# Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

Lecture notes 2020 by Xavier Blase

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## 2 Free electrons in a box

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## 5 Chapter 5 : the tight-binding approximation (applications)

### 5.1 The 1D chain with 2 atoms per cell.

We now study a slightly more complex chain of atoms alternating atoms of type A and atoms of type B with an interatomic distance "a". Any unit cell, say the n-th unit cell, contains 2 atoms, one of type A in position $(\tau_A + 2na)$ and one of type B in position $(\tau_B + 2na)$. The primitive lattice vector is $\mathbf{a}_1 = 2a\hat{x}$. The reciprocal space primitive lattice vector is $\mathbf{b}_1 = (2\pi/2a)\ \hat{x} = (\pi/a)\ \hat{x}$ leading to a Brillouin zone $k \in [-\pi/2a, \pi/2a[$.

We assume here that there is only one atomic orbital per atom that we label orbitals $\phi_A^{at}$ on atoms A and $\phi_B^{at}$ on atoms B. Using the second Bloch theorem, electrons will be described by a wavefunction $\psi_k(r) = e^{ikr}u_k(r)$ where $u_k(r)$ is fully periodic, that is $u_k(r) = u_k(r + 2a)$. Considering for example the n-th unit cell, $u_k(r)$ in this cell can be constructed as any linear combination $\alpha\phi_A^{at}(r - \tau_A - 2na) + \beta\phi_B^{at}(r - \tau_B - 2na)$ of the two atomic orbitals in the cell. To obtain a fully periodic function, this linear combination must be translated by a multiple of 2a all along the chain (see Fig. 12), leading to

$$u(r) = \mathcal{A}\sum_n^{N_C}\Big[\alpha\phi_A^{at}(r - \tau_A - 2na) + \beta\phi_B^{at}(r - \tau_B - 2na)\Big]$$

with $N_C$ the number of unit cells and $\mathcal{A}$ a normalizing factor. By adding the

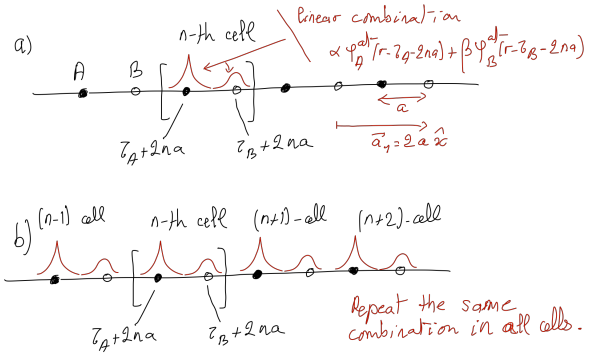


**Figure 1:** Construction of a periodic $u_k(r)$ function: (a) Take a unit cell and make a linear combination of the atomic orbitals in this cell. (b) Repeat this linear combination in all cells.

phase factor $e^{ikr}$, this leads to Bloch states that read:

$$\psi_k(r) = \mathcal{A}e^{ikr}\sum_n^{N_C}\Big[\alpha\phi_A^{at}(r-\tau_A-2na)+\beta\phi_B^{at}(r-\tau_B-2na)\Big]$$

One can write therefore:

$$\psi_k(r) = \alpha\psi_k^A(r)+\beta\psi_k^B(r)$$

where

$$\psi_k^A(r) = \mathcal{A}e^{ikr}\sum_n^{N_C}\phi_A^{at}(r-\tau_A-2na) \quad \psi_k^B(r) = \mathcal{A}e^{ikr}\sum_n^{N_C}\phi_B^{at}(r-\tau_B-2na)$$

Here we see that any Bloch state $|\psi_k\rangle$ can be expressed as a linear combination of two "basis" Bloch states $|\psi_k^A\rangle$ and $|\psi_k^B\rangle$. The state $|\psi_k^A\rangle$ is made of atomic orbitals of type A, and the state $|\psi_k^B\rangle$ of atomic orbitals of type B (see Fig. 2). For more complex systems with more atoms and/or atomic orbitals per unit cell, we can generalize this approach by making one basis Bloch state for each atomic orbital in the unit cell.

The normalization factor $\mathcal{A}$ can be obtained as in the previous chapter. For example imposing $\langle\psi_k^A|\psi_k^A\rangle = 1$ leads to

$$\int dr\left(\mathcal{A}^*e^{-ikr}\sum_{n=1}^{N_C}[\phi_A^{at}]^*(r-\tau_A-2na)\right)\left(\mathcal{A}e^{ikr}\sum_{m=1}^{N_C}\phi_A^{at}(r-\tau_A-2ma)\right)=1$$

where the two $e^{-ikr}$ and $e^{ikr}$ factors cancel each other, leading to:

$$|\mathcal{A}|^2\sum_{n,m}^{N_C}\langle\phi_A^{at}(r-\tau_A-2na)|\phi_A^{at}(r-\tau_A-2ma) = |\mathcal{A}|^2\sum_{n,m}^{N_C}S_{nm}$$

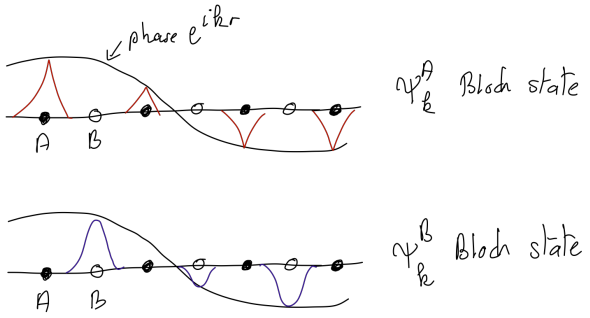


**Figure 2:** (Top) Bloch state $\psi_k^A$ with a periodic repetition of type-A atomic orbitals $\phi_A^{at}$ modulated by the phase factor $e^{ikr}$. (Bottom) Idem for $\psi_k^B$.

with the overlap matrix[1] elements between atomic orbitals

$$S_{nm} = \langle \phi_A^{at}(r - \tau_A - 2na) | \phi_A^{at}(r - \tau_A - 2ma) \rangle = \delta_{nm}$$

nonzero only if the two atomic orbitals are on the same atom (tight-binding approximation). One obtains: $\mathcal{A} = 1/\sqrt{N_C}$ with $N_C = N_A = N_B = N/2$, where $N_A$ is the number of A atoms, $N_B$ is the number of B atoms, and N the total number of atoms. As a result, any Bloch wavefunction $|\psi_k\rangle$ of the crystal is a linear combination of the two basis Bloch states:

$$\psi_k^A(r) = \frac{e^{ikr}}{\sqrt{N_C}} \sum_n^{N_C} \phi_A^{at}(r - \tau_A - 2na) \quad \text{and} \quad \psi_k^B(r) = \frac{e^{ikr}}{\sqrt{N_C}} \sum_n^{N_C} \phi_B^{at}(r - \tau_B - 2na)$$

Before proceeding we note that

$$\langle \psi_k^A | \psi_k^B \rangle = \frac{1}{N_C} \sum_{n,m}^{N_C} \langle \phi_A^{at}(r - \tau_A - 2na) | \phi_B^{at}(r - \tau_A - 2ma) \rangle$$

is necessarily zero since a $\phi_A^{at}$ atomic orbital (on an atom A) can never be on the same atom than a $\phi_B^{at}$ atomic orbital (on an atom B). Again, within the tight-binding approximation (localized tightly bound atomic orbitals) we keep only the "onsite" overlap terms where the two atomic orbitals are on the same atom.

