Solid state physics : electrons and phonons

Master Nanosciences (M1) UGA

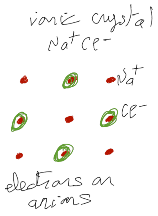
Lecture notes 2020 by Xavier Blase

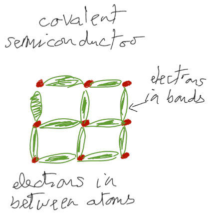
1 Classical electrons and Drude model

2 Free but quantum electrons in a box

3 Chapter 3 : Linear combination of atomic orbitals (LCAO) and the H_2^+ molecule

As we have seen in Chapter 2, the free-electron-in-a-box model cannot predict an energy gap between the highest occupied and lowest unoccupied energy levels in the case of a macroscopic system. In short, this simple model can only describe metals, and not semiconductors or insulators, when the size of the sample becomes large. As a matter of fact, this model is acceptable for well delocalized conduction electrons in simple metals (Na, K, etc.), namely electrons free to move everywhere around atoms. In many systems, such as ionic crystals (e.g. NaCl) or covalent semiconductors (silicon) or insulators (diamond), the valence (outer shell) electrons are rather localized, on the anions in the case of ionic systems (e.g. Cl^- in NaCl = Na^+Cl^-) or in between atoms in the case of covalent systems, namely in the "bonds" connecting the atoms.





A key limitation of the free-electron-in-a-box model is that it only counts the number of electrons per unit volume, the density n=N/V. If one insulator and one metal have roughly the same electronic density, the free-electron-in-a-box model will predict the very same properties. This is wrong : most crystals have roughly the same density (of the order of 10^{23} electrons/cm^3) but very different properties (metals or insulators, magnetic or not, etc.) What is really missing in the previous model is an information on the properties of the atoms, or chemical species, building the crystal. This is what we are going to do now : try to understand the properties of the crystal starting with the properties of the constituting atoms. In this Chapter, we start with the properties of the simplest hydrogen (H) atom that we use to understand the properties of the simplest H_2^+ molecule.

3.1 The isolated hydrogen atom

We will not do here the full theory of the H atom (see your Quantum Mechanical bachelor lecture). We will just provide a brief reminder of its properties. The possible energies ε_n and associated wavefunction $\phi_n(\mathbf{r})$ that the electron can have in the H atom are given by the solutions of the Schrödinger equation.

$$\hat{H}\phi_n(\mathbf{r}) = \varepsilon_n \phi(\mathbf{r}) \quad \text{with} \quad \hat{H} = \frac{-\hbar^2\nabla^2}{2m_e} - \frac{1}{4\pi\epsilon_0}\frac{1}{r}$$

where the potential is the Coulomb potential generated by the proton of the nucleus (r = distance between the electron and the nuclei). The energy solutions are given by:

$$\varepsilon_n = -\frac{\text{Ryd}}{n^2} \quad \text{with} \quad n = 1, 2, 3, \text{etc. the principal quantum number.}$$

and the Rydberg energy: Ryd = 13.6 eV. The associated wavefunctions are:

$$\phi^{at}_{nlm}(\mathbf{r}) = Y_{lm}(\hat{r})R_{nl}(r)$$

with Y_{lm} the spherical harmonics and $R_{nl}(r)$ the radial function. The integers (l,m) are the azimuthal and magnetic quantum numbers with the property that $-l \leq m \leq l$. An atomic wavefunction ϕ^{at}_{nlm} with l=0,1,2, etc. is called an *s, p, d*, etc. atomic orbital (the superscript "at" stands for atomic). The lowest atomic energy level is the *1s* level with n=1 and l=m=0. Its energy is thus ε_{1s} = - 1.0 Ryd and the associated atomic orbital is $\phi^{at}_{1s}(\mathbf{r}) = A\exp(-r/a_0)$ with A a normalization factor and $a_0 = 0.529177\mathring{A}$ the bohr radius.

