Research project : Hartree-Fock calculations in graphene and carbon nanotubes

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Introduction

This project aims at estimating the effect of the interactions between electrons in simple atom lattices as well as in graphene and carbon nanotubes. Few ab initio calculations have been made so far to compute the correction of band structures by taking into account electron-electron correlations. However, band structures describe quite accurately the properties of numerous solids and are widely used to know the properties of the materials at the Fermi level for instance. Band structures can be obtained thanks to experiments, but they aren't always easy. Photo-emissions are quite accurate to estimate the band structure of the occupied states of a solid, namely below the Fermi energy. Description : ARPES method... However, the bands corresponding to empty states (above the Fermi level), turn out to be more difficult to compute. Inverse photo-emission is a way to obtain them : by focusing an electron beam on a solid, the electrons of the beam will tend to occupy the empty states. MORE PRECISE DESCRIPTION... The bandwidth of the bands is a very important quantity, useful when estimating several physical properties. We will study how bandwidth evolves with the correction by Coulomb interaction.

In this project, I have used the Hartree-Fock method to estimate the influence of electron-electron interaction *ab initio*. Hartree-Fock equations can be derived from a variational principle : eigen states are searched within the states making the means value of the hamiltonian stationary. These equations are a set of one-electron wave functions coupled equations : all the wave functions of the electrons in the system play a role in the Schrödinger equation satisfied by any electron. The electron i (in fact we cannot distinguish the electrons, but this gives a better understanding) satisfies the following Schrödinger equation :

$$-\frac{h^2}{2m}\Delta\psi_i(\vec{r}) + U_{ion}(\vec{r})\psi_i(\vec{r}) + \int d\vec{r'}\frac{e^2\sum_j|\psi_j(\vec{r'})|^2}{|\vec{r}-\vec{r'}|}\psi_i(r) - \sum_{jocc.}\delta_{\sigma_i,\sigma_j}\int d\vec{r'}\frac{e^2\psi_j^*(\vec{r'})\psi_i(\vec{r'})}{|\vec{r}-\vec{r'}|}\psi_j(\vec{r}) = \epsilon_i\psi_i(\vec{r}) \tag{1}$$

These equations, derived from a variationnal principle, have a physical meaning. Hartree's term (the third term in the expression above) accounts for electron-electron Coulomb interaction : it is the integral of the Coulomb potential created at position $\vec{r}$ by the distribution of charges of all the others electrons. That is why the total electronic density $n(\vec{r}) = \sum_j |\psi_j(\vec{r'})|^2$ appears, as it sums up this charge distribution. In the equation, we denote $e^2 = \frac{q_e^2}{4\pi\epsilon_0}$. Because the i^{th} electron itself appears in this sum on occupied states, there is a "self-interaction error" : the electron is influenced by the potential it creates itself !

Fock's term (the last term in the member on the left) takes Pauli principle into account, and corrects the self-interaction error made in Hartree's term (thanks to the term for $j = i$). Fock's term is non local :

$$\int V(\vec{r},\vec{r'})\psi_i(\vec{r'})d\vec{r'} \tag{2}$$

and is more difficult to understand thoroughly. It is an exchange term, due to Pauli principle. Hence the contributions to that term only for occupied states with same spin as the i^{th} electron.

A rigorous proof of Hartree-Fock equations can be easily found in litterature, for instance in Ashcroft and Mermin "Solid state physics" book page 332. The idea is to assume that the groud-state wave function can be written as a Slater determinant of one-electron wave functions (in order to be compatible with Pauli principle). However, this is already an assumption because nothing prooves that the total wave-function for a system of N electrons can be decomposed thanks to N one-electron wave-functions. By minimizing the means value of the hamiltonian in this state, and using Lagrange multiplicators to satisfy the constraints of one electron normalized wave functions, we obtain a set of equations on the individual wave functions. The hamiltonian changes, therefore the previous wave functions aren't eigen vectors anymore. The approach I undertook is pertubative : assuming that Hartree-Fock's term induces a slight modification of the eigen function, I computed the correction to the eigen value ; the energy, thanks to **first order perturbation theory**.

The final goal of the project is to apply these numerical methods to compute te correction to the tight-binding energy spectrum of real materials, like graphene or carbon nanotubes. However, it is very useful to start applying these calculations to free electrons, or to low dimensionnal atom lattices. In the first section, I will study somme properties like the density of states of such regular lattices, in the tight-binding approximation. These results will be useful to gain intuition on the future results to be found. I will also present some caracteristic results obtained as we increase the dimension. Then, I will compute thoroughly the correction of the energy spectrum obtained with Hartree-Fock method for a free electron gas, before doing it for the one and two dimensionnal lattice, and eventually for graphene and carbon nanotubes.

Chapter 1

Density of states calculations

1.1 One dimensional lattice

The energy spectrum of a one dimensionnal lattice computed in the tight binding approximation is :

$$E_k = E_0 - t_0 - 2tcos(ka), k \in [-\frac{\pi}{a}, \frac{\pi}{a}[= 1Z.B. \tag{1.1}$$

where the quasi-momentum k spans the First Brillouin Zone. E_0 is the energy of the atomic orbital level. t is the coupling between two neighbouring sites, and t_0 is the coupling in a given site. The lattice is made up of a chain of N atoms, which repeats periodically. This periodicity quantifies k, because of the Periodic Boundary Conditions (PBC).

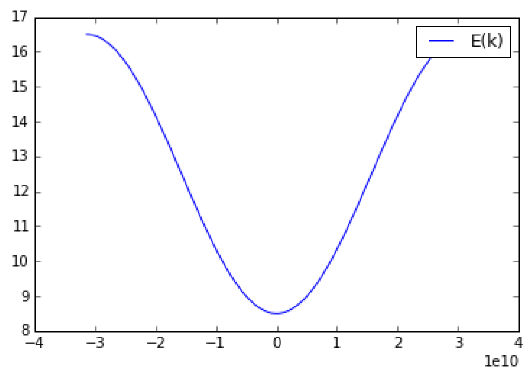

Figure 1.1: Energy spectrum in a one-dimensional lattice under LCAO approximation, for $a = 10^{-10}$ m

Let's do a reminder about the tight-binding approximation. This method assumes that the eigen wave-functions of the hamiltonian have the following form :

$$\psi_k(x) = \frac{1}{\sqrt{N}} \sum_{m=1}^{N} e^{ikma} \chi_m(x) \tag{1.2}$$

where $\chi_m(.)$ is the atomic orbital wave-function of the m^{th} site of the lattice. We assume that either all atoms are of the same type, or that they energy levels are such that **only one energy level per atom plays a role**. Otherwise, the form of the wave-function would be more complicated, including hybridisation between different atomic levels. Several atomic orbital wave-functions $(\chi_m^n)_n$ would be needed.

With these notations :

$$t =< \chi_{m-1}|V_{at}|\chi_m >, t_0 =< \chi_m|V_{at}|\chi_m > \tag{1.3}$$

where V_{at} is the ionic effective potential.

The form of the wave-function derives from Bloch's theorem, and makes the probability amplitude of presence maximal in the neighborhood of the sites of the lattice. An electron having this wave-function is delocalised all over the lattice, but only close to the sites, and not in-between. If we measured the position of the electron, we would find it with very high probability very close to one of the site of the lattice. This is why this method is called "tight-binding", or "Linear Combination of Atomic Orbitals" (LCAO).

In the lattices we have studied, this approximation is well-suited. The opposite approximation, namely "weak-binding", works for solids whose electrons behave nearly like free electrons (plane waves) ; their probability of presence being as important between two atoms than close to an atom. The band structure obtained is the correction computed by a perturbative approach, to the set of free-electrons parabola describing the energy spectrum of these electrons. Each Fourier mode opens a gap at a given node of the spectrum, which gives the final band structure. We assume that electrons in regular lattices, graphene and carbon nanotubes are bound enough to the atoms. Therefore, we won't use this method in the project.

The calculation of the density of states for the one-dimensionnal lattice gives :

$$D(E) = (\frac{dN_<}{dE})(E) = \frac{N}{2\pi t}\frac{1}{\sqrt{1-(\frac{E-(E_0-t_0)}{2t})^2}} \tag{1.4}$$

where $N_<(E)$ is the total number of states having an energy less than E :

$$N_<(E) = N - \frac{N}{\pi}Arccos(\frac{E-(E_0-t_0)}{2t} \tag{1.5}$$

As I will present the calculation in two dimensions, I don't proove these formula in this simple case.

In the following graphs and throughout the whole report, we will use the values $E_0 = 13eV$, $t_0 = 0.5eV$, $t = 2eV$ and $a = 10^{-10}$ m to plot the functions.

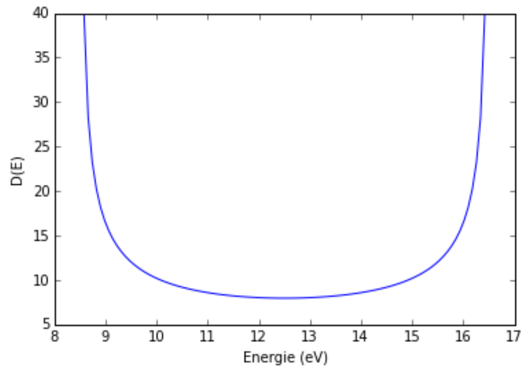

Figure 1.2: Density of energy states $D(E)$ in a one-dimensional lattice under LCAO approximation

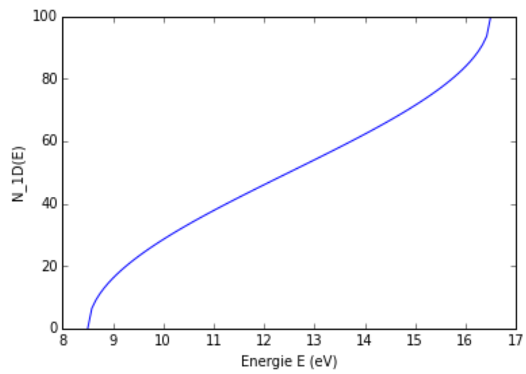

Figure 1.3: Number of energy states $N_<(E)$ in a one-dimensional lattice under LCAO approximation

1.2 Two dimensional lattice

The energy spectrum of electrons in a two dimensional lattice in the tight-binding approximation is :

$$E(k_x, k_y) = E_0 - t_0 - 2t(cos(k_x a) + cos(k_y a)) \in [E_0 - t_0 - 4t, E_0 - t_0 + 4t] \tag{1.6}$$

where $\vec{k} = \begin{pmatrix} k_x \\ k_y \end{pmatrix}$ is the quasi-momemtum of the electron.

