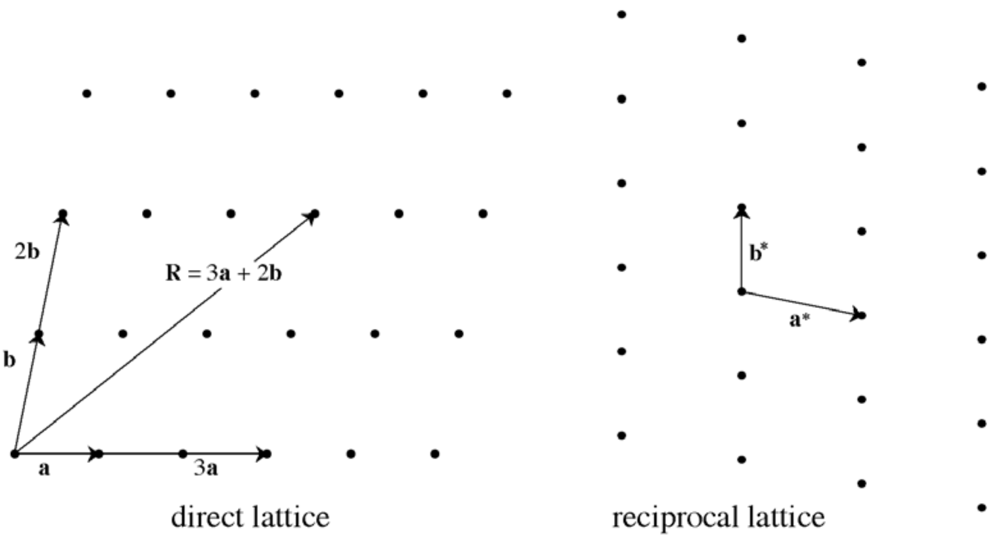
Reciprocal Space and Brillouin Zones in Two and Three Dimensions

As briefly stated at the end of the first section, Bloch's theorem has the following form in two and three dimensions:

$$\varphi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}) = e^{2\pi i \mathbf{k}\cdot\mathbf{R}}\varphi_{\mathbf{k}}(\mathbf{r}) .$$

In this expression, **R** is a lattice vector between a pair of unit cells: $\mathbf{R} = u\mathbf{a} + v\mathbf{b} + w\mathbf{c}$; $u, v,$ and w are integers and the dot product $\mathbf{k}\cdot\mathbf{R} = k_a u + k_b v + k_c w$. (In two dimensions, $\mathbf{R} = u\mathbf{a} + v\mathbf{b}$ and $\mathbf{k}\cdot\mathbf{R} = k_a u + k_b v$.) At this point, we need to clarify the meaning of the vector **k** and find a way to define the two- and three-dimensional Brillouin zones. To do this, let's consider the general, oblique, two dimensional lattice below. For this lattice, the basis vectors, **a** and **b**, are not orthogonal and there is no symmetry relationship between their lengths. An operation that translates by the lattice vector **R** (which we may call $\mathbf{t}^{\mathbf{R}}$) involves *independent* and *commutative* translation operations in the **a** and **b** directions. By an extension of the reasoning used for the one-dimensional translation group, we can deduce that if we operate on a basis function that belongs to the irreducible representation labeled by **k**, we should obtain the following:



direct lattice reciprocal lattice

$$\mathbf{t}^{\mathbf{R}}\phi(\mathbf{k}) = \mathbf{t}^{v\mathbf{b}}\mathbf{t}^{u\mathbf{a}}\phi(\mathbf{k}) = \mathbf{t}^{u\mathbf{a}}\mathbf{t}^{v\mathbf{b}}\phi(\mathbf{k}) = e^{2\pi i\cdot k_a u}e^{2\pi i\cdot k_b v}\phi(\mathbf{k}) \text{ where } \mathbf{R} = u\mathbf{a} + v\mathbf{b}.$$