The next levels are the (n=2, l=0, m=0) *2s* level and the 3-fold degenerate (n=2, l=1, m=-1,0,1) *2p* levels with energy $\varepsilon_{2s} = \varepsilon_{2p}$ = -Ryd / n^2 with (n=2). There is thus a large energy gap (3 Rydb/4) between the lowest *1s* level and the next *2s,2p* levels. In the absence of a very strong perturbation exciting the atom (a laser, etc.), the only electron of the H atom occupies the lowest energy level, namely the ε_{1s} energy level. The electron in this orbital is very localized around the nucleus with $\phi^{at}_{1s}(\mathbf{r}) = A\exp(-r/a_0)$ and the probability to find the electron at a distance r of the nucleus decays exponentially.

3.2 The H_2^+ molecule

Let's consider now the most simple molecule, the H_2^+ cation composed of two protons, in positions $\mathbf{R}_1$ and $\mathbf{R}_2$, and an electron in position $\mathbf{r}$. The Hamiltonian for the electron is:

$$\hat{H} = \frac{-\hbar^2\nabla^2}{2m_e} - \frac{1}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\mathbf{R}_1|} - \frac{1}{4\pi\epsilon_0}\frac{1}{|\mathbf{r}-\mathbf{R}_2|}$$

We call ψ the molecular orbital, namely the wavefunction describing the electron in the molecule. It is an eigenstate of the Hamiltonien, that is a solution of the (static) Schrödinger (or eigenvalue) equation : $\hat{H}|\psi\rangle = \varepsilon|\psi\rangle$ with ε the energy of the electron in the molecule. We started here to use the brackets notations of quantum mechanics.

Considering the two hydrogen atoms, will the electron go into the (1s) level of atoms H in $\mathbf{R}_1$ or in the (1s) level of atoms H in $\mathbf{R}_2$? The answer is that if the two atoms are close enough, the electron will be delocalized over the 2 atoms. Namely, there is a probability to find the electron either on atom 1 with its (1s) atomic wavefunction $\phi_1(\mathbf{r}) = \phi_{1s}^{at}(\mathbf{r}-\mathbf{R}_1)$ or on atom 2 with its (1s) atomic wavefunction $\phi_2(\mathbf{r}) = \phi_{1s}^{at}(\mathbf{r}-\mathbf{R}_2)$. In Quantum Mechanics, this really means that the wavefunction for the electron in the molecule can be written as <u>a linear combination of the atomic orbitals</u> (LCAO):

$$|\psi\rangle = \alpha|\phi_1\rangle + \beta|\phi_2\rangle$$

with (α, β) two unknown coefficients. This linear combination allows the electron to have a probability to be found on one atom or the other.

To get the coefficients (α, β), let's obtain 2 equations by <u>projecting</u> the Schrödinger equation $\hat{H}|\psi\rangle = \varepsilon|\psi\rangle$ onto the atomic orbitals ϕ_1 and ϕ_1, that is in bracket notations :

$$(I)\ \langle\phi_1|\hat{H}|\psi >= \langle\phi_1|\psi > \quad \text{and} \quad (II)\ \langle\phi_2|\hat{H}|\psi >= \langle\phi_2|\psi >$$

that is

$$\begin{aligned} (I) &\quad \alpha H_{11} + \beta H_{12} = \epsilon\,(\alpha S_{11} + \beta S_{12}) \\ (II) &\quad \alpha H_{21} + \beta H_{22} = \epsilon\,(\alpha S_{21} + \beta S_{22}) \end{aligned}$$

where we have introduced the <u>Hamiltonian matrix elements in the atomic basis</u>:

$$H_{ij} = \langle\phi_i|\hat{H}|\phi_j\rangle = \int d\mathbf{r}\ \phi_i^*(\mathbf{r})H(\mathbf{r})\phi_j(\mathbf{r}) \quad \text{with}\ \ (i,j) \in \{1,2\}$$

and the <u>overlap</u> matrix elements :

$$S_{ij} = \langle\phi_i|\phi_j\rangle = \int d\mathbf{r}\ \phi_i^*(\mathbf{r})\phi_j(\mathbf{r})$$

In matrix/vector notations, the two equations (I) and (II) are similar to :

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \varepsilon \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

If the two atomic orbitals ϕ_i and ϕ_j are on the same atom (namely i=j), then H_{ii} is called the onsite Hamiltonian energy that will be labeled ε_0.