We now simplify the upcoming calculations by making another tight-binding approximation on the $e^{ikr}$ phase factor. As in the previous chapter, we assume that the atomic orbitals are very localized (tightly bound to the atoms) and vary much more rapidly than the $e^{ikr}$ phase factor. As a result, when multiplying

[1] Matrice de recouvrement en français

some atomic orbital on a given atom by $e^{ikr}$, we replace "r" in the phase factor by its value at the position of the atom, for example :

$$e^{ikr}\phi_A^{at}(r-\tau_A-2na) \quad \Longrightarrow \quad e^{ik(\tau_A+2na)}\phi_A^{at}(r-\tau_A-2na)$$

The two basis Bloch states become now:

$$\psi_k^A(r) = \frac{1}{\sqrt{N_C}}\sum_n^{N_C} e^{ik(\tau_A+2na)}\phi_A^{at}(r-\tau_A-2na)$$
$$\psi_k^B(r) = \frac{1}{\sqrt{N_C}}\sum_n^{N_C} e^{ik(\tau_B+2na)}\phi_B^{at}(r-\tau_B-2na)$$

This will greatly simplify the calculations to come.[2]

**The bandstructure.** To obtain the two unknown $\alpha$ and $\beta$ coefficients, we proceed somehow similarly than the trick we used for the $H_2^+$ molecule by projecting here the Schrödinger equation

$$\hat{H}|\psi_k\rangle = \varepsilon_k|\psi_k\rangle$$

onto the bra $\langle\psi_k^A|$ and $\langle\psi_k^B|$ leading to the system of 2 equations:

$$(I) \quad \langle\psi_k^A|\hat{H}|\psi_k\rangle = \varepsilon_k\langle\psi_k^A|\psi_k\rangle$$
$$(II) \quad \langle\psi_k^B|\hat{H}|\psi_k\rangle = \varepsilon_k\langle\psi_k^B|\psi_k\rangle$$

Using now $|\psi_k\rangle = \alpha|\psi_k^A\rangle + \beta|\psi_k^B\rangle$ this leads to

$$(I) \quad \alpha H_{AA} + \beta H_{AB} = \varepsilon_k\left(\alpha S_{AA} + \beta S_{AB}\right)$$
$$(II) \quad \alpha H_{BA} + \beta H_{BB} = \varepsilon_k\left(\alpha S_{BA} + \beta S_{BB}\right)$$

with the Hamiltonian matrix elements between the $\psi_k^A$ and $\psi_k^B$ states:

$$H_{AA} = \langle\psi_k^A|\hat{H}|\psi_k^A\rangle \quad H_{AB} = \langle\psi_k^A|\hat{H}|\psi_k^B\rangle \quad H_{BB} = \langle\psi_k^B|\hat{H}|\psi_k^B\rangle \quad H_{BA} = \langle\psi_k^B|\hat{H}|\psi_k^A\rangle$$

with importantly $H_{BA} = H_{AB}^*$ since $\hat{H}$ is hermitian, and further the overlap matrix elements (without the Hamiltonian in the middle):

$$S_{AA} = \langle\psi_k^A|\psi_k^A\rangle \quad S_{AB} = \langle\psi_k^A|\psi_k^B\rangle \quad S_{BB} = \langle\psi_k^B|\psi_k^B\rangle \quad S_{BA} = \langle\psi_k^B|\psi_k^A\rangle$$

We already know by normalization of $\psi_k^A$ and $\psi_k^B$ that $S_{AA} = S_{BB} = 1$ and that further $S_{AB} = 0$.

[2]Note that we did not do this approximation on the phase factor for calculating the norm of $\langle\psi_k^A|\psi_k^A\rangle$ for which the phase factors canceled anyway. But when we define Hamiltonian matrix elements of the type $\langle\psi_k^A|\hat{H}|\psi_k^A\rangle$, the phase factors do not cancel due to the Hamiltonian in the middle that does not commute with the $e^{ikr}$ phase.

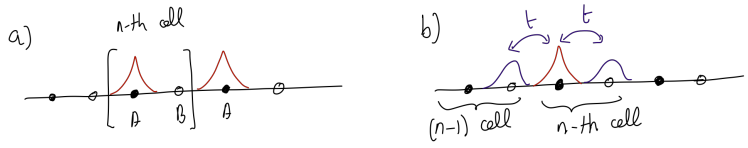


**Figure 3:** (a) Atomic orbitals of the same type of atoms (A or B) cannot be first-nearest-neighbors. (b) Each atomic orbitals of a given type (e.g. $\phi_A^{at}$) has two nearest-neighbor orbitals of the other type (e.g. $\phi_B^{at}$), one in the same cell, the other in another cell.

**NOTE.** Do not confuse the Hamiltonian and overlap matrix elements in the $\psi_k^A$ and $\psi_k^B$ basis (e.g. $H_{AB}$ or $S_{AB}$) with the Hamiltonian and overlap matrix elements in the localized atomic basis, e.g. $\langle\phi_A^{at}(r-\tau_A-2na)|\hat{H}|\phi_B^{at}(r-\tau_B-2ma)\rangle$. We will now express the former with the latter.

Let's calculate first $H_{AA}$ that is:

$$H_{AA} = \frac{1}{N_C}\sum_{n,m}^{N_C} e^{-ik(\tau_A+2na)}e^{ik(\tau_A+2ma)}\langle\phi_A^{at}(r-\tau_A-2na)|\hat{H}|\phi_A^{at}(r-\tau_A-2ma)\rangle$$

Remember that for Hamiltonian matrix elements between atomic orbitals, we keep 2 kind of terms : terms where the 2 atomic orbitals (bra and ket) are on the same atom (onsite energy) AND terms where the atomic orbitals are on first-nearest-neighbor atoms (hoping terms). But in the present case, $\phi_A^{at}$ atomic orbitals can never be on first-nearest-neighbor atoms since two A atoms are separated by a B atom (see Fig. 3a). The only non-zero terms left are the onsite matrix elements for A-type atomic orbitals that we label $\varepsilon_A^0$, that is:

$$\langle\phi_A^{at}(r-\tau_A-2na)|\hat{H}|\phi_A^{at}(r-\tau_A-2ma)\rangle = \delta_{nm}\,\varepsilon_0^A$$

As a result

$$H_{AA} = \frac{1}{N_C}\sum_{n,m}^{N_C} e^{ik(m-n)a}\delta_{nm}\varepsilon_0^A = \frac{1}{N_C}N_C\varepsilon_A^0 = \varepsilon_A^0$$

