Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

Lecture notes 2020 by Xavier Blase

1 Drude classical model

2 Free electrons in a box

3 The H_2^+ molecule

4 Chapter 4 : Bloch theorem and Brillouin zone

As we have seen in Chapter 3, the knowledge of the atomic orbitals and energy levels, namely the wavefunctions and energies solution of the Schrödinger equation for the isolated atoms, allows to obtain much information about the electronic properties of the crystal made out of such atoms. In particular, the molecular or crystal wavefunction, that describes the electrons delocalized over the entire molecule or entire crystal, can be obtained as a first approximation as a linear combination of the atomic orbitals (LCAO) localized on each atom. However in the case of a crystal with of the order of 10^{23} atoms/cm^3, this would lead to a system of 10^{23} equations for 10^{23} unknown coefficients describing the weight of the crystal wavefunction $|\psi\rangle$ on each atomic orbital $|\phi_i^{at}\rangle$ (at=atomic) where the index (i) labels the atom on which the atomic orbital is localized:

$$|\psi\rangle = \sum_{i=1}^{N} \alpha_i |\phi_i^{at}\rangle \quad \text{with} \quad N \simeq 10^{23}$$

We now demonstrate the Bloch theorem that dramatically simplifies the form of the crystal wavefunction in the case of periodic crystals. We start by introducing the language of crystallography used to describe a solid. Rather than giving the position of each of the $N \simeq 10^{23}$ atoms, we give the position of the atoms in the unit cell together with the primitive lattice vectors allowing to reconstruct the entire crystal from the knowledge of the atoms in the unit cell.

4.1 Absolutely minimal crystallography

Definition: A crystal (or lattice) can be constructed from the knowledge of a minimal number of atoms (called the motif) forming the **unit cell** and from the knowledge of the **primitive lattice vectors** that we will write $(\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3})$. All atoms in the crystal can be obtained by translating the atoms in the unit cell by a linear combination of primitive lattice vectors: $\tau_i + \mathbf{R}_{nlm}$ with τ_i the positions of atoms in the unit cell and $\mathbf{R}_{nlm} = n\mathbf{a}_1 + m\mathbf{a}_2 + l\mathbf{a}_3$ with (n,l,m) integers. The $\mathbf{R_{nlm}}$ are called the **lattice vectors**.

The number and disposition of atoms in the unit cell, the length of the primitive lattice vectors and angles between them, define lattices (called Bravais lattices) with different symmetry properties (cubic lattices if the primitive lattice vectors are orthogonal, hexagonale lattices if e.g. two primitive lattice vectors form a 60^o or 120^o angle, etc.) As well known examples, graphene forms a 2-dimensional (2D) hexagonal lattice with 2-atoms per unit cell, while silicon and diamond form a cubic-face center (FCC) crystal with 2 atoms per unit cell. Experimentally, X-ray diffraction allows to determine all these characteristics (just go to the synchrotron in Grenoble).

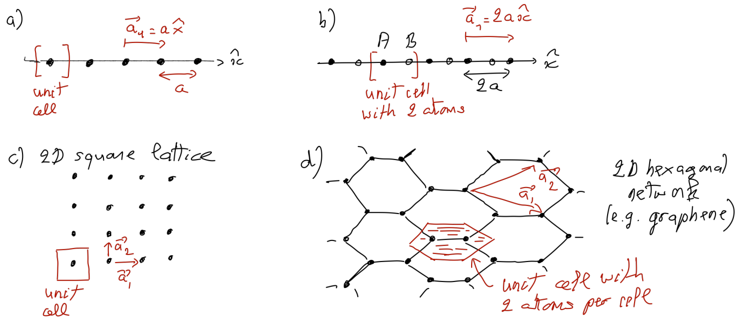

Figure 1: (a) A 1D simple crystal made of identical atoms separated by a length "a" (interatomic distance). By picking one atom forming the unit cell and with a primitive lattice vector $\mathbf{a}_1 = a\hat{\mathbf{x}}$, all atoms can be obtained. Taking $\tau_1 = 0$ the position of the atom in the unit cell, all atoms are in positions $\tau_1 + n\mathbf{a}_1 = na\hat{\mathbf{x}}$. (b) A 1D crystal but with 2 types of alternated atoms (labeled A and B). Here we need to take 2 atoms per cell, one of type A and the other of type B, and the primitive lattice vector is $\mathbf{a}_1 = 2a\hat{x}$ to reconstruct the entire crystal. With τ_A and τ_B the position of the atoms A and B in the unit cell, all atoms of type A are in positions $(\tau_A + n\mathbf{a}_1)$ and all atoms of type B are in positions $(\tau_B + m\mathbf{a}_1)$. (c) A 2D cubic lattice with one atom per cell and orthogonal primitive lattice vectors $\mathbf{a}_1 = a\hat{\mathbf{x}}$ and $\mathbf{a}_2 = a\hat{\mathbf{y}}$. (d) Graphene structure : 2 atoms per unit cell and lattice vectors forming a 60^o angle. The length of the primitive lattice vectors is the 2nd nearest neighbor distance a$\sqrt{3}$ where a is the nearest neighbor interatomic distance.

4.2 The Hamiltonian commutes with the translation operators by any lattice vector

Let's illustrate in Fig. 2 the translation properties of the quantum Hamiltonian:

$$\hat{H}(\mathbf{r}) = \frac{-\hbar^2\nabla^2}{2m_e} + V(\mathbf{r})$$

in the case of a simple 1D crystal made of N identical atoms separated by a distance a. The potential V($\mathbf{r}$) seen by the electrons as a result of the attractive potential from the ions and repulsive potential from the other electrons shows minima at the atomic positions and maxima in between atoms (see potential in blue in Fig. 2). This means as illustrated in the simple 1D case that the potential is invariant by a translation by a distance na, that is a lattice vector for this 1D system. In the general 3D case, this means that :

