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The electronic structure of ideal graphene

1.1 The carbon atom

Carbon is the sixth element in the Periodic Table. It has two stable isotopes, ^{12}C (98.9% of natural carbon) with nuclear spin $I=0$ and, thus, nuclear magnetic moment $\mu_n=0$, and ^{13}C (1.1% of natural carbon) with $I=\frac{1}{2}$ and $\mu_n=0.7024\mu_N$ (μ_N is the nuclear magneton), see Radzig & Smirnov (1985). Like most of the chemical elements, it originates from nucleosynthesis in stars (for a review, see the Nobel lecture by Fowler (1984)). Actually, it plays a crucial role in the chemical evolution of the Universe.

The stars of the first generation produced energy only by proton–proton chain reaction, which results in the synthesis of one α -particle (nucleus ^4He) from four protons, p. Further nuclear fusion reactions might lead to the formation of either of the isotopes ^5He and ^5Li ($p + \alpha$ collisions) or of ^8Be ($\alpha + \alpha$ collisions); however, all these nuclei are very unstable. As was first realized by F. Hoyle, the chemical evolution does not stop at helium only due to a lucky coincidence – the nucleus ^{12}C has an energy level close enough to the energy of three α -particles, thus, the *triple* fusion reaction $3\alpha \rightarrow ^{12}\text{C}$, being resonant, has a high enough probability. This opens up a way to overcome the mass gap (the absence of stable isotopes with masses 5 and 8) and provides the prerequisites for nucleosynthesis up to the most stable nucleus, ^{56}Fe ; heavier elements are synthesized in supernova explosions.

The reaction $3\alpha \rightarrow ^{12}\text{C}$ is the main source of energy for red giants. Carbon plays also an essential role in nuclear reactions in stars of the main sequence (heavier than the Sun) via the so-called CNO cycle.

The carbon atom has six electrons, two of them forming a closed $1s^2$ shell (helium shell) and four filling $2s$ and $2p$ states. The ground-state atomic configuration is $2s^2 2p^2$, with the total spin $S=1$, total orbital moment $L=1$ and total angular moment $J=0$ (the ground-state multiplet $^3\text{P}_0$). The first

excited state, with a $J=1$, 3P_1 multiplet, has the energy $16.4 \text{ cm}^{-1} \approx 2 \text{ meV}$ (Radzig & Smirnov, 1985), which gives an estimate of the strength of the spin-orbit coupling in the carbon atom. The lowest-energy state, with configuration $2s^1 2p^3$, has the energy $33\,735.2 \text{ cm}^{-1} \approx 4.2 \text{ eV}$ (Radzig & Smirnov, 1985), so this is the promotion energy for exciting a 2s electron into a 2p state. At first sight, this would mean that carbon should always be divalent, due to there being two 2p electrons while the 2s electrons are chemically quite inert. This conclusion is, however, wrong. Normally, carbon is tetravalent, due to a formation of hybridized sp electron states, according to the concept of ‘resonance’ developed by L. Pauling (Pauling, 1960; Eyring, Walter & Kimball, 1946).

When atoms form molecules or solids the total energy decreases due to overlap of the electron wave functions at various sites and formation of molecular orbitals (in molecules), or energy bands (in solids); for a compact introduction to chemical bonding in solids, see Section 1.7 in Vonsovsky & Katsnelson (1989). This energy gain can be sufficient to provide the energy which is necessary to promote a 2s electron into a 2p state in the carbon atom.

In order to maximize the energy gained during the formation of a covalent bond, the overlap of the wave functions with those at neighbouring atoms should also be maximal. This is possible if the neighbouring atoms are situated in such directions from the central atoms that the atomic wave functions take on maximum values. The larger these values are the stronger the bond is. There are four basis functions corresponding to the spherical harmonics

$$\begin{aligned}
 Y_{0,0}(\vartheta, \varphi) &= \frac{1}{\sqrt{4\pi}}, \\
 Y_{1,0}(\vartheta, \varphi) &= i\sqrt{\frac{3}{4\pi}} \cos \vartheta, \\
 Y_{1,\pm 1}(\vartheta, \varphi) &= \mp i\sqrt{\frac{3}{8\pi}} \sin \vartheta \exp(\pm i\varphi),
 \end{aligned} \tag{1.1}$$

where ϑ and φ are polar angles. Rather than take the functions $Y_{1,m}(\vartheta, \varphi)$ to be the basis functions, it is more convenient to choose their orthonormalized linear combinations of the form