Similarly for two $\phi_B^{at}$ atomic orbitals on the same atom we define a "B" onsite energy $\varepsilon_B^0 = \langle\phi_B^{at}(r-\tau_B-2na)|\hat{H}|\phi_B^{at}(r-\tau_B-2na)\rangle$ and

$$H_{BB} = \varepsilon_B^0$$

We are now left with calculating :

$$H_{AB} = \frac{1}{N_C}\sum_{n,m}^{N_C} e^{-ik(\tau_A+2na)}e^{ik(\tau_B+2ma)}\langle\phi_A^{at}(r-\tau_A-2na)|\hat{H}|\phi_B^{at}(r-\tau_B-2ma)\rangle$$

$$= \frac{e^{ik(\tau_B-\tau_A)}}{N_C}\sum_{n,m}^{N_C} e^{ik(m-n)2a}\langle\phi_A^{at}(r-\tau_A-2na)|\hat{H}|\phi_B^{at}(r-\tau_B-2ma)\rangle$$

Since orbitals $\phi_A^{at}$ and $\phi_B^{at}$ cannot be on the same atom, there is no onsite contribution. However, $\phi_A^{at}$ and $\phi_B^{at}$ can be first-nearest-neighbors for m=n ($\phi_A^{at}$ and $\phi_B^{at}$ in the same cell) and m=n-1 ($\phi_B^{at}$ in the cell on the "left" of that of $\phi_A^{at}$). This is schematized in Fig. 3b. The matrix elements between these first-nearest-neighbors atomic orbitals are the hoping matrix elements[3] labeled "t" as before:

$$\langle \phi_A^{at}(r-\tau_A-2na)|\hat{H}|\phi_B^{at}(r-\tau_B-2ma)\rangle = t \quad \text{with} \quad (m=n) \text{ or } (m=n-1)$$

We have thus

$$H_{AB} = \frac{e^{ik(\tau_B-\tau_A)}}{N_C}\sum_n^{N_C}\left(e^{ik(0)2a}t + e^{ik(-1)2a}t\right) = e^{ik(\tau_B-\tau_A-a)}2t\cos(ka)$$

that is a complex number. We can now proceed with the system of equations that reads:

$$\begin{aligned}(I) \quad & \alpha(\varepsilon_A^0-\varepsilon_k)+\beta H_{AB}=0\\ (II) \quad & \alpha H_{BA}+\beta(\varepsilon_B^0-\varepsilon_k)=0\end{aligned}$$

leading to the equation for nonzero $(\alpha,\beta)$ solutions

$$(\varepsilon_A^0-\varepsilon_k)(\varepsilon_B^0-\varepsilon_k)-|H_{AB}|^2=0$$

with $(H_{BA}=H_{AB}^*)$ leading to:

$$(\varepsilon_k-\varepsilon_A^0)(\varepsilon_k-\varepsilon_B^0)=4t^2\cos^2(ka)$$

### 5.1.1 The simplest case : A and B are the same atoms

Before considering well known problems and systems in solid state physics, let's first consider the case where A and B are the same atoms. If A and B are the same atoms (same chemical species) and $\phi_A^{at}$ and $\phi_B^{at}$ are the same atomic orbitals, then $\varepsilon_A^0=\varepsilon_B^0$ that we will simplify in $\varepsilon^0$ in this case. Consequently, the electronic energies read:

$$\varepsilon_k = \varepsilon^0 \pm 2t\cos(ka)$$

There are two energies for a given wavevector k, that is two bands in the bandstructure (Fig. 4b). We now remark that if A and B are the same atoms, then we are in the situation of last Chapter with a chain of identical atoms. Last time, we have treated this system considering that we have one atom per unit cell and a primitive lattice vector $\mathbf{a}_1 = a\hat{x}$ with a bandstructure presented in Fig. 4a. In this paragraph, we consider a unit cell with 2-atoms (this is a bit silly here) and a primitive lattice vector $\mathbf{a}_1 = 2a\hat{x}$ with the corresponding bandstructure presented in Fig. 4b. But really the two systems are the same and should have the

[3] Intégrales de saut en français.

same electronic states. This is the case. Considering the 2-atoms/cell system with a Brillouin zone (BZ) $[-\pi/2a, \pi/2a[$, we know that any k-vector outside the BZ is equivalent to a k-vector inside the BZ via a translation by a integer times the reciprocal space primitive lattice vector $\mathbf{b}_1 = (2\pi/2a)\hat{x}$. We can very well consider the "small" Brillouin zone and bring in Fig. 4a all k-points outside $[-\pi/2a, \pi/2a[$ inside $[-\pi/2a, \pi/2a[$ by a translation of $\pm b = \pi/a$. We see that by doing so we can "fold" the band structure from the large BZ to the small one. The two pictures are identical. This process is called **band folding.**

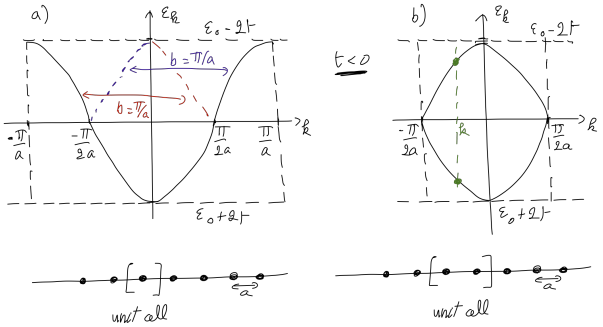


**Figure 4:** (a) Band-structure from previous Chapter for the 1D chain with 1-atom/cell. (b) Band-structure for the 1D chain with 2-atoms/cell. Notice that in a) the Brillouin zone (BZ) is $[-\pi/a, \pi/a[$ while in b) it is twice as small, namely $[-\pi/2a, \pi/2a[$. The green dashed line in b) shows that for a given k there are now 2 different energies, namely the band structure is composed of 2 bands. The red and blue dashed portion of bands in a) show how to fold the largest BZ into the smallest one to recover ... the same band structure in the two cases.

**Complement : effective masses, electrons and holes.** A typical semiconductor such as silicon with a large gap (Fig. 5a) is quite useless for electronics. To be able to tune the current with a gate voltage (the "transistor effect"), a very very few electrons must be added to or removed from the system. This is called n-type or p-type-doping by replacing e.g. a few Si atoms by nitrogen or boron atoms. In a very simplified picture, adding a very few electrons will populate a very few levels at the bottom of the empty band above the gap, that is the conduction band. This is represented in Fig. 5b. These few added electrons have a small k-vector assuming a band structure with a minimum of energy at k=0. This is the case for the 1D chain with 1-atom/cell, yielding $\varepsilon_k = \varepsilon^0 + 2t\cos(ka)$ where $(t < 0)$, that we use for sake of example. We can perform a Taylor expansion at small k of the dispersion relation to obtain :

$$\varepsilon(k) = \varepsilon(0) + k\frac{\partial\varepsilon}{\partial k}\Big|_{k=0} + \frac{k^2}{2}\frac{\partial^2\varepsilon}{\partial k^2}\Big|_{k=0} + ...$$

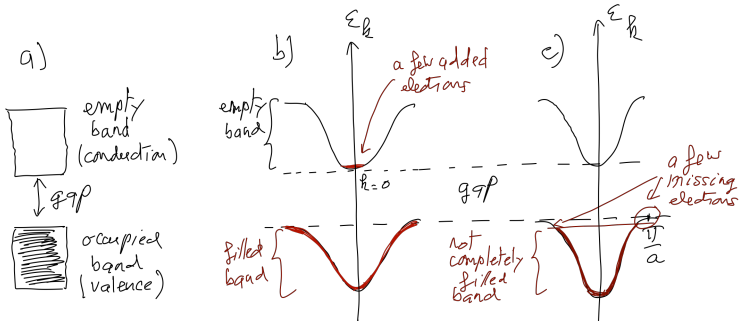


**Figure 5:** (a) A schematic representation of a semiconductor with a filled band (the valence band) and an empty band (the conductions band) separated by an energy gap. b,c) Two bands with minimum at k=0 and maximum at k=$\pm\pi/a$ with a few electrons b) added in the empty conduction bands or c) removed from the top of the filled band.