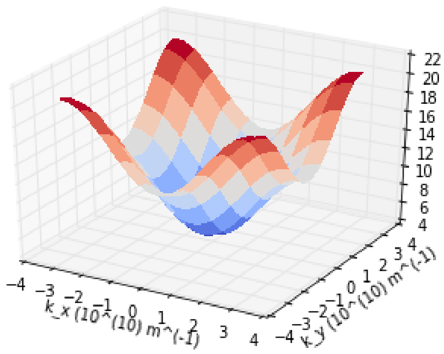

Figure 1.4: Energy spectrum in a square lattice under LCAO approximation

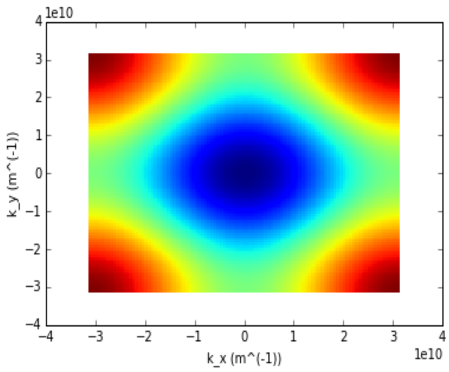

Figure 1.5: Projection of the energy spectrum of a square lattice in the quasi-momentum space

We suppose Periodic Boundary Conditions, such that $k_x = \frac{2\pi m_1}{Na}$, $k_y = \frac{2\pi m_2}{Na}$ with m_1 and m_2 integers. The first Brillouin zone is described by $(k_x, k_y) \in [-\frac{\pi}{a}, \frac{\pi}{a}[^2$.

The number of electronic possible states whose energy is smaller than or equal to E is :

$$N_<^{2D}(E) = \int\int dm_1 dm_2 = \frac{(Na)^2}{(2\pi)^2} \int\int_{\{\vec{k} \in 1.B.Z. | E_{\vec{k}} \leq E\}} dk_x dk_y \tag{1.7}$$

$$= \frac{N^2}{(2\pi)^2} \int\int_{\{\begin{pmatrix} x \\ y \end{pmatrix} \in [-\pi, \pi[^2 | cos(x) + cos(y) \geq \alpha(E)\}} dxdy \tag{1.8}$$

where $\alpha(E) = \frac{E_0 - t_0 - E}{2t} \in [-2, 2]$. This expression of $N_<^{2D}(E)$ as the area of a specific region in the square $[-\pi, \pi]^2$ of the plane is remarkable. We will use it to compute some similar quantities in three dimensions.

$$N_<^{2D}(E) = (\frac{N}{2\pi})^2 \int_{-\pi}^{\pi} (\int_{\{z | cos(z) \geq \alpha(E) - cos(y)\}} dz) dy \tag{1.9}$$

At that stage, as $\alpha(E) - cos(y) = \alpha(E + 2tcos(y))$, we could use for some values of E the expression of the number of states computed in a one dimensional lattice :

$$E + 2tcos(y) \in [E_0 - t_0 - 2t, E_0 - t_0 + 2t] \Rightarrow \int_{\{z|cos(z) \geq \alpha(E) - cos(y)\}} dz = \frac{2\pi}{N} N_<^{1D}(E + 2tcos(y)) \quad (1.10)$$

However it is not mandatory to use to the lower dimension calculations here. After some rewriting and calculations (cf Annexe 1), we find :

$$E \geq E_0 - t_0 \Rightarrow \alpha(E) \leq 0 \Rightarrow N_<^{2D}(E) = \frac{N^2}{\pi^2}(\pi Arccos(\alpha(E)+1) + \int_{-1}^{\alpha(E)+1} \frac{Arccos(\alpha(E) - z)}{\sqrt{1 - z^2}} dz) \quad (1.11)$$

$$E \leq E_0 - t_0 \Rightarrow \alpha(E) \geq 0 \Rightarrow N_<^{2D}(E) = \frac{N^2}{2\pi^2} \int_{\alpha(E)-1}^{1} \frac{Arccos(\alpha(E) - z)}{\sqrt{1 - z^2}} dz \quad (1.12)$$

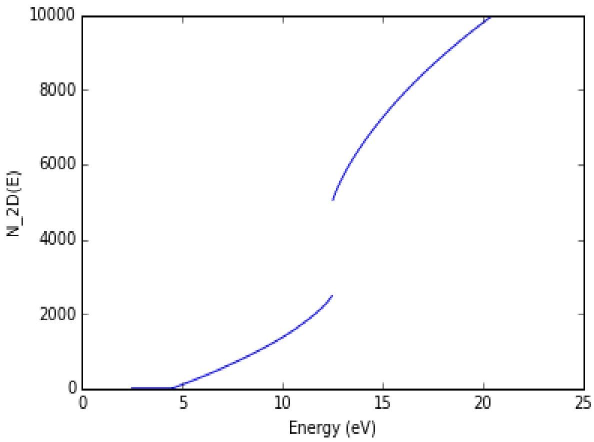

Figure 1.6: Number of energy states in a square lattice under LCAO approximation

We never see the infinite slope of $N_<^{2D}(E)$ in the neighbouring of $E_0 - t_0$, whatever close we look. $N_<^{2D}(E)$ has a square root behavior close to this point.

We notice that $N_<^{2D}(E)$ has a discontinuity in $E_0 - t_0$:

$$lim_{E \longrightarrow (E_0 - t_0)^-} N_<^{2D}(E) = \frac{1}{2} lim_{E \longrightarrow (E_0 - t_0)^+} N_<^{2D}(E) = \frac{N^2}{2\pi^2} \int_{-1}^{1} \frac{Arccos(-z)}{\sqrt{1 - z^2}} dz \quad (1.13)$$

as $\alpha(E) \longrightarrow_{E \longrightarrow E_0 - t_0} 0$.

Moreover, the slope of $N_<^{2D}(E)$ has a discontinuity at $E_0 - t_0 - 4t$:

$$lim_{E \longrightarrow (E_0 - t_0 - 4t)^-} (\frac{dN_<^{2D}}{dE})(E) = 0 \neq lim_{E \longrightarrow (E_0 - t_0 - 4t)^+} (\frac{dN_<^{2D}}{dE})(E) > 0 \quad (1.14)$$

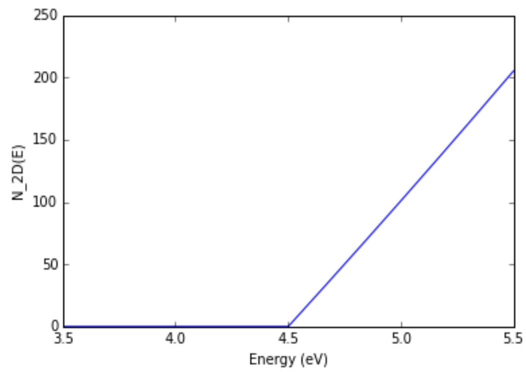

Figure 1.7: Discontinuity of the slope of the number of energy states in a square lattice at the minimal energy $E_0 - t_0 - 4t$

Identically :

$$lim_{E \longrightarrow (E_0 - t_0 + 4t)^+} (\frac{dN_<^{2D}}{dE})(E) = 0 \neq lim_{E \longrightarrow (E_0 - t_0 + 4t)^-} (\frac{dN_<^{2D}}{dE})(E) > 0 \tag{1.15}$$

These discontinuities will be seen directly in the function $E \longmapsto D^{2D}(E)$.

By taking the derivatives of the previous expressions of $N_<^{2D}(E)$, we derive the density of energy states in a square lattice :

$$E > E_0 - t_0 \Rightarrow D^{2D}(E) = \frac{N^2}{2t\pi^2} \int_{-1}^{\frac{E_0 - t_0 + 2t - E}{2t}} \frac{dz}{\sqrt{(1 - z^2)(1 - (\frac{E_0 - t_0 - 2tz - E}{2t})^2)}} \tag{1.16}$$

$$E < E_0 - t_0 \Rightarrow D^{2D}(E) = \frac{N^2}{2t\pi^2} \int_{\frac{E_0 - t_0 - 2t - E}{2t}}^{1} \frac{dz}{\sqrt{(1 - z^2)(1 - (\frac{E_0 - t_0 - 2tz - E}{2t})^2)}} \tag{1.17}$$

We could also directly compute the density of states with the following formula (but we will see that our method enables to deduce the density from the calculations in lower dimensions) :

$$D_{2D}(E) = \int_{1Z.B.} \frac{d^2 k}{V_{BZ}} \delta(\epsilon - \epsilon(\vec{k})) \tag{1.18}$$

The function $E \longmapsto D(E)$ is a **Bessel function**. A computation of an equivalent of $D^{2D}(E)$ when $E \longrightarrow E_0 - t_0$ gives the following result :

$$D^{2D}(E_0 - t_0 + \epsilon) =_{\epsilon \to 0} O(\frac{1}{\sqrt{|\epsilon|}}) \tag{1.19}$$

Thus,

$$N_<^{2D}(E_0 - t_0 + \epsilon) =_{\epsilon \to 0^+} N_<^{2D}((E_0 - t_0)^-) + K\sqrt{\epsilon} \tag{1.20}$$

where K is a constant.

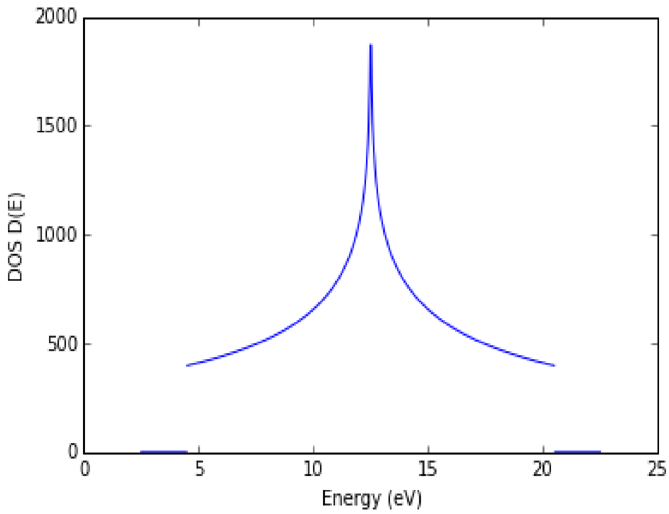

Figure 1.8: Density of energy states in a square lattice under LCAO approximation

Because of the limited resolution in energy, we can't properly see the divergence of $D^{2D}(E)$. We can guess that $D^{2D}(E) \longrightarrow +\infty$ when $E \longrightarrow E_0 - t_0$ thanks to the expression of $D^{2D}(E)$. Indeed both expressions of $D^{2D}(E)$ (for $E \geq E_0 - t_0$ and $E \geq E_0 - t_0$) tend towards :

$$\frac{N^2}{2t\pi^2} \int_{-1}^{1} \frac{dz}{(1-z^2)} = +\infty \tag{1.21}$$

We can also explain this divergence thanks to the saddle points that appear in the energy spectrum, which makes the number of possible energy states increase.

1.3 Three dimensional lattice

Similarly to the lower dimensions, the energy spectrum of electrons in a three dimensional lattice in the tight-binding approximation is :

$$E(k_x,k_y,k_z) = E_0 - t_0 - 2t(cos(k_xa)+cos(k_ya)+cos(k_za)) \in [E_0-t_0-6t, E_0-t_0+6t] \quad (1.22)$$

We suppose Periodic Boundary Conditions, with a cubical lattice of side length Na repeating periodically, such that $k_x = \frac{2\pi m_1}{Na}$, $k_y = \frac{2\pi m_2}{Na}$ and $k_z = \frac{2\pi m_3}{Na}$. The first Brillouin Zone is described by $(k_x,k_y,k_z) \in [-\frac{\pi}{a},\frac{\pi}{a}[^3$.