$$V(\mathbf{r} + \mathbf{R}_{nlm}) = V(\mathbf{r})$$

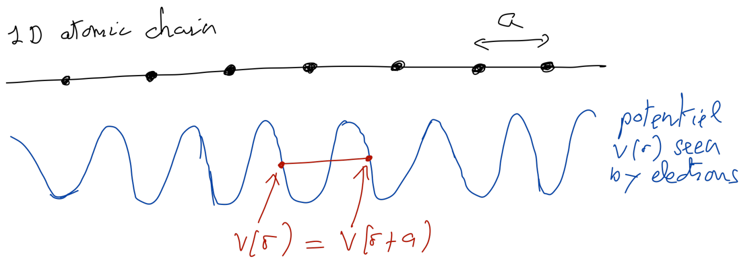

Figure 2: A simple 1D chain of identical atoms. The potential V(r) (in blue) seen by the electrons has its minimum at the atomic position and maximum in the middle of a bond. As a result, V(r+a)=V(r) which means that the potential has the periodicity of the lattice, or is invariant by a translation by a distance na, that is by a lattice vector in this 1D chain.

The same property holds for the kinetic energy operator. As a matter of fact it is obvious that:

$$\frac{d}{dx} = \frac{d}{d(x+a)}$$

that is the derivative operator does not care about the choice of the origin in general. This really means that the kinetic energy operator is invariant by translation. Putting everything together, this means that the Hamiltonian is invariant by a translation by a lattice vector $\mathbf{R}_{nlm}$, namely

$$\hat{H}(\mathbf{r} + \mathbf{R}_{nlm}) = \hat{H}(\mathbf{r}) \quad \text{with} \quad \mathbf{R}_{nlm} = n\mathbf{a}_1 + m\mathbf{a}_2 + l\mathbf{a}_3$$

We can now introduce the translation operator $\hat{T}_{\mathbf{R}_{nlm}}$, namely the translation by a vector $\mathbf{R}_{nlm}$, that acts on any function $f(\mathbf{r})$ as follows:

$$\hat{T}_{\mathbf{R}_{nlm}} f(\mathbf{r}) = f(\mathbf{r} - \mathbf{R}_{nlm})$$

We represent here below (Fig. 3) the action of $\hat{T}_a$ (the translation by a length a) in 1D.

Let's now look at the effect of a translation operator on the action of the Hamiltonian on whatever function:

$$\hat{T}_{\mathbf{R}_{nlm}} \hat{H}(\mathbf{r}) f(\mathbf{r}) = \hat{H}(\mathbf{r} - \mathbf{R}_{nlm}) f(\mathbf{r} - \mathbf{R}_{nlm})$$

Using $\hat{H}(\mathbf{r} - \mathbf{R}_{nlm}) = \hat{H}(\mathbf{r})$ and $f(\mathbf{r} - \mathbf{R}_{nlm}) = \hat{T}_{\mathbf{R}_{nlm}} f(\mathbf{r})$ one obtains:

$$\hat{T}_{\mathbf{R}_{nlm}} \hat{H}(\mathbf{r}) f(\mathbf{r}) = \hat{H}(\mathbf{r}) \hat{T}_{\mathbf{R}_{nlm}} f(\mathbf{r})$$

Since this is true for any function f, this means that $\hat{T}_{\mathbf{R}_{nlm}} \hat{H} = \hat{H} \hat{T}_{\mathbf{R}_{nlm}}$. This means that the two operators commute: $[\hat{H}, \hat{T}_{\mathbf{R}_{nlm}}] = 0$.

We can now use a theorem of quantum mechanics stating that if two operators $\hat{A}$ and $\hat{B}$ commutes, then there exists a common set of eigenvectors, namely:

Theorem. If $[\hat{A}, \hat{B}] = 0$, then it exists a set of states ψ_n such that: $\hat{A}\psi_n = a_n \phi_n$ and $\hat{B}\psi_n = b_n \psi_n$ (the eigenvectors are the same but not necessarily the eigenvalues) The index (n) numbers the different eigenvectors $|\psi_n\rangle$.

Let's apply this result to the Hamiltonian $\hat{H}$ and the translation operator $\hat{T}_{\mathbf{R}_{nlm}}$ where $\mathbf{R}_{nlm}$ is a lattice vector of the crystal (or lattice). There exist eigenstates $|\phi_n\rangle$ of the Hamiltonian, namely wavefunctions describing the electrons in the crystal, that are also eigenstates of the translation operators by a lattice vector. That is:

$$\hat{H}|\psi_n\rangle = \varepsilon_n |\psi_n\rangle \quad \text{and} \quad \hat{T}_{\mathbf{R}_{nlm}} |\psi_n\rangle = c_n(\mathbf{R}_{nlm}) |\psi_n\rangle$$

These eigenstates of the Hamiltonian and of the translation operators are called the Bloch states, from Felix Bloch, Swiss-US physicist who obtained the Nobel prize for the RMN.

Note. We will use the notation ψ for wavefunctions describing electrons in crystals and ϕ for atomic orbitals.

We can gather much information on the translation operator eigenvalues $c_n(\mathbf{R}_{nlm})$. Looking at Fig. 3, it is obvious that a translation does not change the shape of a wavefunction, namely does not change its normalization. This

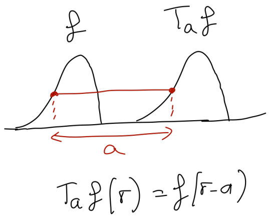

Figure 3: Action of the 1D translation operator T_a (translation by a length a) on a function f(r).

means that if $|\psi_n\rangle$ is normalized, then $\hat{T}_{\mathbf{R}_{nlm}}|\psi_n\rangle = c_n(\mathbf{R}_{nlm})|\psi_n\rangle$ is normalized and necessarily $|c_n(\mathbf{R}_{nlm})|^2 = 1$. This means that the coefficient c is just a phase factor:

$$c_n(\mathbf{R}_{nlm}) = e^{if_n(\mathbf{R}_{nlm})}$$

with $f_n(\mathbf{R}_{nlm})$ some function of the translation vector. Further it is also obvious that a translation by $2\mathbf{R}_{nlm}$ is equivalent to 2 successive translations by $\mathbf{R}_{nlm}$, namely: $\hat{T}_{2\mathbf{R}_{nlm}} = \hat{T}_{\mathbf{R}_{nlm}}\hat{T}_{\mathbf{R}_{nlm}}$ from which we deduce easily that: $c_n(2\mathbf{R}_{nlm}) = c_n(\mathbf{R}_{nlm})c_n(\mathbf{R}_{nlm})$, that is:

$$e^{if_n(2\mathbf{R}_{nlm})} = e^{if_n(\mathbf{R}_{nlm})}e^{if_n(\mathbf{R}_{nlm})} = e^{i2f_n(\mathbf{R}_{nlm})}$$