Since the band has a minimum at (k=0), the first order derivative is zero and the Taylor expansion can be written :

$$\varepsilon(k) = \varepsilon(0) + \frac{\hbar^2 k^2}{2m^*} \quad \text{with} \quad \frac{\hbar^2}{2m^*} = \frac{1}{2}\frac{\partial^2 \varepsilon}{\partial k^2}\Big|_{k=0}$$

The dispersion, namely the dependence of the energy on the wavevector, is the same as that for a free electron, for which $\varepsilon_k = \hbar^2 k^2/2m_e$ with $m_e$ the mass of the electron, but with an "effective" mass $m^*$ related to the curvature of the band at the minimum. In the case of the band structure $\varepsilon_k = \varepsilon^0 + 2t\cos(ka)$, this yields

$$m^* = \hbar^2/2a^2|t|$$

with $|t| = -t$ for $t < 0$. These few added electrons at the bottom of the conduction band can be treated as free electrons with a mass that has been changed by the interaction with the ions and the other electrons. Such effective masses can be much smaller than $m_e$ in many semiconductors and sometimes much larger for "heavy fermions" systems. The mass is controlled by the curvature of the band at its minima, that is here by the hopping term $|t|$. The larger the hoping energy $|t|$, the larger the curvature and the smaller the mass. This translates directly onto the mobility of the electrons in the crystal. A small mass or a large $t$, that is a large probability to jump from one atom to another by unit time, are both consistent with the idea of electrons with large mobilities.

We now assume that we remove a few electrons from the top of the valence (occupied) band (see Fig. 5c). Now the electrons on the highest occupied bands (at the Fermi energy) will have a k-vector very close to $\pm\pi/a$ at the "edge" of the Brillouin zone. We can do a Taylor expansion around this k-vector to obtain an effective mass such that

$$\frac{\hbar^2}{2m^*} = \frac{1}{2}\frac{\partial^2 \varepsilon}{\partial k^2}\Big|_{k=\pm\pi/a}$$

The remarkable property is that the curvature is negative at the top of the band, namely the effective mass $m^*$ is here negative. One way to understand this result is to associate this negative mass to the "holes" at the top of the nearly-completely-filled band. Holes are "missing electrons" and it is not so surprizing that missing electrons should be associated with a negative mass. Under an electric field, electrons and holes move in opposite directions.

## 5.2 The ionicity gap : see Exercise 16

We will see that taking now A and B as different chemical species, yielding different onsite $\varepsilon_A^0$ and $\varepsilon_B^0$ energies, will open a gap at the zone edges between the lower and higher bands of Fig. 4b. This is the ionicity gap. This explains why graphene is (semi)metallic while hexagonal boron-nitride is a large gap insulator, both systems having the very same 2D hexagonal lattice structure.

## 5.3 The Peierls distorsion : see Exercise 17

Polymers are a concret realization of our 1D chain of atoms. It turns out that it is complicated to have conducting polymers because of a phenomenon called Peierls distortion, that is the transformation of a chain of regularly spaced atoms into a chain of dimers. As a matter of fact, the Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers." Exercise 16 explains how this Peierls distorsion transforms the metallic chain of atoms at half-filling into an insulator.

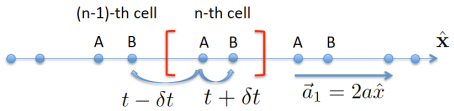


**Figure 6:** Schematic representation of a Peierls distorsion with spontaneous dimerization, i.e. alternating (short and long) interatomic distances and hoping energies.

This is a variation on the 2-atoms/cell with 1-atomic-orbital/atom exercise treated above but with a hoping energy (t+$\delta t$) between the atomic orbitals $\phi_A^{at}(r-\tau_A-2na)$ and $\phi_B^{at}(r-\tau_B-2na)$ in the same n-th cell, and (t-$\delta t$) between the atomic orbital $\phi_A^{at}(r-\tau_A-2na)$ and the atomic orbital $\phi_B^{at}(r-\tau_B-2(n-1)a)$ in the (n-1)-th cell. As such, the onsite energies are not modified but the $H_{AB}$

term now reads:

$$\begin{aligned} H_{AB} &= \frac{e^{ik(\tau_B-\tau_A)}}{N_C}\sum_n^{N_C}\Big(e^{ik(0)2a}(t+dt)+e^{ik(-1)2a}(t-dt)\Big) \\ &= \frac{e^{ik(\tau_B-\tau_A)}}{N_C}N_C e^{-ika}\Big(2t\cos(ka)+2i\delta t\sin(ka)\Big) \\ &= e^{ik(\tau_B-\tau_A-a)}\Big(2t\cos(ka)+2i\delta t\sin(ka)\Big) \end{aligned}$$

The condition to have nonzero $(\alpha,\beta)$ solutions, that is: $(\varepsilon_k-\varepsilon^0)^2-|H_{AB}|^2=0$ becomes:

$$(\varepsilon_k-\varepsilon^0)^2 = 4t^2\cos^2(ka)+4\delta t^2\sin^2(ka)$$

that is two $\varepsilon^+(k)$ and $\varepsilon^-(k)$ solutions:

$$\varepsilon_k = \varepsilon^0 \pm 2t\sqrt{\cos^2(ka)+(\delta t/t)^2\sin^2(ka)}$$

The most important feature is that in the standard chain without dimerization there was no gap between the upper and lower bands. Both $\varepsilon^+(k)$ and $\varepsilon^-(k)$ solutions were equal to the onsite energy $\varepsilon 0$ at BZ boundary $\pm\pi/2a$ (see dashed grey line in Fig. 7). After dimerization, since the $\sin(ka)$ function does not cancel at the BZ boundaries $k=\pm\pi/2$, a $4|\delta t|$ gap opens at BZ boundary between the $\varepsilon^+(k)$ and $\varepsilon^-(k)$ bands. At half filling, when only the lowest band is filled by electrons, the highest band being empty, the system becomes more stable upon dimerization since the electrons gain the energy shaded in light grey in Fig. 7. The system distorts spontaneously and becomes an insulator with a gap, killing the conductivity. This is why it is so difficult to have conducting polymers.

