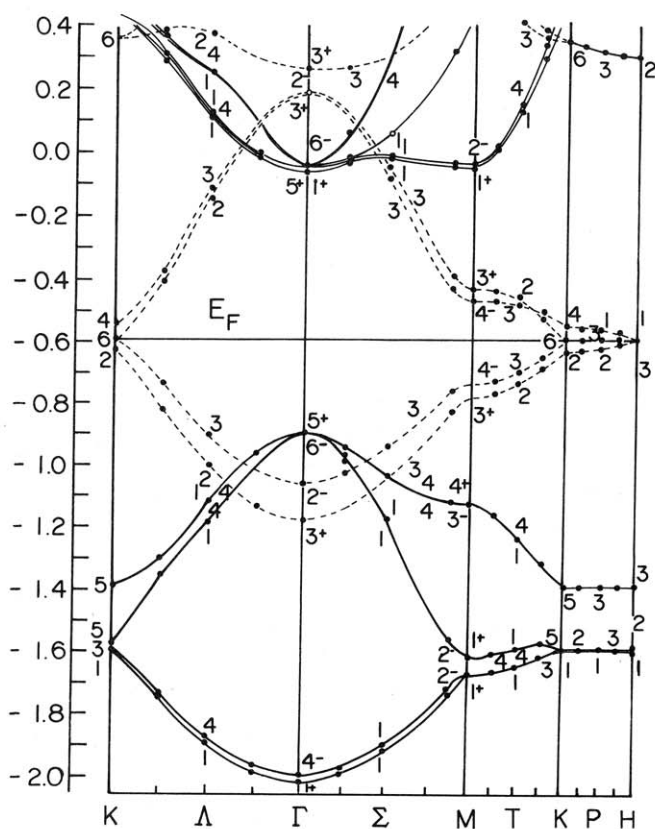


Figure 6. Energy bands of three-dimensional graphite from the calculation by Tatar and Rabii (18). The calculation described in the text can be correlated with the π bands, shown in dotted lines.

available. Consequently the conductivity is also increased. Simon and Andre (17) describe this in detail.

The calculation can be correlated with experimental results and with the results of more sophisticated, state-of-the-art computations (Tatar and Rabii's results (18) shown in Fig. 6). The more exact calculation yields many more bands than ours, originating in s and in-plane p atomic orbitals. There are also asymmetric π bands. Raising of the π degeneracy at the K point is observed. These effects have been described above. Nevertheless, the main features of the π bands are well described by the simple calculation.

Agreement with experiments is also good. Figure 7 compares accepted theoretical results and a very demanding experimental test of them—angle-resolved photoelectron spectroscopy (ARPES) (19). Results of band-theoretical calculations appear in the experiment. Some experimental points do not correlate with band theory. Many are thought to require an explanation by many-electron interactions beyond usual band theory. I feel it is healthy to emphasize

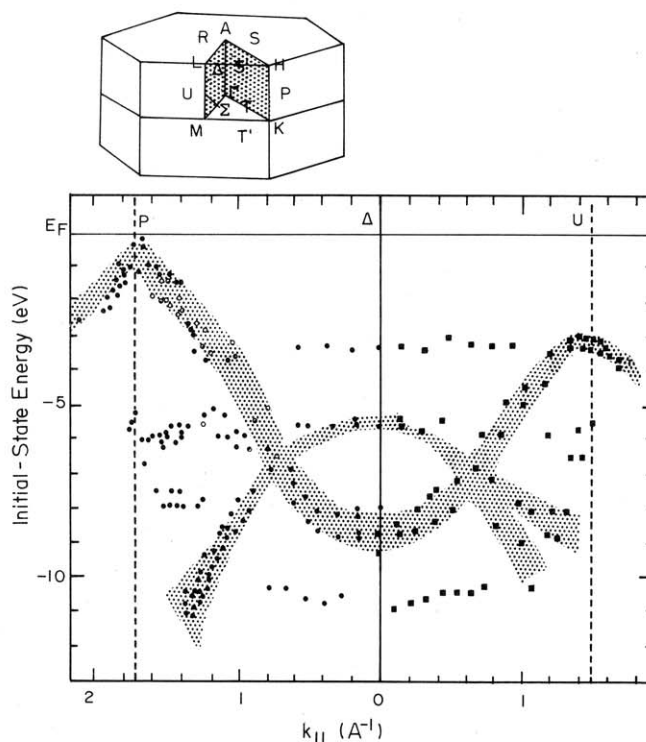


Figure 7. Experimental band-mapping of graphite. Shaded areas represent the generally accepted band structure, with suitable broadening. (Redrawn from Marchand et al. (18).)

this point with students, in order to show that even an easy task such as this gives them a look into what remains a lively field of research.

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