The only possibility for this to be true is that the phase f is a linear function :

$$f_n(\mathbf{R}_{nlm}) = -\mathbf{k}\cdot\mathbf{R}_{nlm} \quad \Longrightarrow \quad \boxed{c_n(\mathbf{R}_{nlm}) = e^{-i\mathbf{k}\cdot\mathbf{R}_{nlm}}}$$

with $\mathbf{k}$ some constant vector (a scalar k in 1D). We deduce that :

$$\hat{T}_{\mathbf{R}_{nlm}}\psi_n(\mathbf{r}) = \psi_n(\mathbf{r}-\mathbf{R}_{nlm}) \quad \text{and} \quad \hat{T}_{\mathbf{R}_{nlm}}\psi_n(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{R}_{nlm}}\psi_n(\mathbf{r})$$

that is : $\psi_n(\mathbf{r}-\mathbf{R}_{nlm}) = e^{-i\mathbf{k}\cdot\mathbf{R}_{nlm}}\psi_n(\mathbf{r})$. Taking $\mathbf{R}_{nlm} \to -\mathbf{R}_{nlm}$ one obtains the first Bloch theorem:

> **Bloch theorem (first)**: the electronic eigenstates $|\psi\rangle$ of the Hamiltonian of a crystal can be taken to be Bloch states that verify:
>
> $$\psi_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_{nlm}) = e^{i\mathbf{k}\cdot\mathbf{R}_{nlm}}\psi_{\mathbf{k}}(\mathbf{r})$$
>
> where $\mathbf{k}$ are called Bloch wavevectors, or wavevectors in short, and $\mathbf{R}_{nlm}$ are the lattice vectors.

Note that we started to use the notation $|\phi_n\rangle$, where n was a generic index numbering the Bloch states, and we now write $\phi_{\mathbf{k}}$ where the wavenumber $\mathbf{k}$ indexes the different Bloch states.

We can now formulate a consequence that is called the second Bloch theorem (the most useful):

> **Bloch theorem (2nd)**: The Bloch states can be written :
>
> $$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$$
>
> where $u_{\mathbf{k}}$ has the full periodicity of the lattice, namely : $u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}_{nlm}) = u_{\mathbf{k}}(\mathbf{r})$ with $\mathbf{R}_{nlm}$ any lattice vector.

Demonstration. We consider the function $u_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{r})$ on which we apply a translation by a lattice vector:

$$\hat{T}_{\mathbf{R}_{nlm}}u_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_{nlm})}\psi_{\mathbf{k}}(\mathbf{r}-\mathbf{R}_{nlm})$$

Using the first Bloch theorem : $\psi_{\mathbf{k}}(\mathbf{r}-\mathbf{R}_{nlm}) = e^{-i\mathbf{k}\cdot\mathbf{R}_{nlm}}\psi_{\mathbf{k}}(\mathbf{r})$ so that:

$$\hat{T}_{\mathbf{R}_{nlm}} u_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_{nlm})} e^{-i\mathbf{k}\cdot\mathbf{R}_{nlm}}\psi_{\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})$$

which demonstrates that $u_{\mathbf{k}}$ is periodic by a lattice vector. This is a crucial result that will dramatically simplify the search for the wavefunctions, and associated energies, for electrons in a crystalline solid. This is what we now illustrate in the case of the 1D chain of atoms with one atomic orbital per atom.

4.3 The 1D chain of identical atoms with one atomic orbital per atom

We now consider a chain of N identical atoms with one atomic orbital ϕ^{at} (at=atom) per atom. Atoms are separated by a distance (a) and the n-th atom is in position na. This is just a generalization of the H_2 molecule with one ϕ^{at}_{1s} atomic orbital per atom : we "just" go from 2 atoms to N atoms with N $\simeq 10^{23}$. As we discussed, writing the crystal wavefunction as a linear combination of these N atomic orbitals would lead to a huge number of coefficients to be found. This is impracticable.

We now use the Bloch theorem. We know that the electronic wavefunction can be written:

$$\psi_k(r) = e^{ikr}u_k(r) \quad \text{with k the (scalar) wavevector in 1D}$$

with u_k a periodic function. We use here in 1D the position r as a scalar (we could use x). Let's try to write $u_k(r)$ as a linear combination of atomic orbitals (LCAO):

$$u_k(r) = \sum_{n=1}^{N} \alpha_n \phi^{at}(r-na)$$

where α_n is the weight (coefficient) of u_k on the atomic orbital $\phi^{at}(r-na)$ located on the atom in position na. Considering now the Fig. 4(a), it is obvious that if the α_n are different, then the function $u_k(r)$ just cannot be periodic, namely $u_k(r+a) \neq u_k(r)$. For u_k to be periodic, the only possibility is that all α_n are the same (see Fig. 4b). This really means that the only possible combination is:

$$u_k(r) = A\sum_{n=1}^{N} \phi^{at}(r-na) \quad \text{with } A = \alpha_n \quad \text{for all n.}$$

that is

$$\psi_k(\mathbf{r}) = Ae^{ikr}\sum_{n=1}^{N} \phi^{at}(r-na)$$

This is extremely simple : there is just one coefficient A to look for and we will obtain it by normalization. By using Bloch theorem, we could go from 10^{23} unknown α_n to only one easy to find.