The form $\mathbf{t}^{\mathbf{R}}\phi(\mathbf{k}) = e^{2\pi i\mathbf{k}\cdot\mathbf{R}}\phi(\mathbf{k})$ makes sense if we define ***k**-space* (often called *reciprocal space*) basis vectors, $\mathbf{a}^*$ and $\mathbf{b}^*$, such that

$$\mathbf{k}\cdot\mathbf{R} = (k_a\mathbf{a}^* + k_b\mathbf{b}^*)\cdot(u\mathbf{a} + v\mathbf{b}) = k_a u + k_b v \text{ for all } u,\ v,\ k_a,\ k_b.$$

This is possible if we demand that $\mathbf{a}^* \perp \mathbf{b}$, $\mathbf{b}^* \perp \mathbf{a}$ and set the magnitudes of $\mathbf{a}^*$ and $\mathbf{b}^*$ so that $\mathbf{a}^*\cdot\mathbf{a} = \mathbf{b}^*\cdot\mathbf{b} = 1$. In three dimensions, the required properties are analogous: $\mathbf{a}^* \perp \mathbf{b},\mathbf{c}$; $\mathbf{b}^* \perp \mathbf{a},\mathbf{c}$; $\mathbf{c}^* \perp \mathbf{a},\mathbf{b}$; $\mathbf{a}^* \bullet \mathbf{a} = \mathbf{b}^* \bullet \mathbf{b} = \mathbf{c}^* \bullet \mathbf{c} = 1$. These are embodied in the definitions

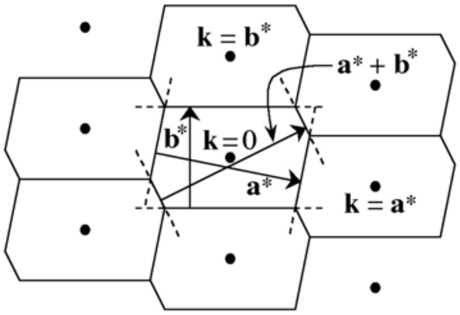
$$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})};\ \mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})};\ \mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{\mathbf{a}\cdot(\mathbf{b}\times\mathbf{c})}$$

where we note that $\mathbf{a}\bullet(\mathbf{b}\times\mathbf{c}) = \mathbf{b}\bullet(\mathbf{c}\times\mathbf{a}) = \mathbf{c}\bullet(\mathbf{a}\times\mathbf{b}) = V$, the volume of the unit cell. The reader should be aware that our definition of the reciprocal space basis vectors ($\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$) differs from that used by most solid state physicists by a factor of 2π, but our statement of Bloch's theorem is equivalent because we include a factor of 2π in the argument of the complex exponential function. The reciprocal space definition used here coincides with that commonly used by crystallographers.