$$H_{11} = H_{22} = \varepsilon_0 \quad \text{onsite energy}$$

By symmetry H_{11} and H_{22} are the same. By normalization of the atomic orbitals:

$$S_{11} = S_{22} = 1$$

Let's consider the terms where $i \neq j$. The Hamiltonian matrix elements H_{12} and H_{21} are called the hopping matrix elements. Since the Hamiltonian is Hermitian, one always have $H_{21} = H_{12}^*$ but here since everything is real, one have:

$$H_{21} = H_{12} = t \quad \text{the hopping energy}$$

The hopping term is responsible for the fact that if one puts the electron on one of the two atoms, it will have a nonzero probability to jump (hop) onto the other atom, namely to be delocalized over the entire molecule. Concerning the S_{12} and S_{21} terms, one will write

$$S_{12} = S_{21} = s \quad \text{the overlap matrix elements between neighbors}$$

namely the overlap between 2 atomic orbitals located on different atoms. Very importantly, since we know how to write the hydrogen atom (1s) orbital and the Hamiltonian, one can calculate (analytically or with a computer) all H_{ij} and S_{ij} terms that depend on the distance $|\mathbf{R}_1 - \mathbf{R}_2|$ between the two atoms. The system of equations thus becomes:

$$\begin{aligned} (I) \quad & \alpha\varepsilon_0 + \beta t = \varepsilon\,(\alpha + \beta s) \\ (II) \quad & \alpha t + \beta\varepsilon_0 = \varepsilon\,(\alpha s + \beta) \end{aligned}$$

namely

$$\begin{aligned} (I) \quad & \alpha(\varepsilon_0 - \varepsilon) + \beta(t - s\varepsilon) = 0 \\ (II) \quad & \alpha(t - s\varepsilon) + \beta(\varepsilon_0 - \varepsilon) = 0 \end{aligned}$$

with non-trivial solutions given by:

$$det \begin{vmatrix} \varepsilon_0 - \varepsilon & t - s\varepsilon \\ t - s\varepsilon & \varepsilon_0 - \varepsilon \end{vmatrix} = 0$$

that is

$$(\varepsilon_0 - \varepsilon)^2 - (t - s\varepsilon)^2 = 0 \quad \Longrightarrow \quad \boxed{\varepsilon = \frac{\varepsilon_0 \pm t}{1 \pm s}}$$

There are two solutions, a low energy one : $\varepsilon_+ = \frac{\varepsilon_0 + t}{1+s}$ (with $t < 0$ and $0 < s < 1$, see below) and a higher energy one: $\varepsilon_- = \frac{\varepsilon_0 - t}{1-s}$. These two levels are called bonding and anti-bonding respectively.

Bonding and anti-bonding levels

Plugging the first (+) solution $\varepsilon = \frac{\varepsilon_0+t}{1+s}$, namely $(\varepsilon - \varepsilon_0) = (t - s\varepsilon)$ into equation (I) above yields: $\alpha = \beta$. The weights of the molecular wavefunction on the two atoms is the same, namely:

$$|\psi_+\rangle = \alpha\left(|\phi_1\rangle + |\phi_2\rangle\right)$$

By normalization, $\langle\psi|\psi\rangle = 1 \Longrightarrow$

$$|\alpha|^2\left(\langle\phi_1|\phi_1\rangle + \langle\phi_1|\phi_2\rangle + \langle\phi_2|\phi_1\rangle + \langle\phi_2|\phi_2\rangle\right) = 1 \implies 2|\alpha|^2\left(1+s\right) = 1$$

so that $\alpha = 1/\sqrt{2(1+s)} \simeq 1/\sqrt{2}$ (within an overall phase factor).

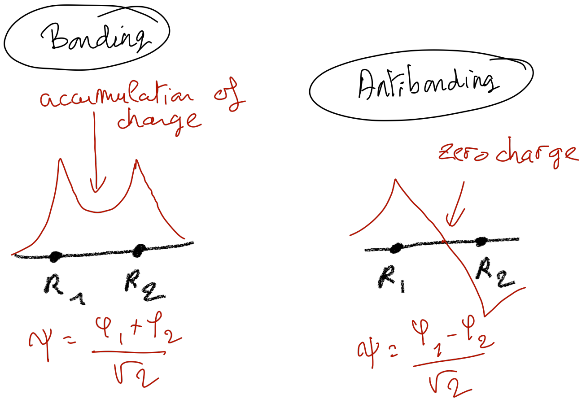


Figure 1: Bonding ψ_+ and antibonding ψ_- molecular wavefunctions in H_2^+. In the bonding state, some charge (electronic density) is localized in between the 2 atoms, that is shared by the two atoms : this is the formation of a chemical bond.