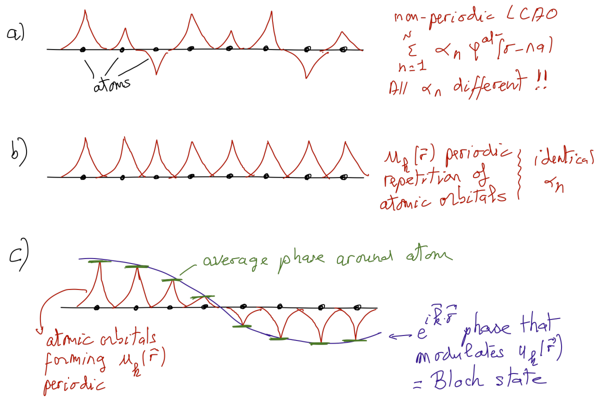

Figure 4: (a) Non periodic linear combination of atomic orbitals $\sum_{n=1}^{N} \alpha_n \phi^{at}(r-na)$ with different coefficients α_n. (b) Only possibility to have a periodic function $u(\mathbf{r})$ written as a linear combination of atomic orbitals : the weight α_n on each atomic orbital must be the same. (c) Bloch state $\psi_k(\mathbf{r}) = e^{ikr}u_k(r)$ where the phase factor modulates the periodic u(r) function. In green, we average the phase factor in the vicinity of an atom to its value at the atomic position (tight-binding approximation).

4.3.1 Normalization and the tight-binding approximation for the overlap matrix

Let's impose normalization for the Bloch state $|\psi_k\rangle$, namely $\langle\psi_k|\psi_k\rangle = 1$. Expanding both the bra and the ket as a function of the atomic orbitals, one obtains:

$$\int dr \left(A^* e^{-ikr} \sum_{n=1}^{N} [\phi^{at}]^*(r-na) \right) \left(A e^{ikr} \sum_{m=1}^{N} \phi^{at}(r-na) \right) = 1$$

taking care of the complex conjugation for the bra. We can see that the two phase factors $e^{-ikr}e^{ikr}$ cancel each other and one is left with:

$$|A|^2 \sum_{n=1}^{N} \sum_{m=1}^{N} \langle \phi_n^{at} | \phi_m^{at} \rangle = 1$$

with the notation $\phi_n^{at}(r) = \phi^{at}(r-na)$ that is the atomic orbital located on atom (n) in position na (idem for m). As defined in the H_2 lecture, the matrix elements $\langle \phi_n^{at} | \phi_m^{at} \rangle$ are called the **overlap matrix elements** noted S_{nm}. It is a measure of how much the two atomic orbitals overlap:

$$S_{nm} = \int dr \phi_n^{at}(r) \phi_m^{at}(r) = \int dr \phi^{at}(r-na) \phi^{at}(r-ma)$$

where we assume real atomic orbitals, and thus no need for the complex conjugate for the bra. If the two orbitals are on the same atom (n=m) then by normalization of the atomic orbitals one has $S_{nn} = 1$. We say that it is the onsite (on-the-same-site) overlap matrix element. If the two orbitals are on first nearest neighbors atoms (m=n±1) then the overlap is small and we write $S_{n,n\pm1} = s$ with s small. If the two orbitals are on atoms located far away (beyond the first neighbor) then there is no point in space where the two orbitals are nonzero together, and $S_{nm} = 0$. The 3 scenarios are summarized in Fig. 5.

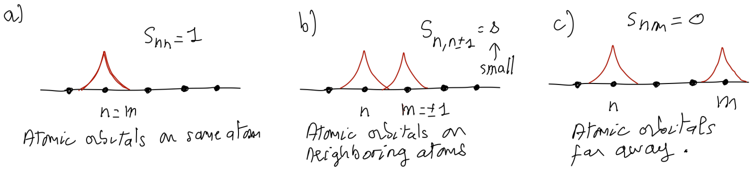

Figure 5: Atomic orbitals ϕ_n^{at} and ϕ_m^{at} are (a) on the same atom, (b) on first-nearest neighbor atoms, and (c) far away.

In the **tight-binding approximation**, we will neglect the first nearest-neighbour $S_{n,n\pm1} = s$ as compared to the onsite $S_{nn} = 1$ term. By tight-binding, we mean that the atomic orbitals are strongly bound to the nuclei, namely rather localized around the nuclei with a limited extent towards neighboring atoms. As a result:

$$\boxed{S_{nm} = \delta_{nm} \qquad \text{Overlap matrix elements in the tight-binding approximation}}$$

with δ_{nm} the Kronecker symbol (δ_{nm}=1 if n=m and δ_{nm}=0 otherwise). As a result, in the tight-binding approximation, the normalization condition becomes:

$$|A|^2 \sum_{n=1}^{N} \sum_{m=1}^{N} \delta_{nm} = 1 \quad \Longrightarrow \quad N|A|^2 = 1 \quad \Longrightarrow \quad A = \frac{1}{\sqrt{N}}$$

(within a constant phase factor). As a result the Bloch states, namely the electronic wavefunctions for this 1D chain of atoms with one atomic orbital per atom, are just:

$$\psi_k(r) = \frac{1}{\sqrt{N}} e^{ikr} \sum_{n=1}^{N} \phi^{at}(r - na)$$

The dependence on the wavevector k means that there are several possible Bloch states that can describe electrons in the crystal. Remember that we have of the order of 10^{23} electrons in the crystal and that we can put only 2 electrons (spin up and down) in one quantum state described by one Bloch state with a given k-vector.

4.3.2 Simplifying the phase factor in the tight-binding approximation

We will keep simplifying the calculations by making the approximation that the e^{ikr} in factor of some atomic orbital $\phi^{at}(r-na)$, centered on atom in position na, can be approximated by e^{ikna}. Considering Fig. 4(c) above, we assume that the phase factor e^{ikr} varies rather smoothly on the extent of the atomic orbital $\phi^{at}(r-na)$ so that we can approximate it by its value at the atomic position (see horizontal green lines in Fig. 4(c) above). As a result:

$$\psi_k(r) = \frac{1}{\sqrt{N}} e^{ikr} \sum_{n=1}^{N} \phi^{at}(r-na) \simeq \boxed{\frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \phi^{at}(r-na)}$$

The terms e^{ikna} are now constants and no longer functions of the position (r).We will be working with this tight-binding form in the following.