The number of electronic possible states whose energy is smaller or equal to E is :

$$N_<^{3D}(E) = \int\int\int dm_1dm_2dm_3 = \frac{(Na)^3}{(2\pi)^3}\int\int\int_{\{\vec{k}\in 1.B.Z.|E_{\vec{k}}\leq E\}} dk_xdk_ydk_z \quad (1.23)$$

$$= (\frac{N}{2\pi})^3 \int\int\int_{\{\begin{pmatrix}x\\y\\z\end{pmatrix}\in[-\pi,\pi[^3|cos(x)+cos(y)+cos(z)\geq\alpha(E)\}} dxdydz \quad (1.24)$$

where $\alpha(E) = \frac{E_0-t_0-E}{2t} \in [-3,3]$.

$$N_<^{3D}(E) = (\frac{N}{2\pi})^3\int_{-\pi}^{\pi}(\int\int_{cos(y)+cos(z)\geq\alpha(E)-cos(x)} dydz)dx \quad (1.25)$$

Let denote :

$$I_x = \int\int_{cos(y)+cos(z)\geq\alpha(E)-cos(x)} dydz \quad (1.26)$$

We notice that

$$\alpha(E) - cos(x) = \frac{E_0-t_0-(E+2tcos(x))}{2t} = \alpha(E+2tcos(x)) \quad (1.27)$$

Let's now compute I_x according to the values of E and x :

$$\alpha(E)-cos(x) \geq 2 \Rightarrow I_x = 0 \quad (1.28)$$

$$\alpha(E)-cos(x) \leq -2 \Rightarrow I_x = \int_{-\pi}^{\pi}\int_{-\pi}^{\pi} dydz = (2\pi)^2 \quad (1.29)$$

If $\alpha(E)-cos(x) \in [-2,2]$, it means that $\alpha(E+2tcos(x)) \in [-2,2]$, which implies that $E+2tcos(x)$ is in the interval $[E_0-t_0-4t, E_0-t_0+4t]$. **We can therefore use the computations of the two-dimensional case to get the results in higher dimension** !
$N_<^{2D}(.)$ is indeed defined on the interval $[E_0-t_0-4t, E_0-t_0+4t]$:

$$\alpha(E)-cos(x)\in[-2,2] \Rightarrow I_x = \int\int_{cos(y)+cos(z)\geq\alpha(E+2tcos(x))} dydz = (\frac{2\pi}{N})^2 N_<^{2D}(E+2tcos(x)) \quad (1.30)$$

thanks to the previous expression 1.8.

After some further calculations, we find :

$$\alpha(E)\leq -1 \Rightarrow N_<^{3D}(E) = \frac{N^3}{\pi}Arccos(\alpha(E)+2) + \frac{N}{\pi}\int_{Arccos(\alpha(E)+2)}^{\pi} N_<^{2D}(E+2tcos(x))dx \quad (1.31)$$

$$\alpha(E)\in[-1,1] \Rightarrow N_<^{3D}(E) = \frac{N}{\pi}\int_0^{\pi} N_<^{2D}(E+2tcos(x))dx \quad (1.32)$$

$$N_<^{3D}(E) = \frac{N}{\pi}(\int_0^{Arccos(\alpha(E))} N_<^{2D}(E+2tcos(x))dx + \int_{Arccos(\alpha(E))}^{\pi} N_<^{2D}(E+2tcos(x))dx) \quad (1.33)$$

$$\alpha(E)\geq 1 \Rightarrow N_<^{3D}(E) = \frac{N}{\pi}\int_0^{Arccos(\alpha(E)-2)} N_<^{2D}(E+2tcos(x))dx \quad (1.34)$$

The order of magnitude of $N_<^{3D}(E)$ is N^3, as we have seen that $N_<^{2D}(E)$ is proportionnal to N^2.

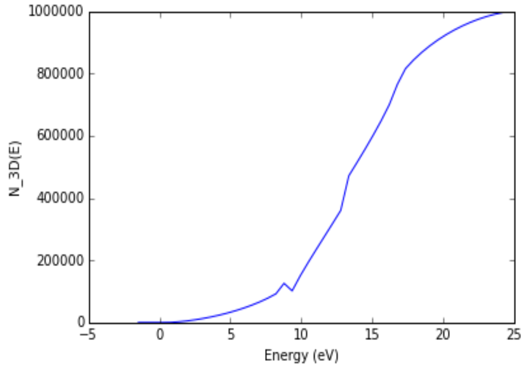

Figure 1.9: Number of energy states in a three dimensional lattice

It is worth to notice that the slope of $N_{<}^{3D}(E)$ is now continuous at the minimal and maximal energies $E_0 - t_0 - 6t$ and $E_0 - t_0 + 6t$, contrary to the two dimensional case.

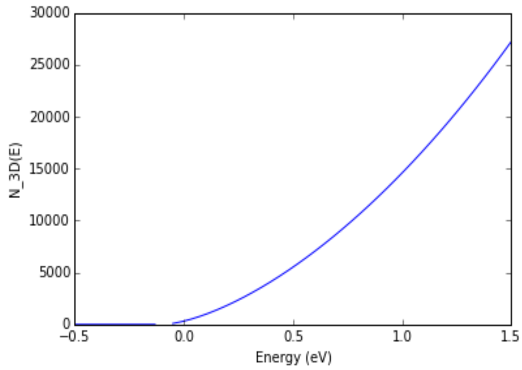

Figure 1.10: Continuity of slope of the number of energy states in a three dimensional lattice at the minimal energy $E_0 - t_0 - 6t$

We can take the derivative of the expression of $N^{3D}(E)$ for $E > E_0 - t_0 + 2t$ and $E < E_0 - t_0 - 2t$. Using that :

$$N_{<}^{2D}(E_0 - t_0 + 4t) = N^2 \tag{1.35}$$

and

$$N_{<}^{2D}(E_0 - t_0 - 4t) = 0 \tag{1.36}$$

we find the following :

$\forall E \geq E_0 - t_0 + 2t$,

$$D^{3D}(E) = \frac{N}{\pi} \int_{Arccos(\frac{E_0 - t_0 + 4t - E}{2t})}^{\pi} D^{2D}(E + 2tcos(x))dx \tag{1.37}$$

$\forall E \leq E_0 - t_0 - 2t$

$$D^{3D}(E) = \frac{N}{\pi} \int_{0}^{Arccos(\frac{E_0 - t_0 - 4t - E}{2t})} D^{2D}(E + 2tcos(x))dx \tag{1.38}$$

The density plot given by these analytical formula is dispayed in Annex 3. These formula seem to give the exact result only for $E \notin]E_0 - t_0 - 2t, E_0 - t_0 + 2t[$. Let's now look at the density obtained with a probabilistic method, consisting of computing the energy for some random quasi-momentum values. This method will be further explained in the following section, for higher dimension lattices.

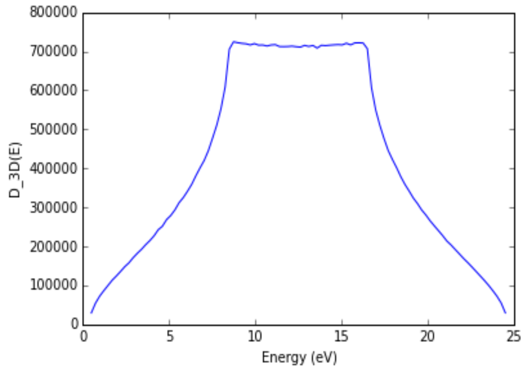

Figure 1.11: Density of states in a three dimensional lattice

This time, contrary to the one and two dimensionnal lattice, the density is continuous.

1.4 Regular lattice in higher dimension

It is interesting to look at the evolution of the density of states in higher dimensions and infinite dimension. Dimensions account for the number of closest neighbours, therefore increasing the dimension should be a way to describe real crystals better, where the atoms of the lattice may be coupled to a good deal of neighbors. Infinite dimension appears in many cases to give conclusions closer to the real three dimensional world than two-dimensional calculations.

To compute the density of states in dimension d, we could carry out the same trick as in 3D, using the results of D.O.S. calculations in lower dimension $d-1$. However a probabilistic method like the Monte-Carlo method is much simpler. Let's briefly explain how it works.

The energy spectrum in dimension d is given by :

$$E(k_1, k_2, .., k_d) = E_0 - t_0 - 2t \sum_{i=1}^{d} cos(k_i a) \tag{1.39}$$

the First Brillouin Zone being$[\frac{-\pi}{a}, \frac{\pi}{a}]^d$.

We consider random variables K_1, K_2,.., K_d, each uniform over $[-\frac{\pi}{a}, \frac{\pi}{a}]$. We choose a number n of random selections of $(K_1, K_2, .., K_d) \in [-\frac{\pi}{a}, \frac{\pi}{a}]^d$. Thus the random variable giving the energy, $E(K_1, K_2, .., K_d)$, is estimated n times.
We also choose the pace of discretization p of the possible interval for the energy, namely $[E_0 - t_0 - 2td, E_0 - t_0 + 2td]$, which is cut into p small intervals.
The distribution of the energy after the n random selections provides histograms telling how many times the random energy estimated was in the interval $[E_0 - t_0 + k\frac{4td}{p}, E_0 - t_0 + (k+1)\frac{4td}{p}]$ for $k \in [0, p-1]$. This histogram is therefore an approximation of the density of states. It would be interesting to be aware of the influence of the two discretizations, represented by n and p, on the precision of the density function computed. Intuitively, n is the most important parameter if p is large enough. (but p does not need to be too big)

Having fixed $E_0 = 13eV$, $t_0 = 0.5eV$, $t = 2eV$ and $a = 10^{-10}m$, we obtain the following results :

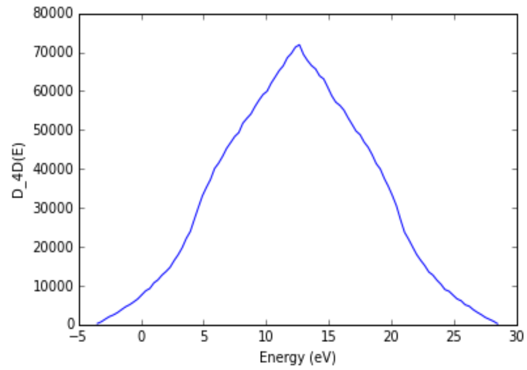

Figure 1.12: Density of states in a four dimensional lattice : n=1000000, p=100

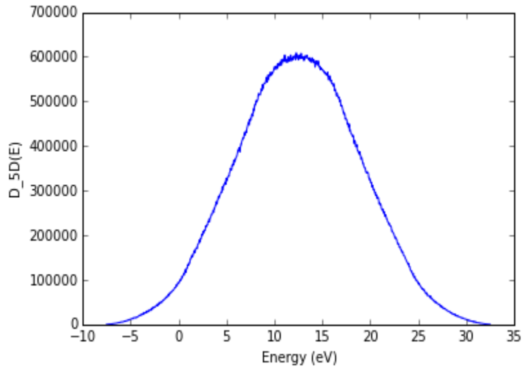

Figure 1.13: Density of states in a five dimensional lattice : n=1000000, p=100

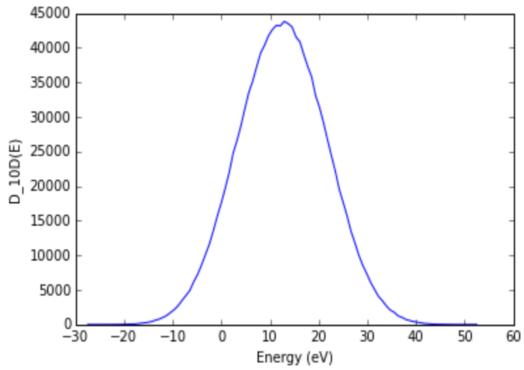

Figure 1.14: Density of states in a ten dimensional lattice : n=1000000, p=100

Each density is plotted over the whole possible interval for the energy : $[E_0 - t_0 - 2td, E_0 - t_0 + 2td]$.