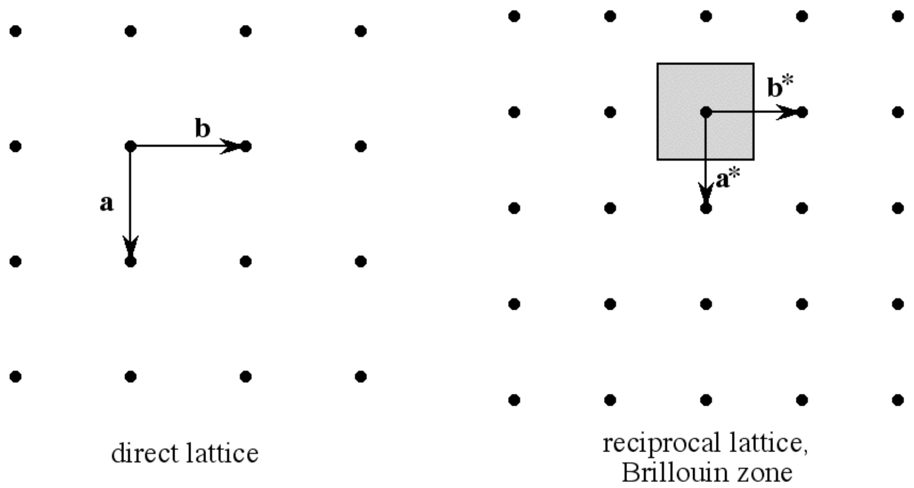
The vectors $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ can be used to build up an entire lattice of points $\{\mathbf{K}_{hkl}\}$ defined such that $\mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, where $h,\ k,$ and l are integers. Each of the vectors in the set, $\{\mathbf{K}_{hkl}\}$, are called reciprocal lattice vectors (RLVs). We show a reciprocal lattice that corresponds to the two-dimensional oblique lattice in Fig. ?. The concept of the reciprocal lattice is of great importance in the theory of diffraction, where the integers $h,\ k,$ and l are known as *Miller indices*. Let's focus on the properties of the factor $e^{2\pi i(\mathbf{k}\cdot\mathbf{R})}$ that appears in Bloch's theorem. If we have two $\mathbf{k}$ vectors ($\mathbf{k}_1$ and $\mathbf{k}_2$) which differ by a RLV $\mathbf{K}_{hkl}$, i.e., $\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{K}_{hkl}$ where $\mathbf{K}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$. Then $e^{2\pi i(\mathbf{k}_1\cdot\mathbf{R})} = \exp\{2\pi i(\mathbf{k}_2 + \mathbf{K}_{hkl})\cdot\mathbf{R}\} = \exp\{2\pi i(\mathbf{k}_2\cdot\mathbf{R})\}\exp\{2\pi i(\mathbf{K}_{hkl}\cdot\mathbf{R})\} = e^{2\pi i(\mathbf{k}_2\cdot\mathbf{R})}$ since $\mathbf{K}_{hkl}\cdot\mathbf{R} = hu + kv + lw = \text{ integer}$. We conclude that $\mathbf{k}_1$ and $\mathbf{k}_2$ are equivalent

RLVs. Any basis function that transforms according to the irreducible representation labeled by $\mathbf{k}_2$ belongs to the equivalent irreducible representation labeled by $\mathbf{k}_1$. More succinctly, $\mathbf{k}_1$ and $\mathbf{k}_2$ are redundant labels for the *same* irreducible representation. In our "listing" of the representations of the one-dimensional translation group, we found that any representation outside of the range $-1/2a < k \leq 1/2a$ is redundant. Similarly, in three dimensions any two **k**-points that are connected by a reciprocal lattice vector are redundant. (The same terminology could be used for the one-dimensional case if we define a set of one dimensional reciprocal lattice vectors with magnitudes $\cdots,\ -2/a,\ -1/a,\ 0,\ 1/a,\ 2/a,\ \cdots$.)

There is a geometric construction that allows us to choose a set of **k**-points that ranges over all necessary values to account for each irreducible representation of translational group once and only once. We do this by constructing a region in reciprocal space that surrounds $\mathbf{k} = 0$ such that all **k**-points enclosed are closer to $\mathbf{k} = 0$ than to any other reciprocal lattice point. As is geometrically evident, this is the region enclosed by the sets of planes that are perpendicular bisectors to the lattice vectors connecting the origin in **k**-space to its nearest neighbor reciprocal lattice points. The region so obtained is the first Brillouin zone. The BZ for the oblique two-dimensional case is illustrated below, the reciprocal lattice vectors that are illustrated show how this region does not enclose any redundant **k**-points. Note that any point in an outlying region of **k**-space is exactly equivalent with one within the BZ.



Brillouin zones for the remaining two-dimensional lattices can be easily constructed by following the same geometrical prescription we have given above. Let's examine the two-dimensional hexagonal lattice. The two lattice vectors **a** and **b** are equal in length and separated by a 120° angle. The reciprocal lattice basis vectors $\mathbf{a}^*$ and $\mathbf{b}^*$ are respectively perpendicular to $\mathbf{a}$ and $\mathbf{b}$, and therefore make a 60° angle to each other. Note that the reciprocal lattice points generated by these basis vectors is also hexagonal, but appears to be rotated by 30° when compared with the direct lattice. The first Brillouin zone is just the hexagon obtained by following the geometrical prescription given above.