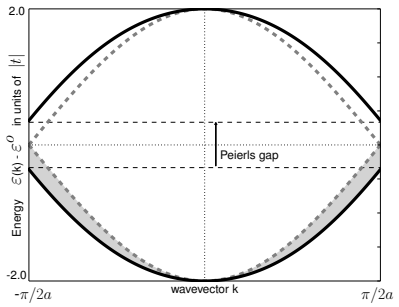


**Figure 7:** Band structure for the dimerized chain that is compared to the undimerized system (dashed grey line). A gap opens at the BZ boundary with stabilization of the electrons in the lower band (see light grey shaded area). The plot corresponds here to a value $\delta t/t = 0.3$ and we represent $(\varepsilon_k-\varepsilon^0)$ in units of the hoping energy $|t|$ where $\varepsilon^0$ is the onsite energy.

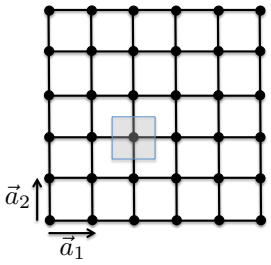


**Figure 8:** Representation of the 2D square lattice with 1 atom per cell. Each cell (or each atom) is indexed by a lattice vector $\mathbf{R}_{ml} = m\mathbf{a}_1 + l\mathbf{a}_2$. A unit cell is represented in grey shaded. The atom in this cell has four nearest neighbours located $\pm\vec{a}_1$ and $\pm\vec{a}_2$ away.

## 5.4 Band structure of the 2D square lattice (the minimal cuprate) : see Exercise 24

The 2D square lattice with interatomic distance "a" is represented in Fig. 8. The primitive lattice vectors are $\mathbf{a}_1 = a\hat{x}$ and $\mathbf{a}_2 = a\hat{y}$. The reciprocal space primitive lattice vectors are $\mathbf{b}_1 = (2\pi/a)\hat{x}$ and $\mathbf{b}_2 = (2\pi/a)\hat{y}$ that verify $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. There is only one atom per unit cell and we further assume in this exercise that there is only one atomic orbital per atom. The only periodic function that can be created as a linear combination of atomic orbitals (LCAO) consists in repeating this atomic function periodically in all cells:

$$u(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{ml} \phi^{at}(\mathbf{r} - \mathbf{R}_{ml}) \quad \text{with} \quad \mathbf{R}_{ml} = m\mathbf{a}_1 + l\mathbf{a}_2$$

where we have included the normalization factor $1/\sqrt{N}$ with N the number of cells or atoms. The $\mathbf{R}_{ml}$ are the lattice vectors pointing to all cells, that is to all atoms assuming that each atom is in position $\tau = 0$ in its cell. The only possible Bloch state for a given $\mathbf{k}$-vector[4] is thus of the form (Bloch theorem) :

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r})$$

with $\mathbf{k} = (k_x, k_y)$ in 2D. Using the tight-binding approximation for the phase factor one obtains:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{ml} e^{i\mathbf{k}\cdot\mathbf{R}_{ml}} \phi^{at}(\mathbf{r} - \mathbf{R}_{ml})$$

The energy $\varepsilon(\mathbf{k})$ associated with $\psi_{\mathbf{k}}$ is simply:

$$\varepsilon(\mathbf{k}) = \langle\psi_{\mathbf{k}}|\hat{H}|\psi_{\mathbf{k}}\rangle = \frac{1}{N} \sum_{ml} \sum_{m'l'} e^{i\mathbf{k}\cdot(\mathbf{R}_{m'l'} - \mathbf{R}_{ml})} \langle\phi^{at}(\mathbf{r} - \mathbf{R}_{ml})|\hat{H}|\phi^{at}(\mathbf{r} - \mathbf{R}_{m'l'})\rangle$$

For a given atom indexed by (ml), the sum over (m'l') gives 5 different non-zero contributions:

[4]Note that since for a given $\mathbf{k}$-vector there is only one possible Bloch state, there is no linear combination to be taken here as we did when there were 2 atoms per cell, namely several atomic orbitals per cell.

- (m'l')=(ml) $\Longrightarrow$ the two atomic orbitals are on the same atom and $\langle \phi^{at}(\mathbf{r}-\mathbf{R}_{ml})|\hat{H}|\phi^{at}(\mathbf{r}-\mathbf{R}_{m'l'}) = \varepsilon_0$ the onsite energy
- the atoms in position $\mathbf{R}_{m'l'}$ are first-nearest-neighbours to $\mathbf{R}_{ml}$ : this happens for $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = \pm\mathbf{a}_1$ and $\pm\mathbf{a}_2$. For these 4 neighbours, the Hamiltonian matrix elements $\langle \phi^{at}(\mathbf{r}-\mathbf{R}_{ml})|\hat{H}|\phi^{at}(\mathbf{r}-\mathbf{R}_{m'l'}) = t$ the hoping matrix element.

One obtains thus:

$$\begin{aligned}\varepsilon(\mathbf{k}) &= \frac{1}{N}\sum_{ml}\Big(e^{i\mathbf{k}\cdot\mathbf{0}}\varepsilon_0 + e^{i\mathbf{k}\cdot\mathbf{a}_1}t + e^{-i\mathbf{k}\cdot\mathbf{a}_1}t + e^{i\mathbf{k}\cdot\mathbf{a}_2}t + e^{-i\mathbf{k}\cdot\mathbf{a}_2}t\Big)\\ &= \frac{1}{N}N\Big(\varepsilon_0 + 2t\cos(k_x a) + 2t\cos(k_y a)\Big)\\ &= \varepsilon_0 + 2t\cos(k_x a) + 2t\cos(k_y a)\end{aligned}$$

The corresponding band structure is represented in Fig. 9(Left) within the Brillouin zone: $(k_x, k_y) \in [-\pi/2a, \pi/2a[$. The energy maxima are $\varepsilon_0 \pm 4t$ and the bandwidth is $8|t|$. At half-filling of the band, the Fermi energy is just $\varepsilon_F = \varepsilon_0$. Instead of trying to show the energy for all $\mathbf{k}$-vectors, it is more traditional to show the band structure $\varepsilon(\mathbf{k})$ for $\mathbf{k}$ running along specific directions in the Brillouin zone. This is what is represented in Fig. 9(Right) where $\mathbf{k}$ spans the directions $\mathbf{X\Gamma}$ and $\mathbf{\Gamma M}$. Such a plot gives much less information that Fig. 9(Left) but is much easier to read.