The density of states looks increasingly like a gaussian when the dimension d increases. The standard deviation σ appears to increase in absolute value as the dimension increases, but the ratio $\frac{\sigma}{4dt}$ of the deviation to the width of the total interval appears to diminish. Let's try to justify this behaviour when d increases.
First, the mean value of the random variable E is $E_0 - t_0$:

$$< -2t \sum_{\nu=1}^{d} cos(K_\nu a) >= 0 \tag{1.40}$$

because

$$\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} cos(k_\nu a) dk_\nu = 0 \tag{1.41}$$

and the random variables K_1, .., K_d are independent.

Then, the standard deviation σ of the distribution of the energy in a d-dimensional lattice is given by:

$$\sigma^2 =< E^2 > - < E >^2 =< E^2 >= 4t^2 \sum_{\nu=1}^{d} \sum_{\nu'=1}^{d} \frac{1}{(\frac{2\pi}{a})^d} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} .. \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} cos(k_\nu a) cos(k_{\nu'} a) dk_1 ... dk_d \tag{1.42}$$

Given that

$$\frac{1}{(\frac{2\pi}{a})^d} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} .. \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} cos(k_\nu a) cos(k_{\nu'} a) dk_1 ... dk_d = \frac{1}{(\frac{2\pi}{a})^2} \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}} cos^2(ka) dk = \frac{1}{2} \tag{1.43}$$

if $\nu = \nu'$, and 0 otherwise, we finally find :

$$\sigma = \sqrt{2d} t \tag{1.44}$$

In fact the hopping in dimension d should be slightly modified in the following way :

$$t = \frac{t}{\sqrt{d}} \tag{1.45}$$

Otherwise, as the standard variation becomes infinite when $d \longrightarrow \infty$, infinite energies could become possible which isn't possible. Under this normalization of the hopping :

$$\sigma = \sqrt{2} \tag{1.46}$$

For any dimension, the distribution of E is symmetric relatively to $E_0 - t_0$.

As $(K_\nu)_{\nu \in [1,d]}$ is a set of indepedent identically distributed random variables, it is also the case for $(X_\nu)_{\nu \in [1,d]} =^{def} (cos(K_\nu a))_{\nu \in [1,d]}$. The variance of X_ν is $\frac{1}{2}$ and its means 0. Therefore according to the Central Limit Theorem, $\frac{\sum_{\nu=1}^{d} cos(K_\nu a)}{d}$ tends to a normally distributed variable when $d \to \infty$. Hence :

$$E_{K_1,\ldots,K_d} \sim_{d \gg 1} -2\sqrt{d} * N(0, 1/2) \tag{1.47}$$

1.5 Graphene

Graphene is a well-known bi-dimensionnal structure which was discovered in 2004. It is made up of atoms of carbon forming a honeycomb lattice.

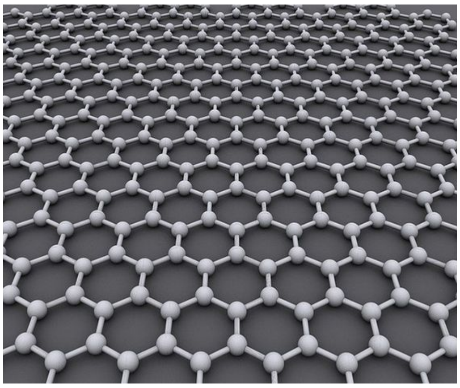

Figure 1.15: View of graphene direct lattice

The energy spectrum of graphene can be easily derived within the tight-binding approximation, thanks to Bloch's theorem. The calculation generalises the one-dimensionnal result, the only difference being that there are more couplings with neighbouring atoms to take into account, and that a unit cell of the direct lattice now contains two carbon atoms. Therefore, there are two possible energy states for each value of the quasi-momemtum, corresponding to two different wave functions $\psi^+_{k_x,k_y}$ and $\psi^-_{k_x,k_y}$. These fonctions have the following form :

$$\psi^+_{k_x,k_y}(\vec{r}) = \frac{1}{\sqrt{2N}} \sum_{\vec{R_n}} e^{i\vec{k}.\vec{R_n}} (\lambda^A_+ \chi^1(\vec{r} - \vec{R_n}) + \lambda^B_+ \chi^2(\vec{r} - \vec{R_n})) \tag{1.48}$$

and

$$\psi^-_{k_x,k_y}(\vec{r}) = \frac{1}{\sqrt{2N}} \sum_{\vec{R_n}} e^{i\vec{k}.\vec{R_n}} (\lambda^A_- \chi^1(\vec{r} - \vec{R_n}) + \lambda^B_- \chi^2(\vec{r} - \vec{R_n})) \tag{1.49}$$

where λ^+_A, λ^-_A and λ^+_B, λ^-_B are constant coefficients. We find that these functions are eigen wave-functions of the tight-binding hamiltonian, with good coefficients $\lambda^{+/-}_A$ and $\lambda^{+/-}_B$, and with the following eigen energies :

$$E^-_{k_x,k_y} = E_0 - t_0 - t\sqrt{3 + 2(2cos(\frac{3a}{2}k_x)cos(\frac{\sqrt{3}a}{2}k_y) + cos(\sqrt{3}ak_y))} \tag{1.50}$$

$$E^+_{k_x,k_y} = E_0 - t_0 + t\sqrt{3 + 2(2cos(\frac{3a}{2}k_x)cos(\frac{\sqrt{3}a}{2}k_y) + cos(\sqrt{3}ak_y))} \tag{1.51}$$

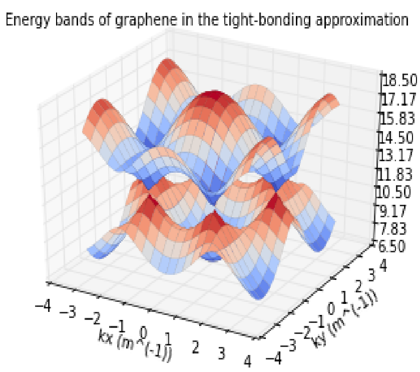

Figure 1.16: Energy spectrum of graphene under tight-binding approximation

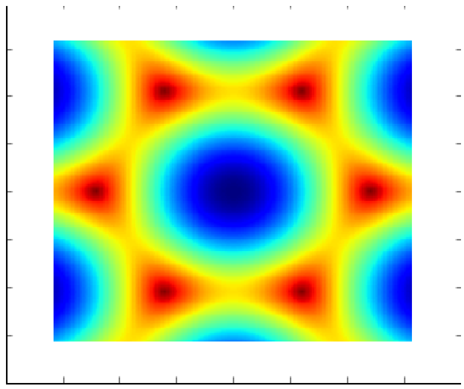

Figure 1.17: Projection of the energy spectrum of graphene in the quasi-momemtum space

As we did for regular lattices, we can estimate the density of states of graphene thanks to a Monte-Carlo method, by randomly choosing vectors $\vec{k}$ in the Brillouin Zone

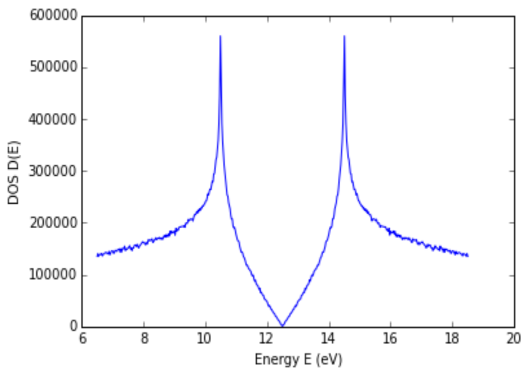

Figure 1.18: Density of states in graphene computed with the Monte-Carlo method with 1000000 random selections

We can see divergences of the density, which remind us of the behovior of the density in two dimensions, where the divergence was due to the saddle-points of the energy band at $E = E_0 - t_0$. For graphene, these singularities, called Van Hove singularities, appear at $E = E_0 - t_0 - t$ and $E = E_0 - t_0 + t$, also because of the saddle points, which make the number of states suddenly growing.

Chapter 2

Taking into account Hartree-Fock potential

2.1 Free electrons in a box

Let's consider free electrons in a box of length L and volume $V = L^3$. The number of electrons is denoted as N. The N electrons occupy N different quantum numbers α_i, each including both spin and momemtum $\vec{k_i}$:

$$\alpha_i = (\vec{k_i}, \sigma_i) \tag{2.1}$$

σ_i is the spin of the i^{th} electron.

The energy spectrum of the electrons when we neglect the interactions between them is :

$$E_{\vec{k}} = \frac{h^2 k^2}{2m} \tag{2.2}$$

corresponding to the hamiltonian $H = \frac{p^2}{2m}$.

Let's denote

$$e^2 = \frac{q_e^2}{4\pi\epsilon_0} = 2.3.10^{-28} SI \tag{2.3}$$

where q_e is the elementary charge of an electron.

If we consider an homogeneous ion potential $v_0(\vec{r})$, Hartree's potential and $v_0(\vec{r})$ exactly compensate each other :

$$v_0(\vec{r}) + V_{Hartree}(\vec{r}) = \int d\vec{r'} \frac{\rho^+(\vec{r'}).(-e^2) + \rho^-(\vec{r'}).e^2}{|\vec{r} - \vec{r'}|} = 0 \tag{2.4}$$

The wave function of an electron with quantum number α_n is

$$\psi_{\vec{k_n}}(\vec{r})|\sigma_n >= \frac{1}{\sqrt{V}} e^{i\vec{k_n}.\vec{r}} |\sigma_n > \tag{2.5}$$

The Fock term applied on $\psi_{\vec{k_n}}(\vec{r})$, knowing the waves functions of the other occupied states, is :

$$(H_{Fock}\psi_{\vec{k_n}})(\vec{r}) = -\sum_j \delta_{\sigma_j,\sigma_n} e^2 \int \frac{\psi^*_{\vec{k_j}}(\vec{r'})\psi_{\vec{k_n}}(\vec{r'})}{|\vec{r} - \vec{r'}|} \psi_{\vec{k_j}}(\vec{r}) \tag{2.6}$$

where the sum on j is a sum **over all occupied states**. This will turn out to be important when we will look at the correction of the energy due to Fock's term for occupied or non-occupied states. This term comes from Pauli principle and Fermi-Dirac statistics : it favors energetically situations with aligned spins of the electrons, because having the same spin implies that the two electrons won't be too close one to each other (thanks to Pauli principle).