$$\begin{aligned}
 \frac{i}{\sqrt{2}} [Y_{1,1}(\vartheta, \varphi) - Y_{1,-1}(\vartheta, \varphi)] &= \sqrt{\frac{3}{4\pi}} \sin \vartheta \cos \varphi, \\
 \frac{i}{\sqrt{2}} [Y_{1,1}(\vartheta, \varphi) + Y_{1,-1}(\vartheta, \varphi)] &= \sqrt{\frac{3}{4\pi}} \sin \vartheta \sin \varphi, \\
 -iY_{1,0}(\vartheta, \varphi) &= \sqrt{\frac{3}{4\pi}} \cos \vartheta,
 \end{aligned} \tag{1.2}$$

which are transformed under rotations as the Cartesian coordinates x , y and z , respectively. Recall that the radial components of the s and p functions in the simplest approximation are equal in magnitude and may be omitted, together with the constant factor $1/\sqrt{4\pi}$, which is not important here. Then the angular dependence of the four basis functions which we will introduce in lieu of $Y_{l,m}(\vartheta, \varphi)$ can be represented as

$$|s\rangle = 1, \quad |x\rangle = \sqrt{3} \sin \vartheta \cos \varphi, \quad |y\rangle = \sqrt{3} \sin \vartheta \sin \varphi, \quad |z\rangle = \sqrt{3} \cos \vartheta. \quad (1.3)$$

We now seek linear combinations of the functions (1.3) that will ensure maximum overlap with the functions of the adjacent atoms. This requires that the value of $\alpha = \max_{\vartheta, \varphi} \psi$ be a maximum. With the normalization that we have chosen, $\alpha = 1$ for the s states and $\alpha = \sqrt{3}$ for the p functions of $|x\rangle$, $|y\rangle$ and $|z\rangle$. We then represent the function $|\psi\rangle$ as

$$|\psi\rangle = a|s\rangle + b_1|x\rangle + b_2|y\rangle + b_3|z\rangle, \quad (1.4)$$

where a and b_i are real-valued coefficients that satisfy the normalization condition

$$a^2 + b_1^2 + b_2^2 + b_3^2 = 1. \quad (1.5)$$

The function $|\psi\rangle$, then, is normalized in the same way as (1.3). This follows from their mutual orthogonality,

$$\int do |\psi(\vartheta, \varphi)|^2 \equiv \langle \psi | \psi \rangle = a^2 \langle s | s \rangle + b_1^2 \langle x | x \rangle + b_2^2 \langle y | y \rangle + b_3^2 \langle z | z \rangle = 4\pi,$$

with do being an element of solid angle. For the time being, the orientation of the axes in our case is arbitrary.

Let us assume that in one of the functions ψ , for which α is a maximum, this maximum value is reached in the direction along the diagonal of the cube $(1, 1, 1)$, with the carbon atom at its centre and with the coordinate axes parallel to its edges (Fig. 1.1). Then $b_1 = b_2 = b_3 = b$. The $(1, 1, 1)$ direction is given by angles ϑ and φ such that

$$\sin \varphi = \cos \varphi = \frac{1}{\sqrt{2}}, \quad \cos \vartheta = \frac{1}{\sqrt{3}}, \quad \sin \vartheta = \sqrt{\frac{2}{3}},$$

so that

$$|x\rangle = |y\rangle = |z\rangle = 1.$$

In addition,

$$\alpha = a + 3b = a + \sqrt{3(1 - a^2)}, \quad (1.6)$$

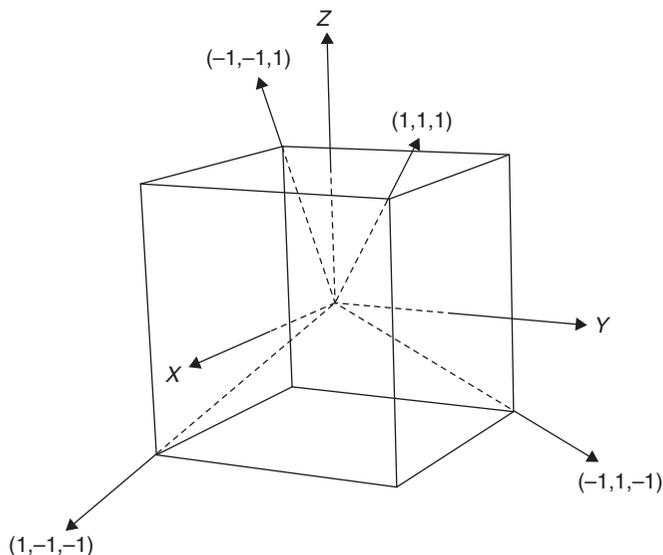


Fig. 1.1. Directions of sp^3 chemical bonds of the carbon atom.