Plugging now the second (-) solution $\varepsilon = \frac{\varepsilon_0-t}{1-s}$, namely $(\varepsilon - \varepsilon_0) = -(t - s\varepsilon)$ into equation (I) above yields: $\alpha = -\beta$. The weights of the molecular wavefunction on the two atoms is the same in absolute value but with an alternated sign, namely:

$$|\psi_-\rangle = \alpha\left(|\phi_1\rangle - |\phi_2\rangle\right) \quad \text{with again by normalization } \alpha \simeq \frac{1}{\sqrt{2}}$$

The wavefunction ψ_+ is called a "bonding" state that accumulates charge at the center of the H-H bond (see red wavefunction below): the two atoms are sharing the electron. On the contrary, because of the minus sign, the ϕ_- wavefunction has a zero at the center of the H-H bond : it is said antibonding since no electron is shared by the 2 atoms.
From the knowledge of the atomic wavefunction and energy levels, we could find the possible energy levels and associated wavefunctions of the molecule.

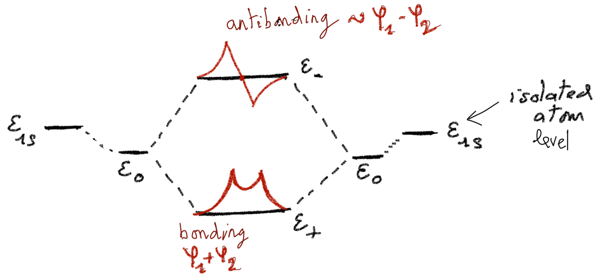


Figure 2: Energy levels / wavefunctions (in red) for H_2^+. The interaction between atoms (quantified by t) transforms the 2 ε_{1s} levels of the isolated atoms into two non-degenerate levels, one at low energy (the bonding level) and one at high energy (the anti-bonding) level.

if one puts one or two electrons on this molecule, they will occupy the lowest energy level ε_+. If one add a third electron, it will occupy the highest level ε_- since one cannot put more than 2 electrons per energy level (Pauli repulsion).

Note on Hamiltonian and overlap matrix elements

In the molecule, the onsite matrix element $H_{11} = \varepsilon_0$ reads:

$$H_{11} = \langle \phi_1 | \hat{H} | \phi_1 \rangle = \langle \phi_1 | \frac{-\hbar^2 \nabla^2}{2m_e} - \frac{1}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_1|} | \phi_1 \rangle - \langle \phi_1 | \frac{1}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_2|} | \phi_1 \rangle$$

Since ϕ_1 is the 1s atomic orbital of atom (1) and $\frac{-\hbar^2 \nabla^2}{2m_e} - \frac{1}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{R}_1|}$ the Hamiltonian of the isolated atom (1), then the first term on the right-hand-side (RHS) of the equation above is just ε_{1s}, that is the 1s isolated atom energy. The second term, namely the effect of the second atom ionic potential on ϕ_1 is a (negative) correction that becomes small if the 2 atoms are separated by a large distance. Thus one can write:

$$H_{11} = \varepsilon_0 = \epsilon_{1s} - \Delta\varepsilon \quad \text{with} \quad \Delta\varepsilon \quad \text{a small positive correction.}$$

Concerning now the hopping energy $H_{12} = t$ and overlap $S_{12} = s$ between atomic orbitals located on neighboring atoms, their magnitude depends on the distance between the two atoms. When the two atoms are very close, $S_{12} = s$ converges towards $S_{11} = 1$ so that s is smaller than one. Similarly, $H_{12} = t$ decays with distance. Since the 1s atomic wavefunctions are positive while the potential is negative, the hopping energy t is negative here.
Typical values in solids (interatomic distances of 2-3 $\mathring{A}$) range from a few tenths to a few eVs for the hopping energy t, while the overlap s is of the order of 0.1-0.2. It is a customary to neglect s in front of $S_{11} = 1$ in the expression above for the energy levels that become:

$$\varepsilon_{\pm} \simeq \varepsilon_0 \pm t$$

namely two levels separated by an energy $2|t|$. The energy t has to be conserved, even when small in front of $H_{11} = \varepsilon_0$, since it is responsible for the lift