As $\forall j,\ \psi_{\vec{k_j}}(\vec{r}) = e^{i\vec{k_j}.\vec{r}}$:

$$(H_{Fock}\psi_{\vec{k_n}})(\vec{r}) = -\sum_j \delta_{\sigma_j,\sigma_n} e^2 \int \frac{e^{i(\vec{k_n}-\vec{k_j}).(\vec{r'}-\vec{r})}}{|\vec{r'}-\vec{r}|}\frac{1}{V}\frac{1}{\sqrt{V}}e^{i\vec{k_n}.\vec{r}}d\vec{r'} \tag{2.7}$$

$$= -\frac{e^2}{V}\frac{V}{(2\pi)^3}\int_{|\vec{k}|<k_F}(\int d\vec{u}\frac{e^{i(\vec{k_n}-\vec{k_j}).\vec{u}}}{|\vec{u}|})d\vec{k}\psi_{\vec{k_n}}(\vec{r}) \tag{2.8}$$

where the integral deals with all vectors $\vec{k}$ which are occupied by one of the electron, which must have, on top of that, the same spin as the n^{th} electron. Switching from the discrete sum over j to the integral over $\vec{k}$ is allowed insofar as the number of occupied states is big enough. (so that the value of $\vec{k_j}$ vectors are very close one to each other) We notice that the self-interaction term doesn't count in the integral as the Lebesgue-measure of a point in three dimensions is 0.

The following term :

$$\int d\vec{u}\frac{e^{i(\vec{k_n}-\vec{k_j}).\vec{u}}}{|\vec{u}|} \tag{2.9}$$

turns out to be the Fourier transform of the funtion $\vec{u} \longmapsto \frac{1}{|\vec{u}|}$. Hence :

$$\int d\vec{u}\frac{e^{i(\vec{k_n}-\vec{k_j}).\vec{u}}}{|\vec{u}|} = \frac{4\pi}{|\vec{k_n}-\vec{k}|^2} \tag{2.10}$$

We conclude that

$$(H_{Fock}\psi_{\vec{k_n}})(\vec{r}) = -\frac{4\pi e^2}{(2\pi)^3}\int_{|\vec{k}|<k_F}\frac{d\vec{k}}{|\vec{k_n}-\vec{k}|^2} \tag{2.11}$$

The energy of this electron now is :

$$\frac{h^2k_n^2}{2m} - \frac{4\pi e^2}{(2\pi)^3}\int_{|\vec{k}|<k_F}\frac{d\vec{k}}{|\vec{k_n}-\vec{k}|^2} =^{def} \frac{h^2k_n^2}{2m} - \Delta(\vec{k_n}) \tag{2.12}$$

The integral deals with all $\vec{k}$ vectors such that $|\vec{k}| < k_F$ only if the electronic states are occupied up to the Fermi energy. For instance in the half-filled case, the integral will adress less $\vec{k}$ states ($\vec{k} : |\vec{k}| < \alpha k_F$ where $\alpha < 1$).

Let's focus on this correction $\Delta(\vec{k})$ to the energy in the free electrons case :

$$\int\int\int_{|\vec{k'}|<k_F}\frac{d\vec{k'}}{|\vec{k}-\vec{k'}|^2} = \int\int\int_{|\vec{v}-\vec{k}|<k_F}\frac{d\vec{v}}{|\vec{v}|^2} \tag{2.13}$$

This integral appears difficult to compute in the general situation where the three components of $\vec{k}$ are different from 0. The expression in spherical coordinates is :

$$\Delta(\vec{k}) = \frac{4\pi e^2}{(2\pi)^3}\int_0^{k_F}\int_0^{\pi}\int_0^{2\pi}\frac{r'^2 sin(\theta')}{k^2+r'^2-2r'[sin(\theta')(k_x cos(\phi')+k_y sin(\phi'))+k_z cos(\theta')]}dr'd\theta'd\phi' \tag{2.14}$$

Computation in the simplified case $\vec{k} = k\vec{e_z}$:
In this case, 2.14 becomes :

$$\Delta(\vec{k}) = \frac{4\pi e^2}{(2\pi)^3}2\pi\int_0^{k_F}\int_0^{\pi}\int_0^{2\pi}\frac{r'^2 sin(\theta')}{k^2+r'^2-2r'kcos(\theta')}dr'd\theta'd\phi' = \frac{4\pi e^2}{(2\pi)^3}2\pi\int_0^{k_F}r^2(\int_0^{\pi}\frac{sin(\theta)}{k^2+r^2-2rkcos(\theta)}d\theta)dr \tag{2.15}$$

$$\Delta(\vec{k}) = \frac{4\pi e^2}{(2\pi)^3}\int_0^{k_F}\int_0^{\pi}r^2\frac{1}{2rk}[ln|k^2+r^2-2rkcos(\theta)|]_0^{\pi}dr' = \frac{4\pi e^2}{(2\pi)^3}\frac{2\pi}{k}\int_0^{k_F}r\ln|\frac{k+r}{k-r}|dr \tag{2.16}$$

Now, we notice that :

$$\frac{d}{dr}((k^2-r^2)\ln|\frac{k+r}{k-r}|) = -2r\ln|\frac{k+r}{k-r}| + 2k \tag{2.17}$$

therefore

$$\frac{d}{dr}\left(-\frac{1}{2}[(k^2-r^2)\ln|\frac{k+r}{k-r}|-2kr]\right)=r\ln|\frac{k+r}{k-r}| \tag{2.18}$$

Using this primitive in 2.16, we finally find :

$$\Delta(\vec{k})=\frac{4\pi e^2}{(2\pi)^3}\left(-\frac{\pi}{k}k_F^2\left(\left(\frac{k}{k_F}\right)^2-1\right)ln|\frac{1+\frac{k}{k_F}}{1-\frac{k}{k_F}}|+2\pi k_F\right) \tag{2.19}$$

$$\Longrightarrow \Delta(\vec{k})=\frac{2e^2}{\pi}k_F\left(\frac{1}{2}+\frac{1-(\frac{k}{k_F})^2}{4\frac{k}{k_F}}ln|\frac{1+\frac{k}{k_F}}{1-\frac{k}{k_F}}|\right)=^{def}\frac{2e^2}{\pi}k_F G(x) \tag{2.20}$$

where $x=\frac{k}{k_F}$ and

$$G(x)=\frac{1}{2}+\frac{1-x^2}{4x}\ln|\frac{1+x}{1-x}| \tag{2.21}$$

Computation using Monte-Carlo techniques :

The computation of the integral $\Delta(\vec{k})$ with a Monte-Carlo method gives the following result :

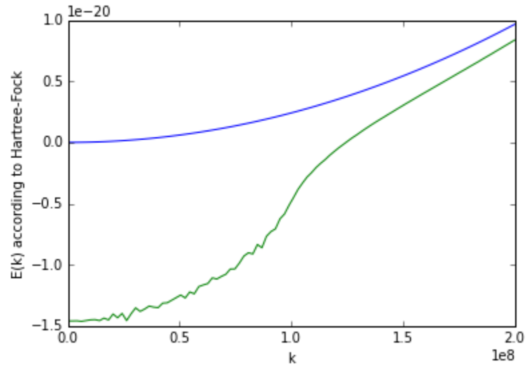

Figure 2.1: Correction the energy of free electrons estimated by Hartree-Fock's term for $k_F=10^8m^{-1}$, computed with a Monte-Carlo approach : n=1000000

The method consists to use random variables K_1,K_2,K_3 uniform over the intervals $[k_x-k_F,k_x+k_F]$, $[k_y-k_F,k_y+k_F]$ and $[k_z-k_F,k_z+k_F]$ respectively. Thus (K_1,K_2,K_3) is a uniform random variable over the cube centered in $\vec{k}$ and of side length k_F. The volume of this cube is therefore $(2k_F)^3$. Let's denote the integrand $f(\vec{k'})=\frac{1}{|\vec{k'}-\vec{k}|^2}$ and n the number of such independent random variables $\vec{K^i}=^{def}(K_1^i,K_2^i,K_3^i)$. Monte-Carlo techniques imply that

$$V_n=^{def}\frac{1}{n}\sum_{i=1}^{n}1_{\vec{K^i}\in B(\vec{k},k_F)}f(\vec{K^i})\longrightarrow_{n\longrightarrow\infty}^{p.s}E(1_{\vec{K}\in B(\vec{k},k_F)}f(\vec{K})) \tag{2.22}$$

where :

$$E(1_{\vec{K}\in B(\vec{k},k_F)}f(\vec{K}))=\frac{1}{(2k_F)^3}\int_{-d}^{d}\int_{-d}^{d}\int_{-d}^{d}1_{\begin{pmatrix}x\\y\\z\end{pmatrix}\in B(\vec{k},k_F)}f(x,y,z)dxdydz \tag{2.23}$$

because the density of the uniform random variable $\vec{K}$ is constant and equal to $\frac{1}{(2k_F)^3}$.

Therefore

$$\int\int\int_{\vec{k'}\in B(\vec{k},k_F)}f(\vec{k'})=\int\int\int_{\vec{k'}\in B(\vec{k},k_F)}\frac{1}{|\vec{k'}-\vec{k}|^2}=(2k_F)^3 lim_{n\longrightarrow\infty}V_n \tag{2.24}$$

The results we obtain are shown above in the plot 2.1. The plot of the energy corrected by Hartree-Fock's term and estimated thanks to a Monte-Carlo approach is smoother for $k>k_F$ than for $k<k_F$. Indeed when $\vec{k}$ becomes greater than k_F in norm, there isn't singularity anymore in the integral, as

$|\vec{k'} - \vec{k}| > 0$ for every $\vec{k'} \in B(\vec{k}, k_F)$.

Let's now compare these results with the exact expression of this triple integral, found by Ashcroft and Mermin :

$$\Delta(\vec{k}) = \frac{2e^2}{\pi} k_F G(\frac{k}{k_F}) \tag{2.25}$$

where $G(.)$ is the following function :

$$G(x) = \frac{1}{2} + \frac{1 - x^2}{4x} \ln |\frac{1 + x}{1 - x}| \tag{2.26}$$

The graph of the function $k \longmapsto G(\frac{k}{k_F})$ is given below (k_F being fixed at $10^8 m^{-1}$) :

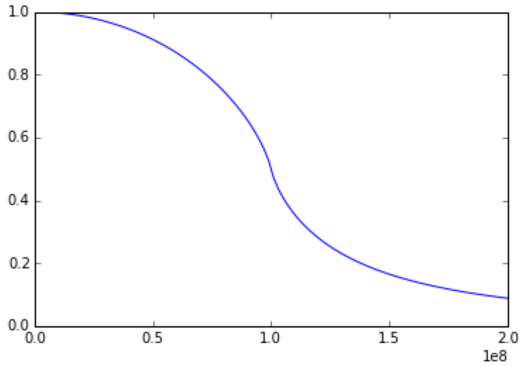

Figure 2.2: Function G

As $G(.)$ takes its values in $[0, 1]$, the correction to the energy of free electrons will be noticed if $e^2 k_F$ and $\frac{h^2 k^2}{2m}$ have the same order of magnitude (let's say 1 eV for instance). We find that :

$$e^2 k_F \sim \frac{h^2 k_F^2}{2m} \Longleftrightarrow k_F \sim 10^8 m^{-1} \tag{2.27}$$

We will therefore choose a Fermi vector of norm close to 10^8 m^{-1} to plot the energies. This is associated with a Fermi velocity of 10^4 m/s approximately.