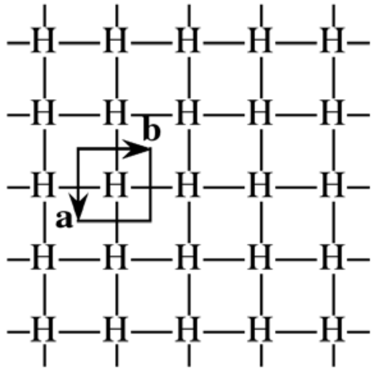


direct lattice

reciprocal lattice,
Brillouin zone

The two-dimensional square lattice is even simpler. The two lattice vectors $\mathbf{a}$ and $\mathbf{b}$ are equal in length and separated by a 90° angle. The reciprocal lattice basis vectors $\mathbf{a}^*$ and $\mathbf{b}^*$ are respectively perpendicular to $\mathbf{a}$ and $\mathbf{b}$, and obviously make a 90° angle to each other. The reciprocal lattice points generated by these basis vectors is also square and is in alignment with the direct lattice, the first Brillouin zone is just a square. When considering these two examples, bear in mind the fact that while the relative orientation of the direct and reciprocal lattices are intimately fixed, the reciprocal lattice does not describe a physical object. Rather, it is an indispensable geometrical construct for dealing with problems in the theory of diffraction, electronic structure or vibrational structure of solids and surfaces. One may think of it as playing a role similar to the role played by the “complex plane” in manipulating complex numbers — the manipulations can be done algebraically (or trigonometrically), but the complex plane is such a useful graphical tool for clarifying the computations it is now virtually inseparable from the field of complex analysis. Those newly initiated to reciprocal space often find it to be a bit mysterious and forbidding, but the price paid for becoming comfortable with reciprocal space is well worth it — and any serious work in crystallography, solid state physics or solid state chemistry requires that the price be paid.

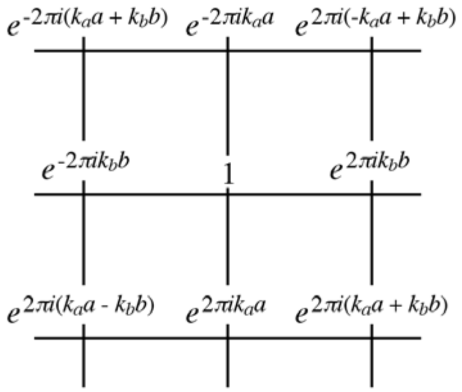
Let's see how energy bands are handled in two dimensional systems. For simplicity we will first consider a hypothetical square layer of hydrogen atoms for which have but one hydrogen per unit cell. We are thus considering the single band that is built up from the hydrogen 1s orbitals. For each $\mathbf{k}$ – point within the BZ, we have just one Bloch basis orbital:



$$\phi(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{2\pi i \mathbf{k}\cdot\mathbf{R}} \phi(\mathbf{R})\,.$$