where we have used the conditions (1.3). The maximum of α as a function of a is reached for $a = \frac{1}{2}$ and is equal to 2. The quantity b in this case is equal to $\frac{1}{2}$. Thus the first orbital with maximum values along the coordinate axes that we have chosen is of the form

$$|1\rangle = \frac{1}{2}(|s\rangle + |x\rangle + |y\rangle + |z\rangle). \quad (1.7)$$

It can be readily shown that the functions

$$\begin{aligned} |2\rangle &= \frac{1}{2}(|s\rangle + |x\rangle - |y\rangle - |z\rangle), \\ |3\rangle &= \frac{1}{2}(|s\rangle - |x\rangle + |y\rangle - |z\rangle), \\ |4\rangle &= \frac{1}{2}(|s\rangle - |x\rangle - |y\rangle + |z\rangle) \end{aligned} \quad (1.8)$$

correspond to the same value $\alpha = 2$. The functions $|i\rangle$ ($i = 1, 2, 3, 4$) are mutually orthogonal. They take on their maximum values along the $(1, 1, 1)$, $(1, \bar{1}, \bar{1})$, $(\bar{1}, 1, \bar{1})$ and $(\bar{1}, \bar{1}, 1)$ axes, i.e., along the axes of the tetrahedron, and, therefore, the maximum gain in chemical-bonding energy corresponds to the tetrahedral environment of the carbon atom. In spite of being qualitative, the treatment that we have performed above nevertheless explains the character of the crystal structure of the Periodic Table group-IV elements (diamond-type lattice, Fig. 1.2) as well as the shape of the methane molecule, which is very close to being tetrahedral.

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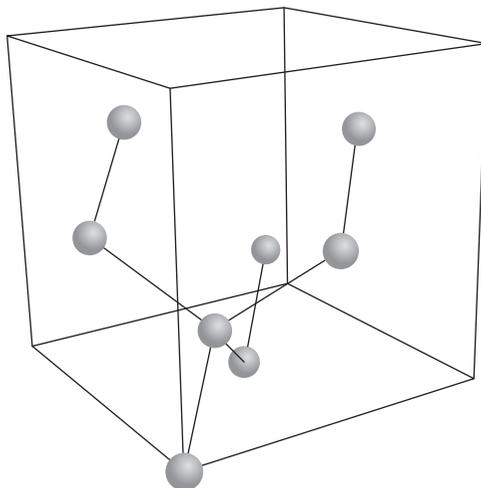


Fig. 1.2. Chemical bonds in the diamond structure.

The wave functions (1.7) and (1.8) correspond to a so-called sp^3 state of the carbon atom, for which all chemical bonds are equivalent. Another option is that *three* sp electrons form hybrid covalent bonds whereas one p electron has a special destiny, being distributed throughout the whole molecule (benzene) or the whole crystal (graphite or graphene). If one repeats the consideration above for a smaller basis including only functions $|s\rangle$, $|x\rangle$ and $|y\rangle$ one finds the following functions corresponding to the maximum overlap (Eyring, Walter & Kimball, 1946):

$$\begin{aligned}
 |1\rangle &= \frac{1}{\sqrt{3}}(|s\rangle + \sqrt{2}|x\rangle), \\
 |2\rangle &= \frac{1}{\sqrt{3}}|s\rangle - \frac{1}{\sqrt{6}}|x\rangle + \frac{1}{\sqrt{2}}|y\rangle, \\
 |3\rangle &= \frac{1}{\sqrt{3}}|s\rangle - \frac{1}{\sqrt{6}}|x\rangle - \frac{1}{\sqrt{2}}|y\rangle.
 \end{aligned}
 \tag{1.9}$$

The corresponding orbits have maxima in the xy -plane separated by angles of 120° . There are called σ bonds. The last electron with the p orbital perpendicular to the plane ($|z\rangle$ function) forms a π bond. This state (sp^2) is therefore characterized by threefold coordination of carbon atoms, in contrast with fourfold coordination for the sp^3 state. This is the case of *graphite* (Fig. 1.3).