Let's plot on a same graph the energy of free independent electrons and the energy computed when taking int account Fock's term, namely :

$$E_{corrige}(k) = \frac{h^2 k^2}{2m} - \frac{q_e^2}{2\pi^2 \epsilon_0} k_F G(\frac{k}{k_F}) \tag{2.28}$$

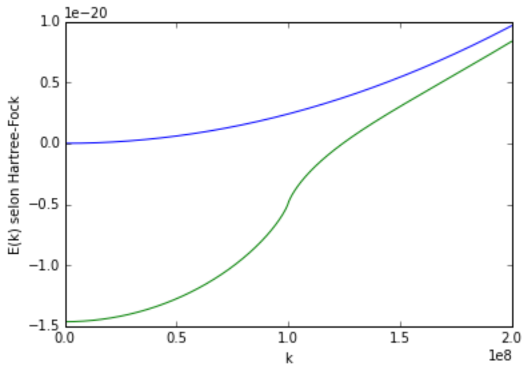

Figure 2.3: Correction of the energy (J) of free electrons by taking into account Hartree-Fock's term for $k_F = 10^8$ m^{-1}

When k_F increases, the correction is slighter :

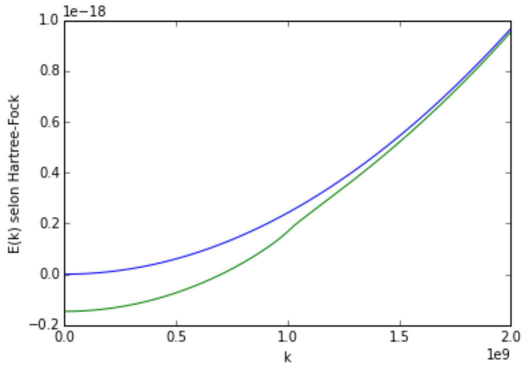

Figure 2.4: Correction of the energy (J) of free electrons by taking into account Hartree-Fock's term for $k_F = 10^9\ m^{-1}$

On the contrary when k_F decreases, **the variation** of the energy of free independent electrons becomes negligible in comparison with **the variation** of the Hartree-Fock energy.

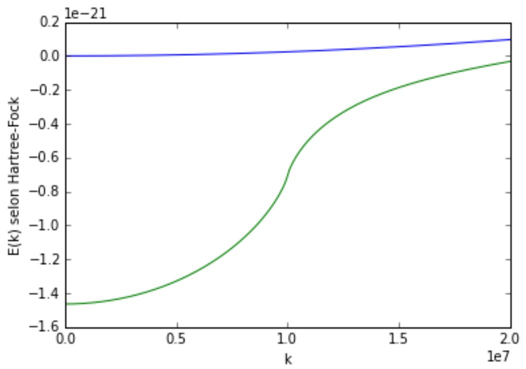

Figure 2.5: Correction of the energy (J) of free electrons by taking into account Hartree-Fock's term for $k_F = 10^7\ m^{-1}$

The behaviour at $k = k_F$ seems peculiar, let's zoom in on it :

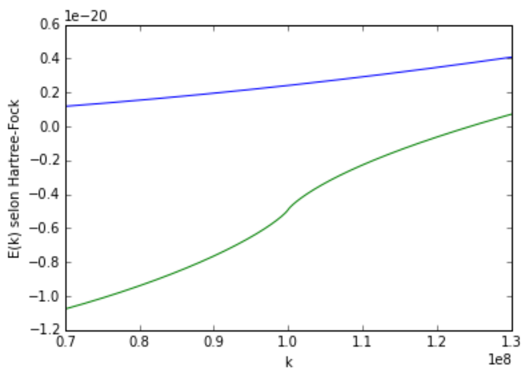

Figure 2.6: Correction of the energy (J) of free electrons by taking into account Hartree-Fock's term for $k_F = 10^8\ m^{-1}$, for k close to k_F

The derivative of the energy computed with Hartree-Fock's method is infinite at $k = k_F$. It tends logarithmically towards ∞ : when we zoom ten times more on the neighboourhood of k_F, the maximal value increases only twofold, which is typical of a logarithmic divergence :

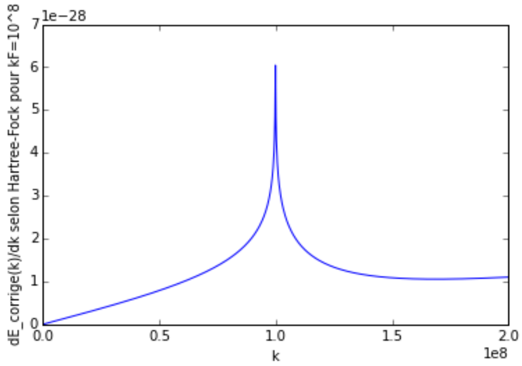

Figure 2.7: Derivative of the energy (J) of free electrons by taking into account Hartree-Fock's term for $k_F = 10^8\ m^{-1}$

Therefore **the Fermi velocity is infinite at** $k = k_F$, which is not physical. This will be corrected by taking screening into account.

The two-fold derivative of this energy is also discontinuous, which is seen by the concavity which suddenly changes at $k = k_F$ (convex for $k < k_F$ and concave for $k > k_F$).

Using that $G(0) = 1$ and $G(1) = \frac{1}{2}$, we find that :

$$E_{corrige}(k = 0) = -\frac{q_e^2}{2\pi^2\epsilon_0}k_F =^{def} A \tag{2.29}$$

and

$$E_{corrige}(k = k_F) = \frac{h^2k_F^2}{2m} - \frac{q_e^2}{4\pi^2\epsilon_0}k_F = \frac{h^2k_F^2}{2m} - \frac{A}{2} \tag{2.30}$$

The band width, namely the difference between the highest and the lowest energy of occupied states is in the filled case :

$$E_{corrige}(k_F) - E_{corrige}(0) = \frac{h^2k_F^2}{2m} + \frac{q_e^2}{4\pi^2\epsilon_0}k_F > \frac{h^2k_F^2}{2m} = E_{ind.electrons}(k_F) - E_{ind.electrons}(0) \tag{2.31}$$

We have Bandwidth(Hartree-Fock)=Bandwidth(independent electrons)+$\frac{A}{2}$.

Therefore the Hartree-Fock's term makes the band-width increase compared with independent electrons, which is seen below :

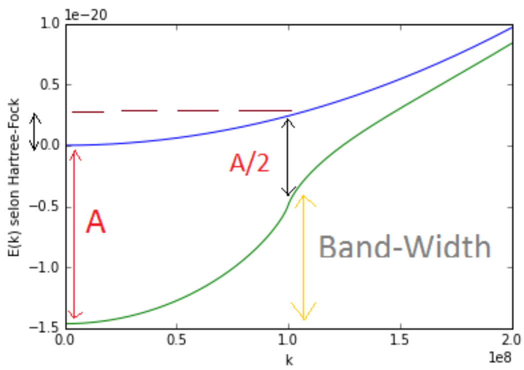

Figure 2.8: Correction of the energy (J) of free electrons by taking into account Hartree-Fock's term for $k_F = 10^8\ m^{-1}$

Some limit computations give :

$$G(\frac{k}{k_F}) - \frac{1}{2} \sim_{k \to k_F} -\frac{2}{k_F}(k_F - k)\ln(|k_F - k|) \tag{2.32}$$

Besides, computing the derivative of $G(.)$ and then the equivalent gives the following :

$$G'(x) \sim -\frac{1}{2}\ln(1-x) \Rightarrow (\frac{d\Delta}{dk})(k) \sim_{k\to k_F} -\frac{q_e^2}{4\pi^2\epsilon_0}\ln|k_F - k| \to \infty \tag{2.33}$$

We recognize the logarithmic divergence we had guessed by zooming on the peak of the derivative of $\Delta(k)$. Such divergence aren't easy to see in plots.

AS we have previously seen, at a fixed k, the correction is bigger when k_F decreases (remaining greater than k) :

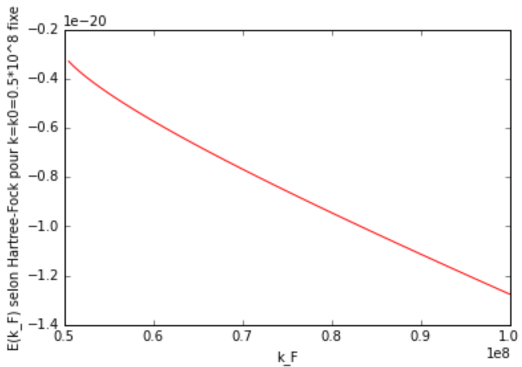

Figure 2.9: Hartree-Fock energy at $k = k_0$ fixed and variable k_F

Remark How do we calculate the Fermi energy ? The number of electrons in the system sets the Fermi vector $\vec{k_F}$. It is unchanged for the same system of electrons where we now consider Hartree-Fock's term. Indeed there are the same number of electrons and the same possible values for the quasi-momentum $\vec{k}$, quantized because of Periodic Boundary Conditions. The energy levels are filled by increasing energy, and the energy is an increasing funtion of $k = ||\vec{k}||$. The Fermi level has then the same quasi-momemtum $\vec{k_F}$ but a different energy level.
The biggest energy of an occupied electronic state previously was $\frac{h^2k_F^2}{2m}$, and is now :

$$max_{\vec{k'}occupied}(\frac{h^2k'^2}{2m} - \frac{4\pi e^2}{(2\pi)^3}\int_{|\vec{k}|<k'}\frac{d\vec{k}}{|\vec{k'}-\vec{k}|^2}) = \frac{h^2k_F^2}{2m} - \frac{4\pi e^2}{(2\pi)^3}\int_{|\vec{k}|<k_F}\frac{d\vec{k}}{|\vec{k_F}-\vec{k}|^2} \tag{2.34}$$

2.1.1 One dimensional lattice

Let k_n be a **possible** quantum state of an electron in this system of N equally spaced atoms. We will make the distinction if the state is occupied or not.
We denote the atomic orbital functions as $\psi_n(.)$. The energy spectrum computed within the tight-binding approximation is

$$E_k = E_0 - t_0 - 2t cos(ka) \tag{2.35}$$

where $k = \frac{2\pi m}{Na}$, $m \in Z$.