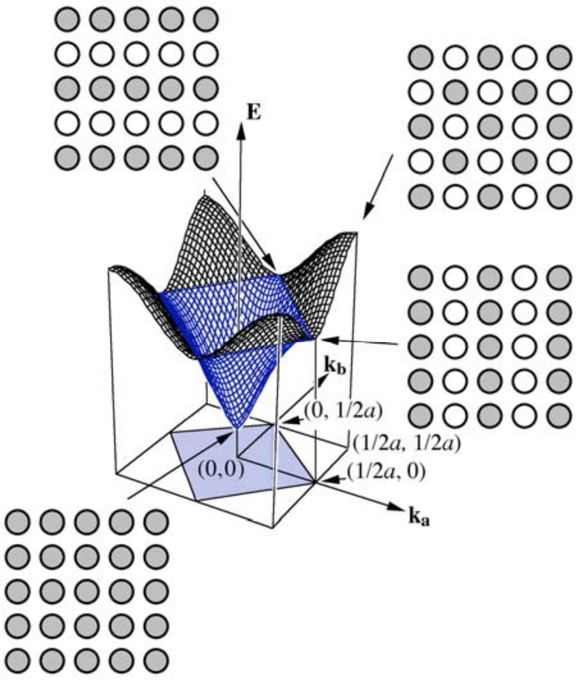
where the sum over $\mathbf{R}$ runs over every unit cell in the plane and $\phi(\mathbf{R})$ symbolizes the H-atom 1s orbital residing in the unit cell at lattice site $\mathbf{R}$. Since there is only one Bloch basis orbital for this problem, the secular determinant for this problem is trivial, but we still must evaluate $H(\mathbf{k})$:

$$H(\mathbf{k}) = \sum_{\mathbf{R}} e^{2\pi i \mathbf{k}\cdot\mathbf{R}} H^{\mathbf{R}}; \quad \text{where } H^{\mathbf{R}} = \langle \phi(0) | \mathcal{H} | \phi(\mathbf{R}) \rangle$$



The diagram here shows the set of coefficients for the factor $e^{2\pi i \mathbf{k}\cdot\mathbf{R}}$ in this equation (the components of $\mathbf{k}$, k_a and k_b, fall in the range $-1/2a < k_a,\ k_b \le 1/2a$). If the nearest neighbor interaction is β, then

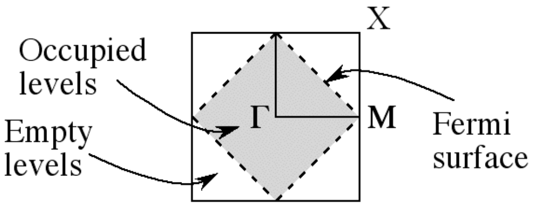
$$H(\mathbf{k}) = \beta(e^{2\pi i k_a a} + e^{-2\pi i k_a a} + e^{2\pi i k_b b} + e^{-2\pi i k_b b}) = 2\beta\{\cos(2\pi k_a a) + \cos(2\pi k_b b)\}$$



The band energy is just equal to

$$H(\mathbf{k}),\ E = 2\beta\{\cos(2\pi k_a a) + \cos(2\pi k_b b)\}$$

which is plotted in Figure 8. We show an energy surface that describes the **k**-dependence of the crystal orbital energy. There is one electron in this system for every hydrogen atom and thus *N* electrons fill *N*/2 crystal orbitals. Since there are *N* crystal orbitals corresponding to the *N* irreducible representations within the first BZ, the energy band is exactly half occupied. The Fermi level is that energy below which fall exactly *N*/2 crystal orbitals. The *Fermi surface* (just a *curve* for this two-dimensional example) is that part of the energy band surface that intersects the Fermi energy. In this 2-D case, the Fermi "surface" is just a square that surrounds the $k = 0$ (Γ point) in the BZ.



Now let's conclude this section with an interesting "real" example, the π-electron band structure of graphite. Graphite is a quasi-2-dimensional solid, with honeycomb sp^2-carbon nets that are layered upon one another with separations of 3.35 Å (Figure 9). The π-electronic structure is very strongly controlled by hexagonal translational symmetry of the 2-dimensional graphene sheets. The conducting properties of graphite and graphite compounds