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Graphene has a honeycomb crystal lattice as shown in Fig. 1.4(a). The Bravais lattice is triangular, with the lattice vectors

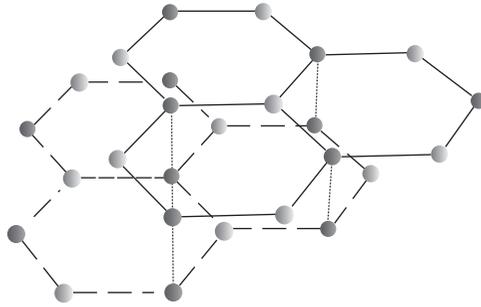


Fig. 1.3. The structure of graphite. Carbon atoms belonging to two different sublattices are shown as black and light grey.

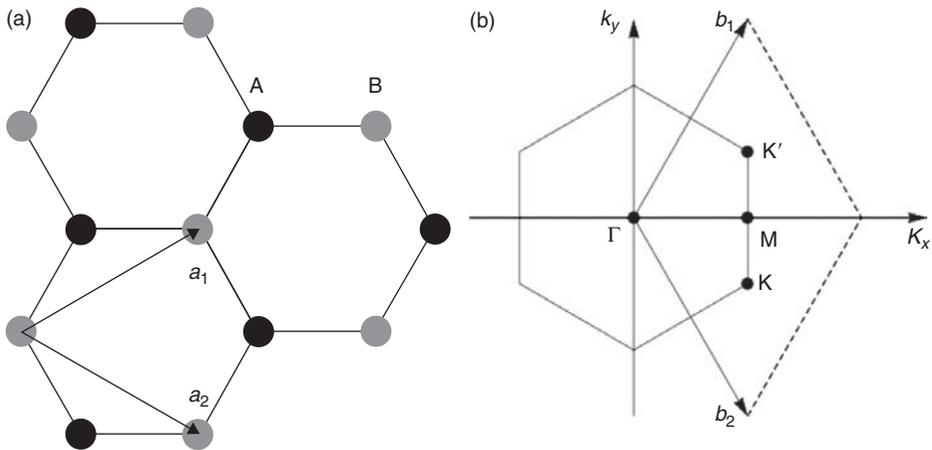


Fig. 1.4. (a) A honeycomb lattice, sublattices A and B are shown as black and grey. (b) Reciprocal lattice vectors and some special points in the Brillouin zone.

$$\vec{a}_1 = \frac{a}{2}(3, \sqrt{3}), \quad \vec{a}_2 = \frac{a}{2}(3, -\sqrt{3}), \quad (1.10)$$

where $a \approx 1.42 \text{ \AA}$ is the nearest-neighbour distance. It corresponds to a so-called conjugated carbon–carbon bond (like in benzene) intermediate between a single bond and a double bond, with lengths $r_1 \approx 1.54 \text{ \AA}$ and $r_2 \approx 1.31 \text{ \AA}$, respectively.

The honeycomb lattice contains two atoms per elementary cell. They belong to two sublattices, A and B, each atom from sublattice A being surrounded by three atoms from sublattice B, and vice versa (a bipartite lattice). The nearest-neighbour vectors are

$$\vec{\delta}_1 = \frac{a}{2}(1, \sqrt{3}), \quad \vec{\delta}_2 = \frac{a}{2}(1, -\sqrt{3}), \quad \vec{\delta}_3 = a(-1, 0). \quad (1.11)$$

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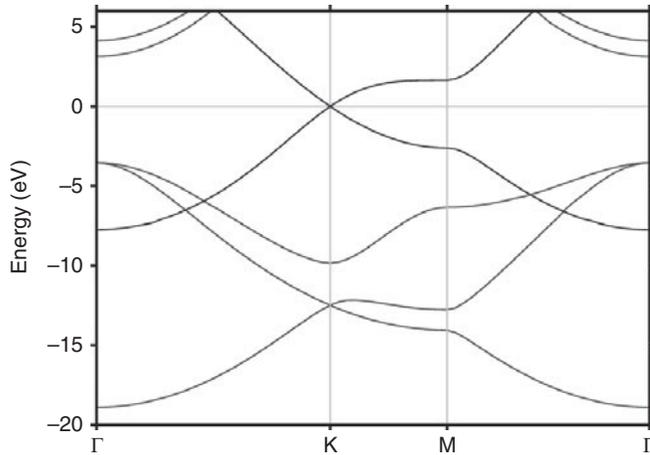


Fig. 1.5. The band structure of graphene (reproduced with permission from Boukhalov, Katsnelson & Lichtenstein, 2008).