An crucial property is that the ensemble of the $\mathbf{k}$-points such that $\varepsilon(\mathbf{k}) = \varepsilon_0$, namely the Fermi "surface", forms a square at half-filling (see Fig. 9). For exemple the $\mathbf{k}$-points $(0, -\pi/a)$, $(\pi/2a, -\pi/2a)$ and $(\pi/a, 0)$ are all on the Fermi surface and are aligned:

- $\varepsilon(0, -\pi/a) - \varepsilon_0 = t\cos(0) + t\cos(-\pi) = 0$
- $\varepsilon(\pi/2a, -\pi/2a) - \varepsilon_0 = t\cos(\pi/2) + t\cos(-\pi/2) = 0$
- $\varepsilon(\pi/a, 0) - \varepsilon_0 = t\cos(\pi) + t\cos(0) = 0$

As such a large portion of the Fermi surface (one side of the square) can be obtained from another large portion of the Fermi surface (the opposite side of the square) by a translation in reciprocal space of magnitude $\Delta\mathbf{k} = \pm(\pi/a, \pi/a)$ or $\Delta\mathbf{k} = \pm(-\pi/a, \pi/a)$. This property is called **nesting of the Fermi surface**. This means in particular that phonons (vibrational modes) with wavevectors $\Delta\mathbf{k}$ and energy $\hbar\Omega_{vib}$ can scatter ("push") a huge amount of electrons from one side of the BZ to the other side, preserving energy and momentum, and bringing electrons from occupied levels to empty ones as required by Pauli repulsion for fermions. This creates an instability of the Fermi surface by interaction of electrons at the Fermi surface with specific phonons: this instability initiates the superconducting transition.

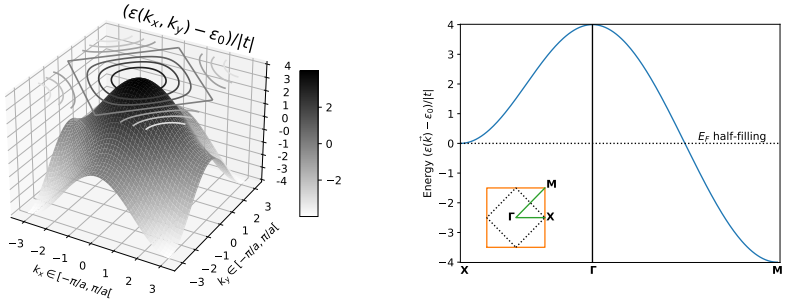


**Figure 9:** Band structure of the 2D square lattice with one atomic orbital per atom. The energy $\varepsilon(k_x, k_y) - \varepsilon_0$ is represented in units of the hoping energy $|t|$. (Left) Band structure for all $\mathbf{k}$-vectors in the BZ. Iso-contours of constant energy are also represented. Notice the square for the $\varepsilon(k_x, k_y) = \varepsilon_0$ isocontour that represents the Fermi surface at half-filling. (Right) Band-structure along specific directions in the BZ as indicated in the Inset by the green lines. $\Gamma$ is the $(k_x, k_y) = (0, 0)$ zone-center, $\mathbf{X}$ is $(k_x, k_y) = (\pi/a, 0)$ and $\mathbf{M}$ is $(k_x, k_y) = (\pi/a, \pi/a)$. The dotted square in the Insert is the ensemble of $\mathbf{k}$-vectors such that $\varepsilon(k_x, k_y) = \varepsilon_0$.

## 5.5 The graphene band structure: see Exercise 23

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov "for groundbreaking experiments regarding the two-dimensional material graphene." Graphene is a 2D materials with 2 carbon atoms (A and B) per unit-cell and an hexagonal structure. We plot below (Fig. 10) in grey a primitive unit cell and the primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. We assume that there is only one atomic orbital $\phi^{at}$ per atom, leading to 2 basis Bloch states:

$$\psi_k^A(r) = \frac{1}{\sqrt{N_C}} \sum_{ml} e^{i\mathbf{k}\cdot(\tau_A + \mathbf{R}_{ml})} \phi_A^{at}(r - \tau_A - \mathbf{R}_{ml})$$

$$\psi_k^B(r) = \frac{1}{\sqrt{N_C}} \sum_{ml} e^{i\mathbf{k}\cdot(\tau_B + \mathbf{R}_{ml})} \phi_B^{at}(r - \tau_B - \mathbf{R}_{ml})$$

with $\mathbf{R}_{ml} = m\mathbf{a}_1 + l\mathbf{a}_2$ a lattice vector pointing to a given unit-cell and $N_C$ the total number of unit cells in the crystal. The basis Bloch states $\psi_k^A$ originates from the periodic repetition of the A-type atomic orbitals modulated by the Bloch phase factor, while $\psi_k^B$ originates from the periodic repetition of the B-type atomic orbitals modulated by the Bloch phase factor. As stated above, one can build one basis Bloch state for each atomic orbital in one unit cell.

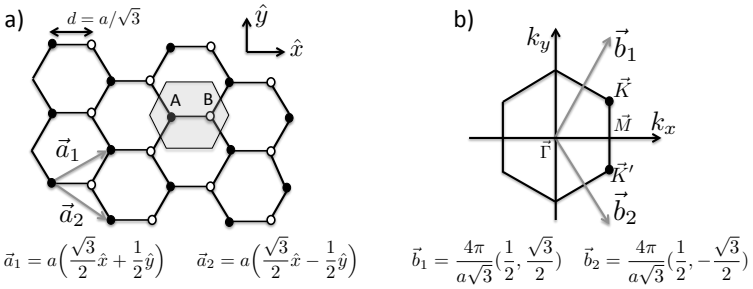


**Figure 10:** (a) Graphene hexagonal lattice with 2 carbon atoms labeled A and B per unit cell. The primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are indicated and a unit-cell is represented in shaded. In this Exercise, the interatomic distance is noted $d$ while -a- is here the length of the primitive lattice vectors. Both are related by $d = a/\sqrt{3}$. For the A-atom in the shaded unit cell, there are 3 first-nearest-neighbours B atoms, one in the same cell and 2 in neighbouring cells. These 2 neighbouring cells are obtained by translating the shaded cell by $-\mathbf{a}_1$ and $-\mathbf{a}_2$, respectively. (b) The hexagonal Brillouin zone with the corner $\mathbf{K} = (2\mathbf{b}_1 + \mathbf{b}_2)/3$. One can verify that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. The primitive lattice vectors make an angle of $60^o$ in real-space and $120^o$ in reciprocal-space.

We must again calculate the Hamiltonian matrix element $H_{AB}$ with here in 2D:

$$\begin{aligned} H_{AB} &= \frac{1}{N_C}\sum_{ml}\sum_{m'l'} e^{-i\mathbf{k}\cdot(\tau_A+\mathbf{R}_{ml})} e^{i\mathbf{k}\cdot(\tau_B+\mathbf{R}_{m'l'})} \langle \phi_A^{at}(r-\tau_A-\mathbf{R}_{ml})|\hat{H}|\phi_B^{at}(r-\tau_B-\mathbf{R}_{m'l'})\rangle \\ &= \frac{e^{i\mathbf{k}\cdot(\tau_B-\tau_A)}}{N_C}\sum_{ml}\sum_{m'l'} e^{i\mathbf{k}\cdot(\mathbf{R}_{m'l'}-\mathbf{R}_{ml})} \langle \phi_A^{at}(r-\tau_A-\mathbf{R}_{ml})|\hat{H}|\phi_B^{at}(r-\tau_B-\mathbf{R}_{m'l'})\rangle \end{aligned}$$