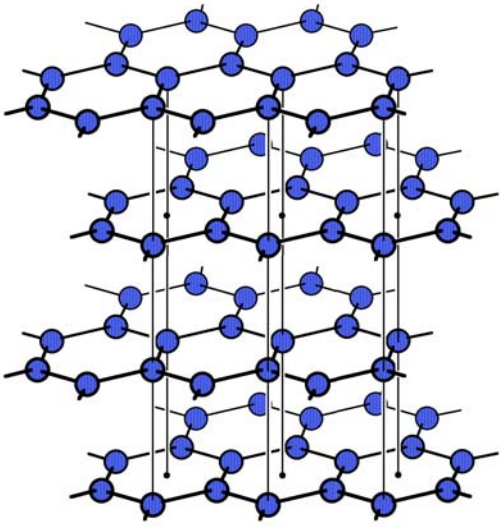
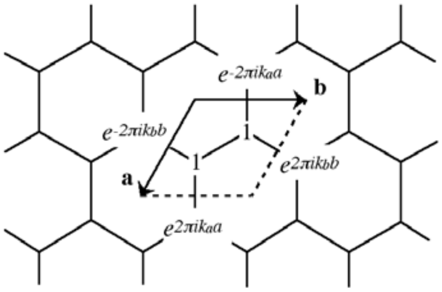


Figure 9. 3-dimensional structure of graphite.

are determined by the π-bands we shall now describe. The π-electronic structure of graphite is jumping-off point used to describe single-walled carbon nanotubes (SWNTs) that are the subject of much current attention. SWNTs are essentially just slices of graphite "chicken-wire" that are rolled-up and stitched together to preserve the local carbon six-membered ring structure of graphite.

We will treat a 2-dimensional π-bonded network — a single layer of graphite. For this problem, there are once again two atoms per unit cell and we will in general have to solve a 2 × 2 Hückel secular determinant.

For each atom in a neighbor cell that is linked to an atom in the origin unit cell, we have shown the phases of the pπ orbitals for atoms in cells adjacent to the origin cell for any given **k**-point ($\mathbf{k} = k_a\mathbf{a}^* + k_b\mathbf{b}^*$). Using this information, it is a simple matter to write down expressions for the matrix elements that appear in the **k** – dependent secular determinant for the graphite pπ bands:



$$H_{11}(\mathbf{k}) = H_{22}(\mathbf{k}) = 0$$
$$H_{12}(\mathbf{k}) = \beta(1 + e^{-2\pi i k_a a} + e^{2\pi i k_b b})$$

Using these matrix elements, we set up and solve the secular equation for any **k** – value:

$$\begin{vmatrix} H_{11}(k) - E & H_{12}(k) \\ H_{21}(k) & H_{22}(k) - E \end{vmatrix} = \begin{vmatrix} 0 - E & \beta(1 + e^{-2\pi i k_a a} + e^{2\pi i k_b b}) \\ \beta(1 + e^{2\pi i k_a a} + e^{-2\pi i k_b b}) & 0 - E \end{vmatrix} = 0$$

$$\text{or} \quad E = \pm\beta\sqrt{3 + 2\cos(2\pi k_a a) + 2\cos(2\pi k_b b) + 2\cos[2\pi(k_a a + k_b b)]}$$

This energy expression has a minimum ($E = -3|\beta|$) for the bonding band and a maximum ($E = 3|\beta|$) for the antibonding bands at **k** = 0. The two bands "touch" at two unique **k** values, $(k_a, k_b) = ({}^1/_{3a}, {}^1/_{3a})$ and $(-{}^1/_{3a}, -{}^1/_{3a})$, which are respectively denoted as **K** and **K′** and reside at the corners of the BZ. The energy bands form surfaces in which the orbital energies can be graphed as a function of **k** throughout the Brillouin zone, this shown in two ways below.