The reciprocal lattice is also triangular, with the lattice vectors

$$\vec{b}_1 = \frac{2\pi}{3a} (1, \sqrt{3}), \quad \vec{b}_2 = \frac{2\pi}{3a} (1, -\sqrt{3}). \quad (1.12)$$

The Brillouin zone is presented in Fig. 1.4(b). Special high-symmetry points K, K' and M are shown there, with the wave vectors

$$\vec{K}' = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \right), \quad \vec{K} = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \right), \quad \vec{M} = \left(\frac{2\pi}{3a}, 0 \right). \quad (1.13)$$

The electronic structures of graphene and graphite are discussed in detail in Bassani & Pastori Parravicini (1975). In Fig. 1.5 we show a recent computational result for graphene. The sp^2 hybridized states (σ states) form occupied and empty bands with a huge gap, whereas π states form a single band, with a conical self-crossing point in K (the same point, by symmetry, exists also in K'). This conical point is a characteristic of the peculiar electronic structure of graphene and the origin of its unique electronic properties. It was first obtained by Wallace (1947) in the framework of a simple tight-binding model. Further this model was developed by McClure (1957) and Slonczewski & Weiss (1958).

Let us start, following Wallace (1947), with the nearest-neighbour approximation for the π states only, with the hopping parameter t . The basis of electron states contains two π states belonging to the atoms from sublattices A and B. In the nearest-neighbour approximation, there are no hopping processes within the sublattices; hopping occurs only between them. The tight-binding Hamiltonian is therefore described by the 2×2 matrix

$$\hat{H}(\vec{k}) = \begin{pmatrix} 0 & tS(\vec{k}) \\ tS^*(\vec{k}) & 0 \end{pmatrix}, \quad (1.14)$$

where \vec{k} is the wave vector and

$$S(\vec{k}) = \sum_{\vec{\delta}} e^{i\vec{k}\vec{\delta}} = 2 \exp\left(\frac{ik_x a}{2}\right) \cos\left(\frac{k_y a \sqrt{3}}{2}\right) + \exp(-ik_x a). \quad (1.15)$$

The energy is, therefore,

$$E(\vec{k}) = \pm t|S(\vec{k})| = \pm t\sqrt{3 + f(\vec{k})}, \quad (1.16)$$

where

$$f(\vec{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right). \quad (1.17)$$

One can see immediately that $S(\vec{K}) = S(\vec{K}') = 0$, which means band crossing. On expanding the Hamiltonian near these points one finds

$$\begin{aligned} \hat{H}_{K'}(\vec{q}) &\approx \frac{3at}{2} \begin{pmatrix} 0 & \alpha(q_x + iq_y) \\ \alpha^*(q_x - iq_y) & 0 \end{pmatrix}, \\ \hat{H}_K(\vec{q}) &\approx \frac{3at}{2} \begin{pmatrix} 0 & \alpha^*(q_x - iq_y) \\ \alpha(q_x + iq_y) & 0 \end{pmatrix}, \end{aligned} \quad (1.18)$$

where $\alpha = e^{5i\pi/6}$, with $\vec{q} = \vec{k} - \vec{K}$ and $\vec{k} - \vec{K}'$, respectively. The phase $5\pi/6$ can be excluded by a unitary transformation of the basis functions. Thus, the effective Hamiltonians near the points K and K' take the form

$$\hat{H}_{K,K'}(\vec{q}) = \hbar v \begin{pmatrix} 0 & q_x \mp iq_y \\ q_x \pm iq_y & 0 \end{pmatrix}, \quad (1.19)$$

where

$$v = \frac{3a|t|}{2} \quad (1.20)$$

is the electron velocity at the conical points. The possible negative sign of t can be excluded by an additional phase shift by $-\pi$.