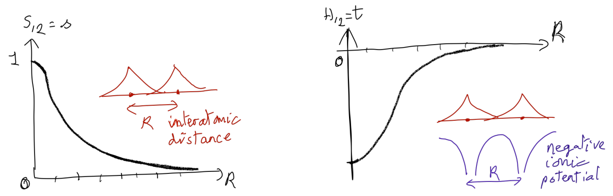


Figure 3: Decay with interatomic distance of (Left) the overlap $S_{12} = s$ and (Right) hopping $H_{12} = t$. In red the 1s wavefunctions and in blue the (negative) ionic potential.

of degeneracy of atomic orbitals and the formation of bands.

Note on the hopping matrix element $H_{12} = t$

The time-dependent Schrödinger equation reads:

$$i\hbar \frac{\partial |\psi(t)\rangle}{\partial t} = \hat{H}|\psi(t)\rangle \quad \Longrightarrow |\psi(t+dt)\rangle = |\psi(t)\rangle + \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle$$

Assume that at time (t) the electron is localized on the atom (1), that is in the atomic orbital $\phi_1 \;\; \rightarrow \;\; |\psi(t)\rangle = |\phi_1\rangle$. Then at time (t+dt) the molecular wavefunction will read:

$$|\psi(t+dt)\rangle = |\phi_1\rangle + \frac{1}{i\hbar}\hat{H}|\phi_1\rangle$$

Its "weight" on the atomic orbital ϕ_2 that measures the probability to find the electron on atom (2) in orbital ϕ_2 reads:

$$\langle\phi_2|\psi(t+dt)\rangle = \langle\phi_2|\phi_1\rangle + \frac{1}{i\hbar}\langle\phi_2|\hat{H}|\phi_1\rangle = s + \frac{t}{i\hbar} \simeq \frac{t}{i\hbar}$$

One can see that the probabiility that an electron jumps from atom 1 to atom 2 (by tunneling) is proportional to the hopping matrix element t.

3.3 Towards solids with 10^{23}/cm^3 atoms (qualitative)

Let's assume now that we form a solid by bringing N atoms close to each other (see Figure 4 below for a 1D solid), with $N \simeq 10^{23}$. We can do the very same reasoning, building the crystal wavefunction ψ as a linear combination of the N atomic orbitals ϕ^{at}:

$$\psi(\mathbf{r}) = \sum_{i=1}^{N} \alpha_i \phi^{at}(\mathbf{r} - \mathbf{R}_i)$$

The linear combination means again that the electron can delocalizes all over the N atoms. The atomic orbital $\phi^{at}(\mathbf{r} - \mathbf{R}_i)$ localized on the atom located in $\mathbf{R}_i$ has an energy ε^{at} when the atoms are separated by a large distance (it could be

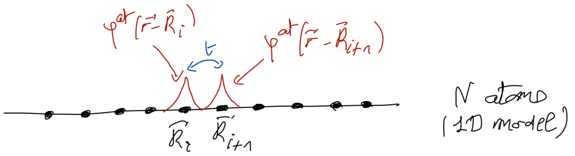


Figure 4: Symbolic representation of a 1D solid with N atoms in positions $\{\mathbf{R}_i\}$ (i=1 to N). There is one atomic orbital $\phi_i^{at}(\mathbf{r}) = \phi^{at}(\mathbf{r} - \mathbf{R}_i)$ on each atom, for example a 1s atomic orbital (in red on the picture). We represent (in blue) the hopping term t between neighboring atoms which is responsible for the delocalization of the electrons over all atoms.

a 1s, 2s, 2p etc. atomic energy level). When the atoms are brought close to each other and start interacting, the N degenerate ε^{at} levels of the isolated atoms form a "band" of N levels that spread over an energy range (<u>the band width</u>) of the order of the hopping energy t, namely the Hamiltonien matrix element between neighboring atoms : $t = \langle\phi_i^{at}|\hat{H}|\phi_{i\pm1}^{at}\rangle$ with $\phi_i^{at}(\mathbf{r}) = \phi^{at}(\mathbf{r} - \mathbf{R}_i)$. This is how energy bands form in a solid (see Fig. 5).