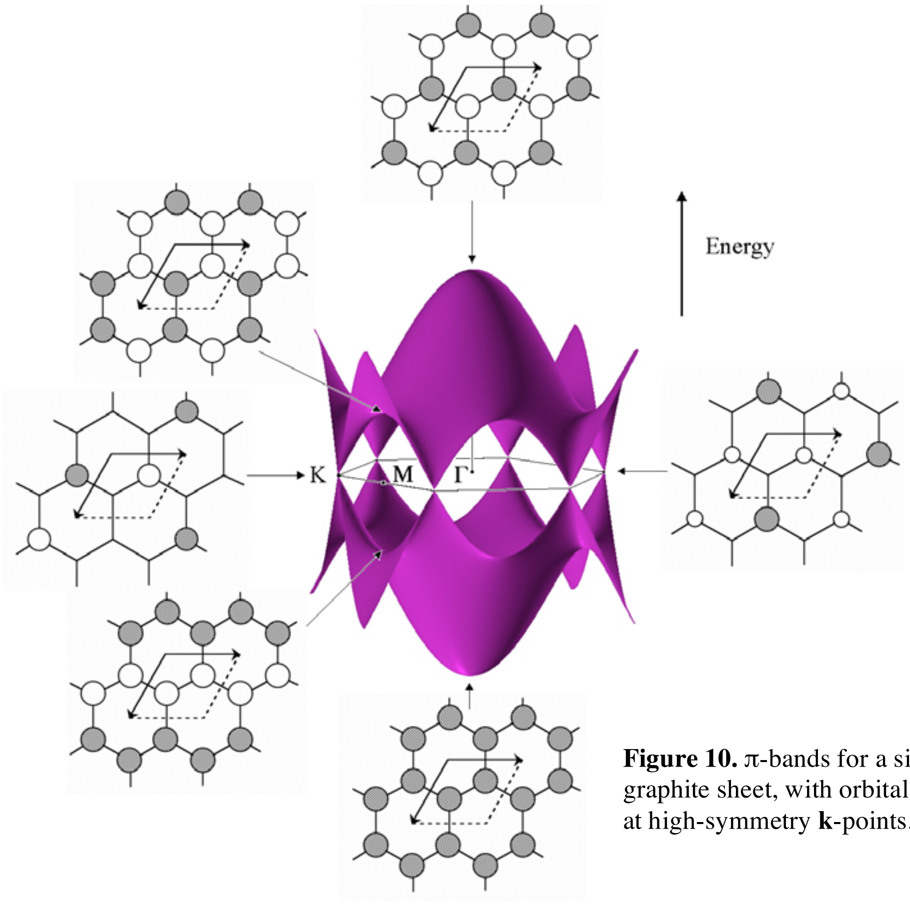


Figure 10. π-bands for a single graphite sheet, with orbitals shown at high-symmetry **k**-points.

First we show the two surfaces, the nodal characteristics of the π orbitals at the high symmetry points, **Γ**, **M**, and **K**. The reader should be able to see by inspection that the bonding/antibonding character in the crystal orbitals rationalizes their energy ordering. Since there are two carbon atoms per unit cell, there are two electrons to be accommodated and the bottom band is therefore entirely filled while the top band is entirely empty. The Fermi level lies at E = 0 and bisects the two bands, running through just the points **K** and **K´**.

Alternatively, one can look at a diagram of energy contours for the lower π band (the upper band is its "mirror image" with respect to energy. The contours represent "cuts" made by slicing through the previously illustrated surfaces with planes at constant energies. The periodicity of the bands throughout **k**-space should be evident and is, of course, just another illustration of the essential redundancy of any representations of the translational group once one moves beyond the first BZ. The contour diagram shows clearly that the point M is a saddle point on this 2-dimensional surface and as such is a point where the density of states has a singularity (referred to as a Van Hove singularity).

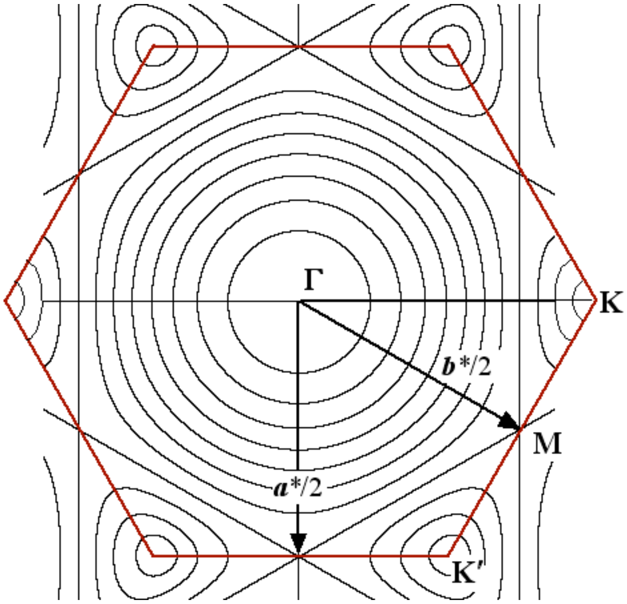


Figure 11. Contours for the lower π-band for a single graphite sheet.