$$(H_{Fock}\psi_{\vec{k_n}})(\vec{r}) = -\sum_{jocc.}\delta_{\sigma_j,\sigma_n}e^2\int d\vec{r}\frac{\psi^*_{\vec{k_j}}(\vec{r'})\psi_{\vec{k_n}}(\vec{r'})}{|\vec{r}-\vec{r'}|}\psi_{\vec{k_j}}(\vec{r}) \tag{2.36}$$

where the sum on j is a sum **over all occupied states**.

$$\forall j, \psi_{k_j}(r) = \frac{1}{\sqrt{N}}\sum_n e^{ik_jna}\psi_n(r) \tag{2.37}$$

Hence :

$$\psi^*_{k_j}(r')\psi_{k_n}(r') = \frac{1}{N}\sum_n e^{i(k_n-k_j)na}|\psi_n(r')|^2 \tag{2.38}$$

because $\psi^*_{n_1}(r')\psi_{n_2}(r') = 0$ if $n_1 \neq n_2$ as we suppose that atomic orbitals don't overlap.

$$(H_{Fock}\psi_{k_n})(r) = -\sum_{jocc.} \delta_{\sigma_j,\sigma_n}[\frac{e^2}{N}\sum_{m=1}^{N}(\int d\vec{r'}\frac{|\psi_m(r')|^2}{|\vec{r}-\vec{r'}|})e^{i(k_n-k_j)ma}]\psi_{k_j}(r) \tag{2.39}$$

Let denote :

$$\Gamma_{n,j}(r) = \frac{e^2}{N}\sum_{m=1}^{N}(\int d\vec{r'}\frac{|\psi_m(r')|^2}{|\vec{r}-\vec{r'}|})e^{i(k_n-k_j)ma} \tag{2.40}$$

so that:

$$(H_{Fock}\psi_{k_n})(r) = -\sum_{jocc.} \delta_{\sigma_j,\sigma_n}\Gamma_{n,j}(r)\psi_{k_j}(r) \tag{2.41}$$

If the state k_n is indeed occupied, the state labelled by the index n is reached in the sum over j. We thus distinguish two terms in the previous expression : the self-interaction (for $j = n$) term and the rest :

$$-\frac{e^2}{N}\int d\vec{r'}\frac{(\sum_{m=1}^{N}|\psi_m(r')|^2)}{|\vec{r}-\vec{r'}|}\psi_{k_n}(r) - \sum_{jocc.,j\neq n}\delta_{\sigma_j,\sigma_n}[\frac{e^2}{N}\sum_{m=1}^{N}(\int d\vec{r'}\frac{|\psi_m(r')|^2}{|\vec{r}-\vec{r'}|})e^{i(k_n-k_j)ma}]\psi_{k_j}(r) \tag{2.42}$$

$$(H^{Fock}_{auto-interaction}\psi_{k_n})(r) = -\frac{e^2}{N}\int d\vec{r'}\frac{(\sum_{m=1}^{N}|\psi_m(r')|^2)}{|\vec{r}-\vec{r'}|}\psi_{k_n}(r) \tag{2.43}$$

On the other side, we must express Hartree's potential :

$$(V_{Hartree}\psi_{k_n})(r) = e^2\int d\vec{r'}\frac{\rho(r')}{|r-r'|}\psi_{k_n}(r) \tag{2.44}$$

where $\rho(.)$ is the electronic density :

$$\rho(r') = \sum_{jocc.}^{N}|\psi_{k_j}(r')|^2 \tag{2.45}$$

The equation 2.1.1 implies that

$$\forall j, |\psi_{k_j}(r')|^2 = \frac{1}{N}\sum_{m=1}^{N}|\psi_m(r')|^2 \tag{2.46}$$

which is the same for all occupied electronic states.

We deduce that

$$\rho(r') = \frac{N_e}{N}\sum_{m=1}^{N}|\psi_m(r')|^2 \tag{2.47}$$

with N_e **the number of electrons** in the system, which differs from the number of occupied states N^{occ}, as we can put two electrons in each state. We thus have :

$$(V_{Hartree}\psi_{k_n})(r) = e^2\frac{N_e}{N}\int d\vec{r'}\frac{(\sum_{m=1}^{N}|\psi_m(r')|^2)}{|\vec{r}-\vec{r'}|}\psi_{k_n}(r) \tag{2.48}$$

We must not forget that this expression includes a self-interaction term if k_n is an occupied state (as $|\psi_{k_n}(r')|^2$ appears in the expression of $\rho(r')$ in this case):

$$(V^{Hartree}_{self-interaction}\psi_{k_n})(r) = e^2\int d\vec{r'}\frac{|\psi_{k_n}(r')|^2}{|r-r'|}\psi_{k_n}(r) \tag{2.49}$$

$$= -e^2\delta_{\sigma_n,\sigma_n}\int d\vec{r'}\frac{\psi^*_{k_n}(r')\psi_{k_n}(r')}{|r-r'|}\psi_{k_n}(r) \tag{2.50}$$

$$= -\frac{e^2}{N}\int d\vec{r'}\frac{(\sum_{m=1}^{N}|\psi_m(r')|^2)}{|\vec{r}-\vec{r'}|}\psi_{k_n}(r) \tag{2.51}$$

$$= -(H^{Fock}_{self-interaction}\psi_{k_n})(r) \tag{2.52}$$

if k_n is an occupied state.

We have proved that the Fock term allows to get rid of the self-interaction problem :

$$(V^{Hartree}_{self-interaction} + H^{Fock}_{self-interaction})\psi_{k_n}(r) = 0 \tag{2.53}$$

If k_n is not an occupied state, the self-interaction terms both in Hartree's potential and in Fock's term don't exist. The equation 2.1.1 implies that $\psi_{k_n}(r)$ remains an eigen vector af $H^{Fock}_{self-interaction} + V_{Hartree}$:

$$(H^{Fock}_{self-interaction} + V_{Hartree})\psi_{k_n}(r) = e^2\frac{N_e-1}{N}\int d\vec{r'}\frac{(\sum_{m=1}^{N}|\psi_m(r')|^2)}{|\vec{r}-\vec{r'}|}\psi_{k_n}(r) \tag{2.54}$$

Among the four components of the Hartree-Fock term :
$H^{Fock}_{self-interaction}$, $H^{Fock}_{without-self-interaction}$, $V^{Hartree}_{self-interaction}$, $V^{Hartree}_{without-self-interaction}$, only two remain :

$$H^{Fock}_{without-self-interaction} + V^{Hartree}_{without-self-interaction} \tag{2.55}$$

At the first order, the variation of the energy of the electronic state k_n state **due to Fock's term** is

$$\Delta(E_{k_n})_{Fock} =< \psi_{k_n}|H^{Fock}_{without-self-interaction}|\psi_{k_n} > \tag{2.56}$$

$$= \int \psi^*_{k_n}(r)(H^{Fock}_{w.s.i.}\psi_{k_n})(r)d\vec{r} = -\sum_{j=1,j\neq n,jocc.}\delta_{\sigma_j,\sigma_n}\int \psi^*_{k_n}(r)\Gamma_{n,j}(r)\psi_{k_j}(r)d\vec{r} \tag{2.57}$$

thanks to 2.1.1.

Let's compute $\int \psi^*_{k_n}(r)\Gamma_{n,j}(r)\psi_{k_j}(r)d\vec{r}$:

$$\int \psi^*_{k_n}(r)\Gamma_{n,j}(r)\psi_{k_j}(r)d\vec{r} = \frac{1}{N}\sum_{l=1}^{N}e^{i(k_j-k_n)la}\int d\vec{r}|\psi_l(r)|^2\Gamma_{n,j}(r) \tag{2.58}$$

thanks to the non-overlapping assumption ($\psi^*_{l_1}(r)\psi_{l_2}(r) = 0$ if $l_1 \neq l_2$). Therefore, using the expression 2.1.1 of $\theta_{n,j}(.)$:

$$\int \psi^*_{k_n}(r)\Gamma_{n,j}(r)\psi_{k_j}(r)d\vec{r} = \frac{e^2}{N^2}\sum_{l=1}^{N}\sum_{m=1}^{N}[\int d\vec{r}|\psi_l(\vec{r})|^2(\int d\vec{r'}\frac{|\psi_m(\vec{r'})|^2}{|r-r'|})]e^{i(k_n-k_j)(m-l)a} \tag{2.59}$$

We conclude that for a one dimensional lattice (seen in a three-dimensional space) :

$$\Delta(E_{k_n})_{Fock} = -\sum_{j=1,j\neq n,jocc.}\delta_{\sigma_j,\sigma_n}\frac{e^2}{N^2}\sum_{l=1}^{N}\sum_{m=1}^{N}[\int d\vec{r}|\psi_l(\vec{r})|^2(\int d\vec{r'}\frac{|\psi_m(\vec{r'})|^2}{|r-r'|})]e^{i(k_n-k_j)(m-l)a} \tag{2.60}$$

The knowledge of the orbital functions $\psi_l(.)$ appears necessary to estimate this correction to the energy.

We also have to consider the variation of the energy of the electronic state k_n state **due to Hartree's term and the self-interaction Fock term** (if there is one, namely if k_n is an occupied state) :

$$\Delta(E_{k_n})_{Hartree} =^{def} < \psi_{k_n}|H^{Fock}_{s.i.} + V^{Hartree}|\psi_{k_n} >=< \psi_{k_n}|V^{Hartree}_{w.s.i.}|\psi_{k_n} > \tag{2.61}$$

$$\Rightarrow \Delta(E_{k_n})_{Hartree} = \int d\vec{r}\psi^*_{k_n}(\vec{r})(e^2\frac{N_e-\delta^{occ.}_{k_n}}{N}\int d\vec{r'}\frac{\sum_{m=1}^{N}|\psi_m(\vec{r'})|^2}{|\vec{r}-\vec{r'}|})\psi_{k_n}(\vec{r}) \tag{2.62}$$

Therefore, using 2.46, if k_n is not an occupied state :

$$\Delta(E_{k_n})_{Hartree} = e^2\frac{N_e}{N^2}\sum_{l=1}^{N}\sum_{m=1}^{N}[\int d\vec{r}|\psi_l(\vec{r})|^2\int d\vec{r'}\frac{(|\psi_m(\vec{r'})|^2)}{|\vec{r}-\vec{r'}|}] \tag{2.63}$$

On the contrary, if k_n is an occupied state :

$$\Delta(E_{k_n})_{Hartree} = e^2 \frac{N_e - 1}{N^2} \sum_{l=1}^{N} \sum_{m=1}^{N} [\int d\vec{r} |\psi_l(\vec{r})|^2 \int d\vec{r'} \frac{(|\psi_m(\vec{r'})|^2)}{|\vec{r} - \vec{r'}|}] \tag{2.64}$$

To sum it all, the total correction to the energy at the first order (treating Hartree-Fock's terms as perturbations):

$$\Delta(E_{k_n}) = \Delta(E_{k_n})_{Hartree} + \Delta(E_{k_n})_{Fock} \tag{2.65}$$

namely :

$$e^2 \frac{N_e - \delta_{k_n}^{occ}}{N^2} \sum_{l=1}^{N} \sum_{m=1}^{N} [\int d\vec{r} |\psi_l(\vec{r})|^2 \int d\vec{r'} \frac{(|\psi_m(r')|^2)}{|\vec{r} - \vec{r'}|}] - \sum_{j \neq n, jocc.} \delta_{\sigma_j,\sigma_n} \frac{e^2}{N^2} \sum_{l=1}^{N} \sum_{m=1}^{N} [\int d\vec{r} |\psi_l(\vec{r})|^2 (\int d\vec{r'} \frac{|\psi_m(\vec{r'})|^2}{|r - r'|})] e^{i(k_n - k_j)(m-l)a} \tag{2.66}$$

where $e^2 = \frac{q_e^2}{4\pi\epsilon_0}$ and $\delta_{k_n}^{occ} = 1$ if k_n is indeed occupied, and equals 0 otherwise. Therefore **the correction to the energy due to Hartree's potential and Fock's term is different for free and occupied states**.