4.3.3 The energy ε_k and the band-structure for the 1D chain

We now want to know the energy for an electron described by the Bloch state $\psi_k(r)$. This is very easy now since $|\psi_k\rangle$ is a normalized eigenstate of the Hamiltonian :

$$\hat{H}|\psi_k\rangle = \varepsilon_k|\psi_k\rangle \quad \Longrightarrow \quad \langle\psi_k|\hat{H}|\psi_k\rangle = \varepsilon_k\langle\psi_k|\psi_k\rangle = \varepsilon_k$$

Using the tight-binding approximation, one obtains:

$$\varepsilon_k = \frac{1}{N} \sum_{n=1}^{N} \sum_{m=1}^{N} e^{-ikna} e^{ikma} \langle\phi_n^{at}|\hat{H}|\phi_m^{at}\rangle$$

where the minus sign in the phase factor e^{-ikna} comes from the complex conjugation for the bra. Since the phase factors (e.g. e^{-ikna}) are constants, they could be taken out of the integral over space $\langle\phi_n^{at}|\hat{H}|\phi_m^{at}\rangle$. We now have the matrix elements of the Hamiltonian in the atomic basis:

$$H_{nm} = \langle\phi_n^{at}|\hat{H}|\phi_m^{at}\rangle \qquad \textbf{Hamiltonian matrix elements}.$$

As for the H_2 molecule we will distinguish 3 cases (see Fig. 6):

- $m = n \quad \Longrightarrow \quad H_{nn} = \varepsilon_0$ (onsite matrix element).
- $m = n \pm 1 \quad \Longrightarrow \quad H_{nm} = t$ (hopping matrix element between nearest-neighbors).
- $|m-n| > 1 \quad \Longrightarrow \quad H_{nm} = 0$ (no possible hopping : the atoms are too distant !)

As explained in the case of the H_2 molecule, if we know how to write the atomic orbitals, and since we know how to write the Hamiltonian, the energies ε_0 (onsite energy) and t (hopping) can be easily calculated by a standard computer.

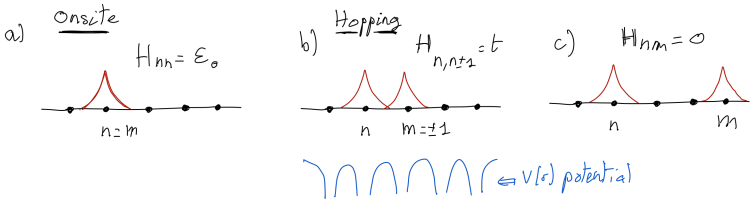

Figure 6: Atomic orbitals ϕ_n^{at} and ϕ_m^{at} are (a) on the same atom, (b) on first-nearest neighbor atoms, and (c) far away.

We can now calculate the energy ε_k by considering the 3 possible cases (m=n-1,n,n+1) for a given n in the double sum:

$$\begin{aligned} \varepsilon_k &= \tfrac{1}{N} \textstyle\sum_{n=1}^{N} \; \sum_{m=n,n\pm1} \; e^{ik(m-n)a} H_{mn} \\ &= \tfrac{1}{N} \textstyle\sum_{n=1}^{N} \; \left(e^{ik(0)a} \varepsilon_0 + e^{ika} t + e^{-ika} t \right) \end{aligned}$$

where the first, second and third term in the parenthesis correspond to (m=n), (m=n+1) and (m=n-1), respectively. Since the terms in the parenthesis do no depend on the index (n), the $\sum_{n=1}^{N}$ leads to N-times the same factor, and:

$$\varepsilon_k = \frac{1}{N} \times N \times \left(\varepsilon_0 + t(e^{ika} + e^{-ika}) \right) = \varepsilon_0 + 2t\cos(ka)$$

This confirms the qualitative discussion given above : the N atomic orbitals yield a **band of energy** with a **band width** proportional to the hopping matrix element $H_{n,n\pm1} = t$. Again, we did not have to solve a huge system, just apply the Bloch theorem !! The dependence and the plot of the energy ε_k as a function of k is called the **band structure** of the system or the dispersion relation between energy and wavevector (see Fig. 7b).

We close this paragraph by a summary of the tight-binding approximations we adopted to conduct the calculation of the properties of this 1D chain of atoms with one orbital per cell.

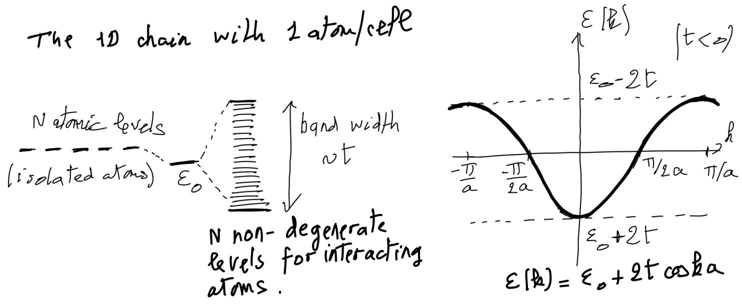

Figure 7: (Left) Qualitative discussion: upon interaction, N isolated atomic energy levels lead to a band of N non-degenerate levels with a band width proportional to the hopping energy t. (Right) Band-structure, i.e. the electronic energy ε_k as a function of k, for the 1D chain of atoms with 1 atom/cell and one atomic orbital per atom. The band width is precisely 4t, confirming the qualitative picture.

Summary of tight-binding approximations

The Bloch states can be approximated by :

$$\psi_k(r) \simeq \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikna} \phi^{at}(r - na)$$

with the phase factor e^{ikr} taken at the atomic position na when in factor with $\phi^{at}(r - na)$.

The overlap matrix elements can be approximated as:

$$S_{nm} = \langle \phi_n^{at} | \phi_m^{at} \rangle = \delta_{nm}$$

The Hamiltonian matrix elements are given by:

$$\begin{aligned} H_{nm} = \langle \phi_n^{at} | \hat{H} | \phi_m^{at} \rangle &= \quad \varepsilon_0 \quad (m = n) \\ &= \quad t \quad (m = n \pm 1) \\ &= \quad 0 \quad (|m - n| > 1) \end{aligned}$$

We will keep the same kind of approximations in all cases treated during this class.