On taking into account the next-nearest-neighbour hopping t' , one finds, instead of Eq. (1.16),

$$E(\vec{k}) = \pm t|S(\vec{k})| + t'f(\vec{k}) = \pm t\sqrt{3 + f(\vec{k})} + t'f(\vec{k}). \quad (1.21)$$

The second term breaks the electron–hole symmetry, shifting the conical point from $E=0$ to $E=-3t'$, but it does not change the behaviour of

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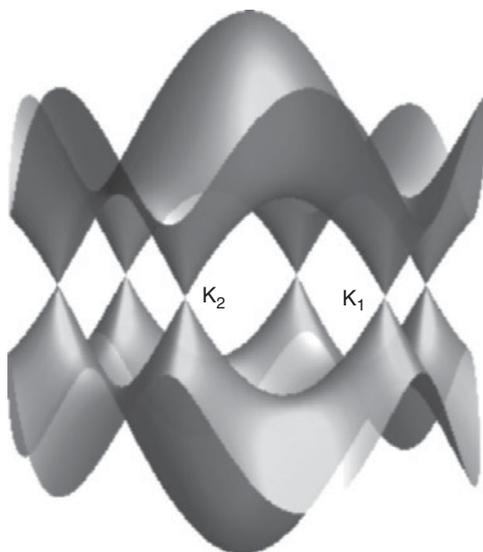


Fig. 1.6. The electron energy spectrum of graphene in the nearest-neighbour approximation.

the Hamiltonian near the conical points. Actually, this behaviour is symmetry-protected (and even topologically protected), as we will see in the next section.

The points K and $-K'$ differ by the reciprocal lattice vector $\vec{b} = \vec{b}_1 - \vec{b}_2$, so the point K' is equivalent to $-K$. To show this explicitly, it is convenient sometimes to use a larger unit cell in the reciprocal space, with six conical points. The spectrum (1.16) in this representation is shown in Fig. 1.6.

The parameters of the effective tight-binding model can be found by fitting the results of first-principles electronic-structure calculations. According to Reich *et al.* (2002), the first three hopping parameters are $t = -2.97$ eV, $t' = -0.073$ eV and $t'' = -0.33$ eV. The smallness of t' means that the electron-hole symmetry of the spectrum is very accurate not only in the vicinity of the conical points but also throughout the whole Brillouin zone.

There are saddle points of the electron energy spectrum at M (see Figs. 1.5 and 1.6), with Van Hove singularities in the electron density of states, $\delta N(E) \propto -\ln|E - E_M|$ (Bassani & Pastori Parravicini, 1975). The positions of these singularities are

$$E_{M-} = t + t' - 3t'' \approx -2.05 \text{ eV}$$

and

$$E_{M+} = -t + t' + 3t'' \approx 1.91 \text{ eV}.$$

1.3 Massless Dirac fermions in graphene

Undoped graphene has a Fermi energy coinciding with the energy at the conical points, with a completely filled valence band, an empty conduction band and no band gap in between. This means that, from the point of view of a general band theory, graphene is an example of a *gapless semiconductor* (Tsdirilkovskii, 1996). Three-dimensional crystals, such as HgTe and α -Sn (grey tin) are known to be gapless semiconductors. What makes graphene unique is not the gapless state itself but the very special, chiral nature of the electron states, as well as the high degree of electron–hole symmetry.

For any realistic doping, the Fermi energy is close to the energy at the conical point, $|E_F| \ll |t|$. To construct an effective model describing electron and hole states in this regime one needs to expand the effective Hamiltonian near one of the special points K and K' and then make the replacements

$$q_x \rightarrow -i \frac{\partial}{\partial x}, \quad q_y \rightarrow -i \frac{\partial}{\partial y},$$

which corresponds to the effective mass approximation, or $\vec{k} \cdot \vec{p}$ perturbation theory (Tsdirilkovskii, 1982; Vonsovsky & Katsnelson, 1989). From Eq. (1.19), one has

$$\hat{H}_K = -i\hbar v \vec{\sigma} \nabla, \quad (1.22)$$

$$\hat{H}_{K'} = \hat{H}_K^T, \quad (1.23)$$

where

$$\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (1.24)$$

are Pauli matrices (only x - and y -components enter Eq. (1.22)) and T denotes a transposed matrix. A complete low-energy Hamiltonian consists of 4×4 matrices taking into account both two sublattices and two conical points (in terms of semiconductor physics, two valleys).

In the basis

$$\Psi = \begin{pmatrix} \psi_{KA} \\ \psi_{KB} \\ \psi_{K'A} \\ \psi_{K'B} \end{pmatrix}, \quad (1.25)$$

where ψ_{KA} means a component of the electron wave function corresponding to valley K and sublattice A, the Hamiltonian is a 2×2 block supermatrix,

$$\hat{H} = \begin{pmatrix} \hat{H}_K & 0 \\ 0 & \hat{H}_{K'} \end{pmatrix}. \quad (1.26)$$