The detailed information provided by these depictions of energy surfaces are not usually available, and of course are not possible for three-dimensional crystals where **k**-space is three-dimensional as well. Instead, the **k**-dependence of the energy bands is indicated by plotting band energies along lines that connect high-symmetry points. The **k**-dependence can be ignored altogether by simply plotting the density of states, in which the number of band orbitals is displayed as a function of energy — as shown for the graphite π bands here.

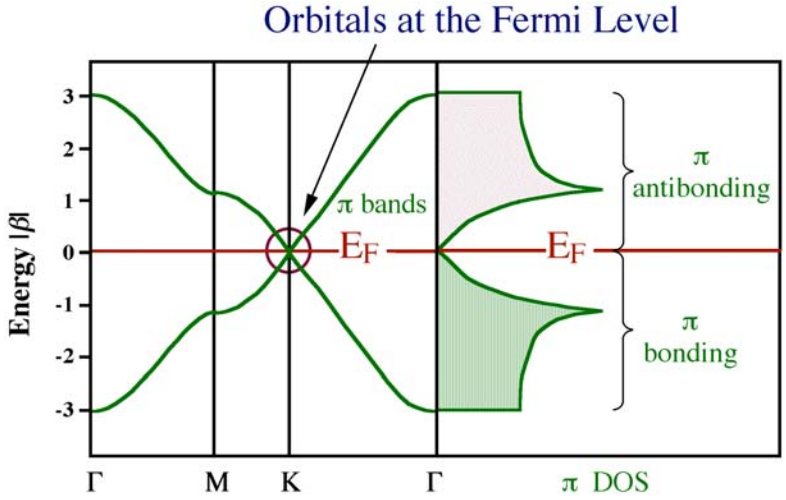


Figure 12. “Spaghetti” diagram for the π-bands of a single graphite sheet, plus the π density of states.

The detailed features of the density-of-states (DOS) function can be understood most clearly by examination of the band surface picture or the contour plot. We have already indicated that the van Hove singularities at E = ±β are associated with the saddle points on the band surfaces. The DOS at a given energy is proportional to the area of the surface obtained by cutting a slice through the surface of thickness dE at E. The contribution to the DOS at a given point on the surface is inversely proportional to the gradient at the point, so to get the DOS one needs to integrate over the line over all points at that energy. For our graphite example, that would in principle mean that we would perform a line-integral over an individual contour line in Figure 11:

$$\mathrm{DOS} = \oint_{E} \frac{dS}{\nabla f}$$

where *f* is the energy band function. (In 3-dimensions, this becomes an integral over the surface at energy E.) The van Hove singularities are a consequence of the vanishing of the gradient of the energy surface at the saddle points. There are no singularities due to the band maximum (minimum) because the length of the energy contours vanishes at the same rate as the gradient vanishes as one approaches the maximum (minimum) from below (above). The DOS for graphite goes to zero at the Fermi level because the energy contours contract to the single points (**K** and **K**´) where the π and π* bands touch.

In “real-life” cases, energy dispersions curves and DOS diagrams are not obtained by solving the band energies in closed form. Rather, DOS functions are obtained by performing calculations on a computer using a grid of **k**-points that is evenly spread over the BZ. The discrete distribution of energy levels so obtained is an approximation of the true continuous DOS. The quality of the computed approximate DOS depends on the fineness of the **k**-point grid and unless the grid is very fine, features such as singularities are rounded off.