Question : the energy ε_k in Fig. 7b is a continuous function of k. What we really need however are N discrete energy levels originating from the interaction between N atomic levels ! How can we go from a continuous function to a discrete set of N energies ? We answer this question here below by introducing the

Brilluoin zone and by descretizing the k-vectors thanks to boundary conditions as we did for the free-electrons-in-a-box model.

Complement : highest known superconducting temperature T_C with hydrogen under pressure. We have studied here above a crystal made out of simple atoms with one orbital per atom following our study of H_2^+. This may seem a bit too simple but in fact recent experiments, following theoretical predictions, have shown that the material with the largest T_C on earth (about 200 K) is just "metallic hydrogen", that is hydrogen atoms put under pressure ["Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system", A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov and S. I. Shylin, Nature volume 525, pages 73-76 (2015)]. This is much larger than the previous record of about 170 K for complex "cuprates" such as Hg-Ba-Ca-Cu-O also put under pressure. Putting pressure is a way to force H_2 molecules (which are very stable) to form a hydrogen crystal with a hopping parameter (t) that increases under pressure, that is increases when the distance between atoms decreases : it is the hopping parameter (t) that is responsible for electron delocalization over the entire crystal, namely a metallic character that is needed for a superconducting transition. Hydrogen is not alone in these high T_C compounds, mixed with some sulfur in the cited Nature paper, but really it is hydrogen that is responsible for the exceptional superconducting properties. Towards room temperature T_C at ... ambiant pressure ?

4.4 Discretizing the k-vectors : the Brillouin zone (BZ)

We start this section by considering the case discussed here above of the 1D chain of atoms with one-atom/cell. The primitive lattice vector is $\mathbf{a}_1 = a\hat{x}$ where a is the interatomic distance. Let's introduce now the scalar b=$2\pi/a$. It is homogeneous to the inverse of a length, that is homogeneous to a wavevector k in 1D (in 1D scalars and vectors are the same). If we now consider the energies for electrons in the 1D chain, one discovers easily that:

$$\varepsilon(k+b) = \varepsilon_0 + 2t\cos[(k+b)a] = \varepsilon_0 + 2t\cos[ka+2\pi] = \varepsilon_0 + 2t\cos[ka] = \varepsilon(k)$$

The two wavevectors k and (k+b) give the same energy ! We can even go further by considering now the corresponding Bloch states for this 1D chain:

$$\begin{aligned}\psi_{k+b}(r) &= \frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{i(k+b)na}\phi^{at}(r-na) \\ &= \frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{i(kna+n2\pi)}\phi^{at}(r-na) \\ &= \frac{1}{\sqrt{N}}\sum_{n=1}^{N} e^{ikna}\phi^{at}(r-na) = \psi_k(r)\end{aligned}$$

We see that the two quantum states $\psi_{k+b}(r)$ and $\psi_k(r)$ are the same quantum states and should not be counted twice. Similarly $\psi_{k+nb}(r)$ and $\psi_k(r)$ are the same quantum states (n some integer). One way to make sure that we do not count several times the same quantum state is to restrict k to $[-b/2, +b/2[$ or $]-b/2, +b/2]$. By doing so we are sure that 2 k-vectors in this interval cannot differ by b (since the range is smaller than b if one excludes one of the extreme values $\pm b/2$). Further, it is easy to see that any k-vector outside $[-b/2, +b/2[$ is equal to a given k-vector inside $[-b/2, +b/2[$ plus or minus some multiple of b, namely is equivalent to a k-vector inside $[-b/2, +b/2[$. In short, only k-vectors in $[-b/2, +b/2[$ need to be considered. This k-vector interval is called the **Brillouin zone** in reciprocal space for this 1D chain of atoms with 1-atom/cell (from Léon Brillouin a French physicist).

Formal definition of the Brillouin zone.

The space of the **k**-wavevectors is called the **reciprocal space.** We define the **reciprocal space primitive lattice vectors** $(\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3)$ that are related to the primitive lattice vectors $(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ of the crystal (in real-space) by the condition:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$$

The set of **k**-vectors labeled $\mathbf{G}_{nlm} = n\mathbf{b}_1 + l\mathbf{b}_2 + m\mathbf{b}_3$ form the lattice vectors of the reciprocal space lattice. The Brillouin zone is the unit-cell of the reciprocal space lattice. Synchrotron diffraction gives a representation of such a reciprocal space lattice.

All this is very formal so let's just simply define the Brillouin zone for the systems we will be considering in the next lectures, namely the 1D chain with 1 and 2 atoms per cell and the 2D square lattice (see Fig. 9 below). We will also be considering the graphene system (as an exercise) which is a 2D hexagonal lattice with 2 atoms per cell. Its unit cell and Brillouin zone are represented on the right.

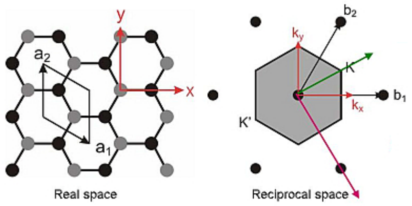

Figure 8: Unit cell and Brillouin zone of graphene (the 2 atoms in the unit cell are both carbon atoms) or hexagonal boron-nitride (the 2 atoms in the unit cell are B and N).

Discretization of k-vectors.