For the A atom in the cell indexed by the lattice vector $\mathbf{R}_{ml}$ (say the grey shaded unit cell in Fig. 10), there are 3 first-nearest-neighbour B-atoms, one in the same cell with $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = 0$, and 2 others such that $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = -\mathbf{a}_1$ and $(\mathbf{R}_{m'l'} - \mathbf{R}_{ml}) = -\mathbf{a}_2$, leading to:

$$\begin{aligned} H_{AB} &= \frac{e^{i\mathbf{k}\cdot(\tau_B-\tau_A)}}{N_C}\sum_{ml}\left(e^{i\mathbf{k}\cdot(\mathbf{0})}t + e^{i\mathbf{k}\cdot(-\mathbf{a}_1)}t + e^{i\mathbf{k}\cdot(-\mathbf{a}_2)}t\right) \\ &= \frac{e^{i\mathbf{k}\cdot(\tau_B-\tau_A)}}{N_C} N_C\left(1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2}\right)t \\ &= t f(\mathbf{k}) e^{i\mathbf{k}\cdot(\tau_B-\tau_A)} \quad \text{with} \quad f(\mathbf{k}) = 1 + e^{-i\mathbf{k}\cdot\mathbf{a}_1} + e^{-i\mathbf{k}\cdot\mathbf{a}_2} \end{aligned}$$

The band structure is given again by the condition:

$$(\varepsilon_k - \varepsilon^0)^2 - |H_{AB}|^2 = 0$$

with $H_{AA} = H_{BB} = \varepsilon^0$ the onsite energy associated with the $\phi^{at}$ atomic orbital

(a carbon $2p_z$ atomic orbital in the case of graphene). Simple algebra leads to:

$$|H_{AB}|^2 = |t|\Big(3 + 2\cos(\mathbf{k}\cdot\mathbf{a}_1) + 2\cos(\mathbf{k}\cdot\mathbf{a}_2) + 2\cos[\mathbf{k}\cdot(\mathbf{a}_2 - \mathbf{a}_1)]\Big)$$

leading to the band structure containing again 2 bands

$$\varepsilon_k = \varepsilon^0 \pm t\sqrt{3 + 2\cos(\mathbf{k}\cdot\mathbf{a}_1) + 2\cos(\mathbf{k}\cdot\mathbf{a}_2) + 2\cos[\mathbf{k}\cdot(\mathbf{a}_2 - \mathbf{a}_1)]}$$

In $\mathbf{k} = \mathbf{0}$ (the Brillouin zone center), one obtains $\varepsilon(\mathbf{k} = \mathbf{0}) = \varepsilon^0 \pm 3t$. In the Brillouin-zone "corner" $\mathbf{K} = (2\mathbf{b}_1 + \mathbf{b}_2)/3$ with $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$, one obtains:

$$\begin{aligned}\cos(\mathbf{K}\cdot\mathbf{a}_1) &= \cos(4\pi/3) = -0.5\\ \cos(\mathbf{K}\cdot\mathbf{a}_2) &= \cos(2\pi/3) = -0.5\\ \cos[\mathbf{K}\cdot(\mathbf{a}_2 - \mathbf{a}_1)] &= \cos(-2\pi/3) = -0.5\end{aligned}$$

leading to:

$$|f(\mathbf{K})|^2 = 0 \quad \Longrightarrow \quad \varepsilon_K = \varepsilon^0$$

that is the same energy for the two $\varepsilon_K^+$ and $\varepsilon_K^-$ solutions : the lower and upper subbands touch at $\mathbf{K}$. The corresponding band structure is indicated in Fig. 11.

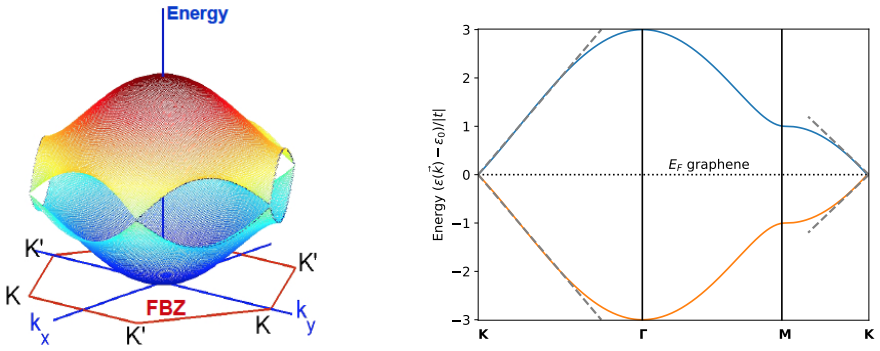


**Figure 11:** Band structure of graphene : the upper and lower subbands (the $\varepsilon_k^+$ and $\varepsilon_k^-$ solutions) touch at the BZ corners $\mathbf{K}$ and $\mathbf{K}'$ with an energy $\varepsilon^0$ that is also the Fermi level energy : in graphene, only the lowest subband is filled. Graphene is called a semi-metal with very few electrons (electrons with a wavevector at the BZ corner) being allowed to "jump" into the empty conduction bands. We represent in (Left) the full band structure and (Right) the band-structure along the **KΓMK** directions (see Fig. 10b). In dashed grey, the linear fit of the bands around the $\mathbf{K}$-vector.

Graphene is in the situation of a half-filled band with the Fermi level located at $\varepsilon_F = \varepsilon^0$. Namely, only the lowest "subband" is filled. The "Fermi surface", that is the surface such that $\varepsilon(\mathbf{k}) = \varepsilon_F = \varepsilon^0$ is limited to discrete $\mathbf{k}$-vectors at the BZ corners. Graphene is called a semi-metal since only very few electrons with a wavevector at the BZ corners can jump into the empty bands.

An interesting property is that the dispersion around $\mathbf{k} = \mathbf{K}$ is linear, namely the energy depends linearly with the norm of $\mathbf{q}$ with $\mathbf{k} = \mathbf{K} + \mathbf{q}$ in the vicinity of $\mathbf{K}$. Indeed the Taylor expansion of the exponential function for the norm of q going to zero yields:

$$e^{-i\mathbf{k}\cdot\mathbf{a}_1} = e^{-i\mathbf{K}\cdot\mathbf{a}_1}e^{-i\mathbf{q}\cdot\mathbf{a}_1} = e^{-i4\pi/3}\Big(1 - i\mathbf{q}\cdot\mathbf{a}_1\Big) = \Big(\frac{-1}{2} + i\frac{\sqrt{3}}{2}\Big)\Big(1 - i\mathbf{q}\cdot\mathbf{a}_1\Big)$$

$$e^{-i\mathbf{k}\cdot\mathbf{a}_2} = e^{-i\mathbf{K}\cdot\mathbf{a}_2}e^{-i\mathbf{q}\cdot\mathbf{a}_2} = e^{-i2\pi/3}\Big(1 - i\mathbf{q}\cdot\mathbf{a}_2\Big) = \Big(\frac{-1}{2} - i\frac{\sqrt{3}}{2}\Big)\Big(1 - i\mathbf{q}\cdot\mathbf{a}_2\Big)$$

so that

$$f(\mathbf{K}+\mathbf{q}) = \frac{i}{2}\mathbf{q}\cdot(\mathbf{a}_1+\mathbf{a}_2) + \frac{\sqrt{3}}{2}\mathbf{q}\cdot(\mathbf{a}_1-\mathbf{a}_2) = \frac{i}{2}\mathbf{q}\cdot(\sqrt{3}a\hat{x}) + \frac{\sqrt{3}}{2}\mathbf{q}\cdot(a\hat{y})$$

namely

$$f(\mathbf{K}+\mathbf{q}) = \frac{a\sqrt{3}}{2}(iq_x + q_y)$$

As a result

$$\varepsilon(\mathbf{K}+\mathbf{q}) - \varepsilon^0 = \pm t\sqrt{|f(\mathbf{K}+\mathbf{q})|^2} = \pm t\frac{a\sqrt{3}}{2}|q| = \pm\hbar v_F|q| \quad \text{with} \quad v_F = \frac{a\sqrt{3}|t|}{2\hbar}$$