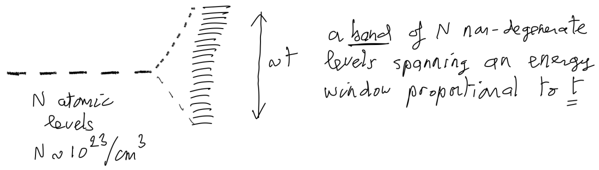


Figure 5: When the atoms are far from each other, the N atoms yield N degenerate atomic levels. When the atoms are brought close to each other and start interacting, these N atomic levels transform into N non-degenerate levels forming a band with an energy width proportionnal to the overlap energy t. The closest are the atoms, the larger is the energy t and the band width.

Let's now put electrons. If each atom comes with 1 electron, one has N electrons to distribute over N levels. Since we put 2 electrons (spin up and down) per level, this means that the lowest (N/2) levels are filled, while the upper (N/2) levels are empty : the band is "half-filled." The energy gap between the highest occupied level and the lowest unoccupied level is of the order of (t/N) with t equal at most to a few eVs and $N \simeq 10^{23}$. This forms an energy gap much much smaller than k_BT : a crystal with a half-filled band is metallic (see Fig. 6-Left). Let's assume now that each atom brings 2 electrons. Then the band is completely filled. What can we say about the energy gap ? where is the closest empty level above the highest filled level in the band ?

To answer this question, one must consider the bands form by the other atomic levels, e.g. the 2s band (formed by 2s atomic orbitals) that stands above

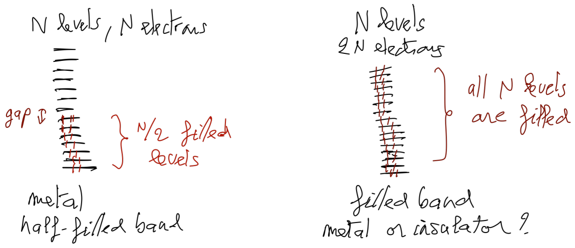


Figure 6: (Left) N electrons on N levels form a metallic half-filled band. (Right) 2N electrons on N levels form a completely filled band. Metallic or insulating ?

the 1s band (see Fig. 7). If the 1s and 2s band widths are small as compared to the energy difference between the ε_{1s} and ε_{2s} isolated atoms energy levels, then the gap is large and the system is insulating. If the band width of each band is large as compared to $\varepsilon_{2s} - \varepsilon_{1s}$, then the two bands overlap and there is no energy gap : the system is metallic. Note that the band width, proportional to the hopping energy t, increases when the distance between atoms decreases. As such, by putting pressure onto a solid, bringing atoms closer from each other, one may increase t and turns a semiconductor into a metal.

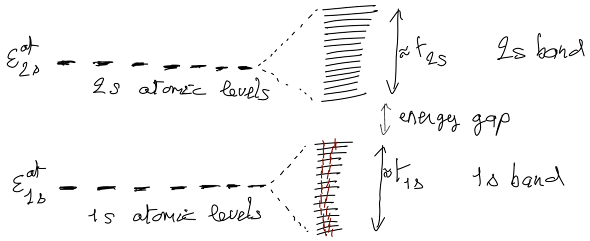


Figure 7: Two bands : the 2s band above the 1s band. Depending on the energy difference $\varepsilon_{2s} - \varepsilon_{1s}$ between the atomic 1s and 2s energy levels, as compared to the band width of each band, the system can be insulating or metallic. The band width can be increased by bringing the atoms closer and closer. The difference $\varepsilon_{2s} - \varepsilon_{1s}$ depends on the type of atoms (the chemical species) forming the crystal.

To conclude this section, let's note however that there is a problem with this approach: to get the 10^{23} energy levels and unknown coefficients α_i, one must solve a system of 10^{23} equations with 10^{23} unknown (the α_i coefficients). This is huge even for the best computers that are petaflopic, namely that can perform 10^{15} floating point operations per second ! We must be more clever and simplify the problem !! This is the scope of the next chapter devoted to the Bloch theorem.