Back to our study of the 1D chain with 1 atom/cell, we could reduce the k-vectors to the Brillouin zone $[-\frac{b}{2}, \frac{b}{2}[= [-\frac{\pi}{a}, \frac{\pi}{a}[$. However we still have a continuum energy $\varepsilon(k)$, namely an infinite number of possible energy levels, not N discrete energy levels as expected from the linear combination of N atomic orbitals. As we did for the free-electrons-in-a-box model, we use now boundary

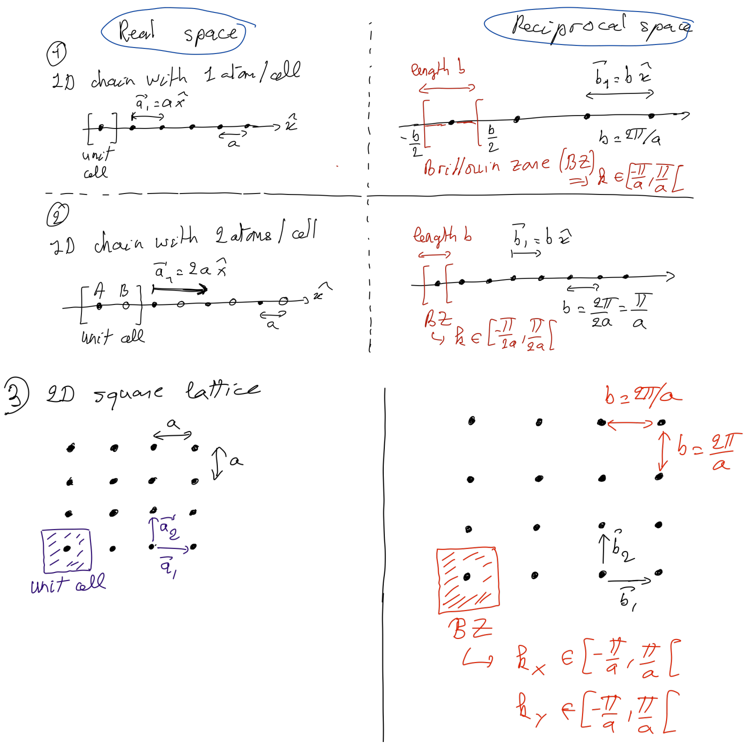

Figure 9: Real-space crystal and reciprocal space for (1) the 1D chain of atoms with 1 atom/cell, (2) the 1D chain of atoms with 2 atoms/cell, (3) the 2D square lattice.

conditions to discretize the possible k-vectors inside the Brillouin zone. The idea is that the electrons do not go spontaneously outside the crystal so that the wavefunction $\psi_k(r)$ must cancels on the ”surface” of the crystal. For a 1D crystal with N atoms and an interatomic distance -a- we can assume that the crystal starts at r=0 and stops at r=L with L=Na. We could thus impose $\psi_k(r=0)=0$ and $\psi_k(r=Na)=0$.

A preferred way of imposing boundary conditions is to use periodic boundary conditions (PBC) or Born and von Karman (BVK) conditions that can be ”pictured” by folding the surface onto itself in all directions. This is what is illustrated in Fig. 10(a,b) in the case of our finite 1D chain. The nice thing about this simple trick is that you can have a finite size crystal that is fully periodic. In the case of the ”straight” 1D chain, a translation by $\mathbf{a}_1 = a\hat{x}$ does not yield exactly the same crystal at the surface, so that the Bloch theorem based on the commutation of the Hamiltonian with the translation operator is somehow violated at the surface. This is actually not a big problem (there are 2 atoms at the surface versus typically 10^{23} in the chain) but it is slightly ”inelegant”.

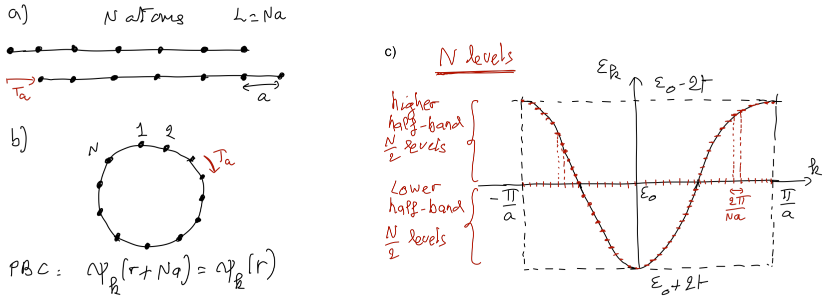

Figure 10: (a) Chain of N atoms not strictly invariant by a translation. (b) Chain with periodic boundary condition finite and periodic by translation. (c) Discretized k-points and energy levels.

The periodic boundary conditions where the crystal is folded onto itself allows to have a finite (N) number of atoms and perfect translation symmetry.

The periodic boundary condition implies that the positions r and $(r + L)$ are exactly the same positions, so that one need to impose: $\psi_k(r) = \psi_k(r + Na)$. Using the 2nd Bloch theorem this means that: $e^{ikr}u(r) = e^{ik(r+Na)}u(r + Na)$, namely $e^{ikr}u(r) = e^{ikNa}e^{ikr}u(r)$ where we used the fact that $u(r)$ is fully periodic, that is $u(r + Na) = u(r)$. Therefore $e^{ikNa} = 1$ and $kNa = n2\pi$ where n is an integer $\Longrightarrow k = n(2\pi/Na)$. As a result of the discretization of the k-vectors, the number of k-vectors in the Brillouin zone of length $b = 2\pi/a$ is just

$$\frac{2\pi/a}{2\pi/Na} = N$$

This is exactly the result we were expecting. There are only N possible energy levels $\varepsilon(k)$ associated with the N possible values of k.

The band structure ε_k is thus no longer a continuum of energies, but a set of N discrete energy levels (see Fig. 10c). The energy spacing between these levels is extremely small, since it is equal to the band width proportional to t (at most a few eVs) divided by N which is of the order of 10^{23} in solids. This is dramatically small, much smaller than room temperature, and just cannot be seen experimentally in macroscopic systems. Experimentally, the band structure can be obtained by photoemission that can be performed e.g. at the ESRF synchrotron in Grenoble. However, it is crucial to know how many levels are available in the band if we want to know how to put the electrons on the energy levels and see if the system is metallic or insulating. This is what we now discuss.

Half-filled band. We now assume that there is one electron per atomic level in the isolated atoms limit, that is a total of N electrons in the system. Since one energy level can accommodate 2 electrons (one spin up, one spin down), the N electrons will occupy the lowest (N/2) levels in the atomic chain. The band is half-filled. The Fermi level ε_F, defined as the energy of the highest occupied level, is the energy in the middle of the band, that is $\varepsilon_F = \varepsilon_0$.