The linearity of the dispersion around the **K**-vector (corner of the BZ) is represented in Fig. 11(Right) with the dashed grey lines. In relativistic theory, one has the fundamental relation relating total energy, momentum, and mass of particles : $E^2 = (pc)^2 + (mc^2)^2$. For a massless particle: E = ±pc, namely a linear relation between energy and impulsion. With p = ħq in the vicinity of $\vec{K}$ and replacing the light velocity c by the Fermi velocity: $v_F \simeq$ c/300 in graphene, one obtains a behaviour for graphene electrons at the Fermi energy similar to massless relativistic fermions.

## 5.6 The 1D chain of atoms with s-p hybridization (a model Silicon): see Exercise 19

We study as in class the electronic properties of a 1D chain of N identical atoms within the tight-binding model. The distance between atoms is noted a. In the first question we assume there is one s-orbital $\phi_s^{at}$ per atom (as in class).

1) In the first question, we assume that there is one orbital per atom $\phi_s^{at}(x-na)$ where the subscript "s" indicates a s-type atomic orbital. The onsite energy for these s atomic orbitals is taken to be $\varepsilon_0^s = -\varepsilon_0$ and the nearest neighbour hopping energy is $t = -\gamma$ with $\gamma$ positive. We follow the lecture notes to find the s-band structure:

$$\varepsilon_s(k) = -\varepsilon_0 - 2\gamma\cos(ka) \qquad \text{with} \quad k \in [-\frac{\pi}{a}, \frac{\pi}{a}[$$

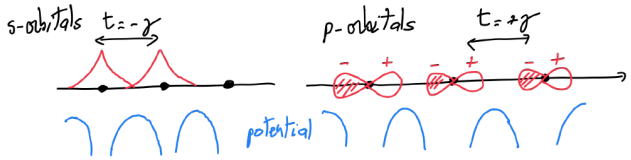


**Figure 12:** (Left) 1D chain with s-orbitals on each atom. (Right) 1D chain with p-orbitals on each atom. The p-orbitals change sign on each side of the atom on which they are centered explaining the change in sign of the hoping term as compared to s-orbitals.

The band-width of the s-band is $4\gamma$ with a minimum at $-\varepsilon_0 - 2\gamma$ and a maximum at $-\varepsilon_0 + 2\gamma$.

2) The second question with p-orbitals is very similar but changing the sign of the onsite and hoping energies, leading to:

$$\varepsilon_s(k) = \varepsilon_0 + 2\gamma\cos(ka) \qquad \text{with} \quad k \in [-\frac{\pi}{a}, \frac{\pi}{a}[$$

The band-width of the p-band is again $4\gamma$ with a minimum at $\varepsilon_0 - 2\gamma$ and a maximum at $\varepsilon_0 + 2\gamma$.

At $\gamma = 0$ then all levels in the s-band have an energy $\varepsilon_0^s = -\varepsilon_0$ and all levels in the p-band have an energy $\varepsilon_0^p = \varepsilon_0$. The two band overlap when the minimum of the p-band and the maximum of the s-band are equal, namely when:

$$-\varepsilon_0 + 2\gamma = \varepsilon_0 - 2\gamma \quad \Longrightarrow \quad \gamma = \varepsilon_0/2$$

3) We now allow the s- and p-electrons to interect with the nearest neighbour interaction $\langle\phi_s^{at}(x-na)|\hat{H}|\langle\phi_p^{at}(x-(n\pm1)a) = \pm\gamma$. There is no onsite interaction between s and p orbitals for symmetry reasons. The system to solve is:

$$\begin{aligned}\alpha H_{ss} + \beta H_{sp} &= \varepsilon\alpha \\ \alpha H_{ps} + \beta H_{pp} &= \varepsilon\beta\end{aligned}$$

The quantity $H_{ss} = \langle\phi_s^{at}(x-na)|\hat{H}|\phi_s^{at}(x-na)\rangle$ is just the energy $\varepsilon_s(k)$ of the first question. Similarly, the quantity $H_{pp} = \langle\phi_p^{at}(x-na)|\hat{H}|\phi_p^{at}(x-na)\rangle$ is just the energy $\varepsilon_p(k)$ of the second question. It remains to calculate the s-p coupling matrix element:

$$\begin{aligned}H_{sp} = \langle\psi_s|\hat{H}|\psi_p\rangle &= \frac{1}{N}\sum_{n=1}^{N}\sum_{m=1}^{N} e^{-ikna}e^{ikma}\langle\phi_s^{at}(x-na)|\hat{H}|\phi_p^{at}(x-ma)\rangle \\ &= \frac{1}{N}\sum_{n=1}^{N}\left(e^{ika}\gamma + e^{-ika}(-\gamma)\right) = \gamma 2i\sin(ka)\end{aligned}$$

For the $\alpha$ and $\beta$ solutions to be non-zero we must have:

$$(H_{ss} - \varepsilon)(H_{pp} - \varepsilon) - |H_{sp}|^2 = 0$$

with $H_{ps} = H_{sp}^*$, leading to:

$$(\varepsilon - \varepsilon_s(k))(\varepsilon - \varepsilon_p(k)) = 4\gamma^2 \sin^2(ka)$$

We can introduce $\varepsilon_{av} = (\varepsilon_s + \varepsilon_p)/2$ and $\Delta\varepsilon = \varepsilon_p - \varepsilon_s$ (dropping for brievety the k index) so that

$$(\varepsilon - \varepsilon_s(k))(\varepsilon - \varepsilon_p(k)) = (\varepsilon - \varepsilon_{av} - \Delta\epsilon/2)(\varepsilon - \varepsilon_{av} + \Delta\epsilon/2)$$

of the form (a-b)(a+b) leading to:

$$(\varepsilon - \varepsilon_s)(\varepsilon - \varepsilon_p) = (\varepsilon - \varepsilon_{av})^2 - (\Delta\epsilon/2)^2$$

so that

$$\varepsilon = \varepsilon_{av} \pm \sqrt{(\Delta\epsilon/2)^2 + 4\gamma^2 \sin^2(ka)}$$