The band gap between the highest occupied and lowest unoccupied level is as discussed above dramatically small. **The half-filled band is metallic**. Systems like alkali metals (lithium, sodium, potassium, etc.) with a single electron in the highest occupied atomic 2s, 3s or 4s levels are metallic because of this.

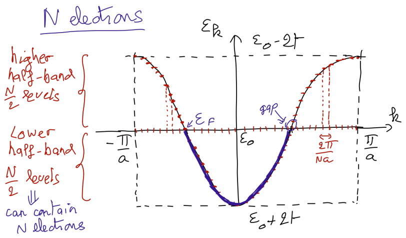

Figure 11: Occupied levels in blue.

Filled band. We now assume that there are two electrons per atomic level in the isolated atoms limit, that is a total of 2N electrons on the atomic chain. All N levels in the band will be occupied. The band is completely filled and we do not know how far above in energy is the next unoccupied level. The next unoccupied level belongs to a band located higher in energy and formed by a linear combination of higher atomic levels. This is the well known case of diamond where two bands originating from the 2s and 2p atomic levels can be formed. Similarly, the silicon band structure originates from the bands formed by the 3s and 3p electrons. This is what is illustrated in Fig. 12.

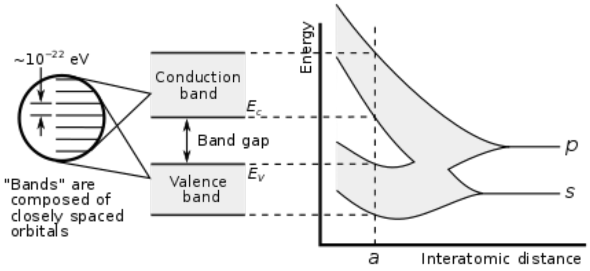

Figure 12: Evolution of the s and p bands in diamond or silicon as a function of the interatomic distance. Energy levels are shaded in grey. The experimental interatomic distance is indicated by the vertical dashed line indicating a non-zero gap (from *https://en.wikipedia.org/wiki/Electronic_band_structure*).

At very large interatomic distance, the atoms are isolated and there are discrete atomic s and p levels separated by an energy $\Delta\varepsilon_{sp}^{at} = \varepsilon_p^{at} - \varepsilon_s^{at}$ (with at = atom) When atoms are brought closer to each other, the s-band and p-bands widens proportionally to the hopping energy t that increases when the distance between atoms decreases. At some point, when t becomes comparable to $\Delta\varepsilon_{sp}^{at}$, the gap between the s- and p-bands closes and the system becomes metallic. However, in the case of diamond and silicon, bringing the atoms even closer induces a reopening of the gap by a phenomenon of "sp-hybridization" and for experimental interatomic distances "a" (see vertical dashed line in Fig. 12), silicon and diamond are a semiconductor and insulator, respectively. This phenomenon of sp-hybridization is treated in a simplified way in Exercise 19 (The 1D chain of atoms with s-p hybridization : a model Silicon).

Complement: Silicon band structure. We provide in Fig. 13 the band structure of silicon along high-symmetry directions in the Brillouin zone (BZ) represented in the left. Silicon crystallizes in a face-centered cubic crystal with 2-atoms/cell and the corresponding Brillouin zone of independent **k**-vectors is a "truncated octahedron". High-symmetry **k**-points in the BZ are given names and the energy levels $\varepsilon_{n\mathbf{k}}$ are plotted along directions connecting these high-symmetry **k**-points. In the plot given, the zero of energy is set to the top of the occupied bands, called also the valence bands. The band gap is shaded in grey. Above the band gap are the empty bands (or conduction bands). One can see that the band width of the valence bands is of the order of 12 eVs while the band gap is of about 1.1 eV.

The index "n" in $\varepsilon_{n\mathbf{k}}$ indicates different bands : with the 3s, $3p_x$, $3p_y$, $3p_z$ atomic levels one can generate the four occupied valence bands represented in the picture (in the **k**-points U and K the 4 bands are non-degenerate and are all visible. For other **k**-points they have the same energy: they are degenerate and one see less bands). With these 4 bands, the Brillouin zone can accommodate N-times 8 electrons, where N is the number of unit cells and 8 the number of 3s, $3p_x$, $3p_y$, $3p_z$ electrons given by the 2 atoms in one unit cell.

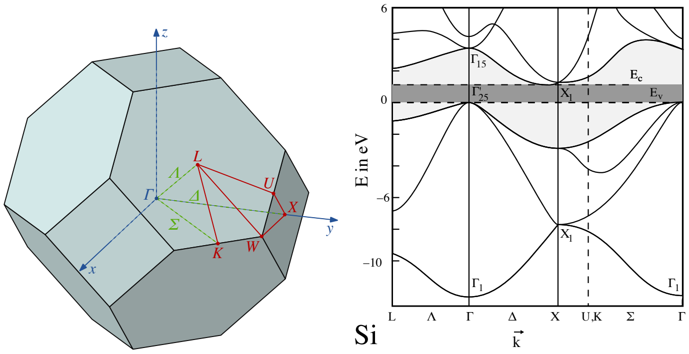

Figure 13: Brillouin zone and band structure of silicon. In grey the band gap between occupied and unoccupied levels (about 1.1 eV). The bands originating from the 1s and 2s, 2p atomic levels are completely filled and much much lover in energy (not represented). They are called the core bands.

As a final remark, one note that the highest occupied level $\varepsilon_{n\mathbf{k}}$ can be found for the Brillouin zone-center $\mathbf{k} = (0, 0, 0)$ wavevector (labelled the Γ point), while the lowest energy unoccupied level can be obtained for a **k**-point somewhere in between Γ and X. The gap is said to be **indirect**. This is an important matter for optical absorption since a photon, characterized by a large energy but an extremely small wavevector, can change by absorption the energy but not the wavevector of an electron.