Both terms coming from Hartree's term and from Fock's term have the same order of magnitude. Indeed for both, $\frac{e^2}{N^2}$ is a prefactor. The first term has a prefactor of order N_e, the number of occupied states, but the second term coming from Fock's term calculations involves a sum over the occupied states labeled by j, and there are $N^{occ} = \frac{N_e}{2}$ such non-zero terms.

We also notice that the double integral involving the atomic orbital wave functions $\psi_m(.)$ and $\psi_l(.)$ appears in both term. An another expression of the energy correction would be :

$$\frac{e^2}{N^2} \sum_{l=1}^{N} \sum_{m=1}^{N} (\int d\vec{r} |\psi_l(\vec{r})|^2 \int d\vec{r'} \frac{(|\psi_m(\vec{r'})|^2)}{|\vec{r} - \vec{r'}|})(N_e - \delta_{k_n}^{occ} - \sum_{j \neq n, jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n - k_j)(m-l)a}) \tag{2.67}$$

Let's adopt the following notation :

$$I_{l,m} = \int d\vec{r} \int d\vec{r'} \frac{|\psi_m(\vec{r'})|^2 |\psi_l(\vec{r})|^2}{|\vec{r} - \vec{r'}|} \tag{2.68}$$

and

$$\Theta_{l,m}^n = (N_e - \delta_{k_n}^{occ} - \sum_{j \neq n, jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n - k_j)(m-l)a}) \tag{2.69}$$

As the correction to the energy is a real number, by taking the imaginary part, we obtain that :

$$\sum_{j \neq n, jocc.} \delta_{\sigma_j,\sigma_n} sin((k_n - k_j)(m-l)a) = 0 \tag{2.70}$$

so that it is the same to write $\Theta_{l,m}^n$ with exponential or cosine.

We notice the symetry of the roles played by l and m : $I_{l,m} = I_{m,l}$.

The equation 2.67 can be rewritten as :

$$\Delta(E_{k_n}) = \frac{e^2}{N^2} \sum_{l=1}^{N} \sum_{m=1}^{N} I_{l,m} \Theta_{l,m}^n \tag{2.71}$$

A little calculation, using that $k_n = \frac{2\pi}{Na} p_n$ (p_n being an integer) for a one-dimensionnal lattice, gives the following :

$$l = m \Rightarrow \Theta_{l,m}^n = N_e - N^{occ} = \frac{N_e}{2} \tag{2.72}$$

if (k_n, σ_n) is not an occupied state.

If $l \neq m$ and all the N possible states are occupied, each by two electrons with opposite spins, :

$$\Theta^n_{l,m} = N_e - \delta^{occ}_{k_n} + 1 \approx N_e = 2N^{occ} \tag{2.73}$$

because

$$\sum_{j=1,jocc.}^{N} e^{i\frac{2\pi}{N}(n-j)(m-l)} = e^{i\frac{2\pi}{N}n(m-l)} \sum_{j=1,jocc.}^{N} (e^{i\frac{2\pi}{N}(l-m)})^j = 0 \tag{2.74}$$

in this specific case.

Invariance by translation

We can simplify the expression 2.71 using the periodic boundary conditions. Let l_0 be an integer in $[1, N]$. Let's prove that

$$\sum_{m=1}^{N} I_{l_0,m}\Theta^n_{l_0,m} \tag{2.75}$$

does not depend on the integer l_0.

$$I_{l_0+1,m} = \int d\vec{r} \int d\vec{r'} \frac{|\psi_m(\vec{r'})|^2|\psi_{l_0+1}(\vec{r})|^2}{|\vec{r}-\vec{r'}|} = \int d\vec{r} \int d\vec{r'} \frac{|\chi(\vec{r'}-ma\vec{e_x})|^2|\chi(\vec{r}-(l_0+1)a\vec{e_x})|^2}{|\vec{r}-\vec{r'}|} \tag{2.76}$$

where $\chi(.)$ is the atomic orbital of the site at the origin of the lattice.

Thanks to the new variable $\vec{u} = \vec{r} - a\vec{e_x}$:

$$I_{l_0+1,m} = \int d\vec{u} \int d\vec{r'} \frac{|\chi(\vec{r'}-ma\vec{e_x})|^2|\chi(\vec{u}-l_0a\vec{e_x})|^2}{|\vec{u}-(\vec{r'}-a\vec{e_x})|} \tag{2.77}$$

and $\vec{v} = \vec{r'} - a\vec{e_x}$:

$$I_{l_0+1,m} = \int d\vec{u} \int d\vec{v} \frac{|\chi(\vec{v}-(m-1)a\vec{e_x})|^2|\chi(\vec{u}-l_0a\vec{e_x})|^2}{|\vec{u}-\vec{v}|} = \int d\vec{u} \int d\vec{v} \frac{|\psi_{m-1}(\vec{v})|^2|\psi_{l_0}(\vec{u})|^2}{|\vec{u}-\vec{v}|} \tag{2.78}$$

We have proven that

$$I_{l_0+1,m} = I_{l_0,m-1} \tag{2.79}$$

Moreover

$$\Theta^n_{l_0+1,m} = (N^{occ} - \delta^{occ}_{k_n} - \sum_{j\neq n,jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n-k_j)(m-l_0-1)a}) = \Theta^n_{l_0,m-1} \tag{2.80}$$

Therefore :

$$\sum_{m=1}^{N} I_{l_0+1,m}\Theta^n_{l_0+1,m} = \sum_{m=1}^{N} I_{l_0,m-1}\Theta^n_{l_0,m-1} \tag{2.81}$$

The Periodic Boundary Conditions give :

$$I_{l_0,0} = \int d\vec{r} \int d\vec{r'} \frac{|\psi_0(\vec{r'})|^2|\psi_{l_0}(\vec{r})|^2}{|\vec{r}-\vec{r'}|} = \int d\vec{r} \int d\vec{r'} \frac{|\psi_N(\vec{r'})|^2|\psi_{l_0}(\vec{r})|^2}{|\vec{r}-\vec{r'}|} = I_{l_0,N} \tag{2.82}$$

because the N^{th} atom of the lattice also is the atom labelled by 0 in the PBC approximation.

$$\Theta^n_{l_0,N} = (N_e - \delta^{occ}_{k_n} - \sum_{j\neq n,jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n-k_j)(N-l_0)a}) = (N_e - \delta^{occ}_{k_n} - \sum_{j=1,j\neq n,jocc.} \delta_{\sigma_j,\sigma_n} e^{-i(k_n-k_j)l_0a}) \tag{2.83}$$

because $(k_n - k_j)Na = \frac{2\pi(p_n-p_j)}{Na}Na = 2\pi(p_n - p_j)$ where p_n and p_j are integers.

In the end, 2.81 becomes :

$$\sum_{m=1}^{N} I_{l_0+1,m}\Theta^n_{l_0+1,m} = \sum_{m=1}^{N} I_{l_0,m}\Theta^n_{l_0,m} \tag{2.84}$$

Therefore

$$\Delta(E_{k_n}) = \frac{e^2}{N} \sum_{m=1}^{N} I_{l_0,m} \Theta^n_{l_0,m} \tag{2.85}$$

for any l_0.

To compute $\Delta(E_{k_n})$, I first tried Monte-Carlo methods. We'll see that it is not necessary to have a simple estimation of the correction to the energy, but such methods can turn out to be useful in the case of complicated atomic localised orbitals.

Stochastics methods :
My first idea was to find a simple way to compute the integrals $I_{l,m}$, as we need them to estimate the global correction to the energy. I used Monte-Carlo methods. Nevertheless, because of the divergence of the integrand at some points, the convergence speed wasn't good enough. M. Ferrero then told me about **Metropolis algorithm**.

We write the correction due to Hartree-Fock's term in the following way :

$$\Delta(E_{k_n}) = e^2 \sum_{m=1}^{N} \int d\vec{r} \int d\vec{r'} \frac{(N_e - \delta^{occ}_{k_n} - \sum_{j \neq n, j occ.} \delta_{\sigma_j,\sigma_n} e^{i(k_n - k_j)ma})}{|\vec{r} - \vec{r'}|} \frac{|\psi_0(\vec{r})|^2 |\psi_m(\vec{r'})|^2}{N} \tag{2.86}$$

Let denote

$$\pi(m, \vec{r}, \vec{r'}) = \frac{|\psi_0(\vec{r})|^2 |\psi_m(\vec{r'})|^2}{N} > 0 \tag{2.87}$$

and

$$F(m, \vec{r}, \vec{r'}) = \frac{\Theta^{1D}_{0,m}}{|\vec{r} - \vec{r'}|} = \frac{(N_e - \delta^{occ}_{k_n} - \sum_{j \neq n, j occ.} \delta_{\sigma_j,\sigma_n} e^{i(k_n - k_j)ma})}{|\vec{r} - \vec{r'}|} \tag{2.88}$$

We notice that $\pi(.)$ is a density of probability :

$$\int \int d\vec{r} d\vec{r'} \sum_m \pi(m, \vec{r}, \vec{r'}) = 1 \tag{2.89}$$

Indeed, $\psi_m(.)$ is an atomic orbital and is therefore normalised :

$$\int d\vec{r'} |\psi_m(\vec{r'})|^2 = 1 \tag{2.90}$$

We want to compute

$$\frac{\Delta(E_{k_n})}{e^2} = \sum_m \int \int d\vec{r} d\vec{r'} F(m, \vec{r}, \vec{r'}) \pi(m, \vec{r}, \vec{r'}) \tag{2.91}$$

We use the **ergodic theorem** : if $(X_n)_{n \geq 0}$ is a recurrent, irreductible and positive Markov chain ; $\pi(.)$ being its unique invariant probability measure :

$$\frac{1}{M} \sum_{i=1}^{M} F(X_i) \longrightarrow_{M \longrightarrow \infty} E_\pi(F) = \sum_m \int \int d\vec{r} d\vec{r'} F(m, \vec{r}, \vec{r'}) \pi(m, \vec{r}, \vec{r'}) \tag{2.92}$$

Let's give a hint to understand this theorem. When computing the means of the values of $F(.)$ over the Markov chain, we are somehow counting the number of points of the Markov chain close to x (given by the density $\pi(x) = lim_{n \longrightarrow +\infty} P(X_n = x)$), and multiplying it by the value of F there : $\pi(x)F(x)$. Then we sum over the contributions x. The closest the distribution of the points of the Markov chain is to the density $\pi(.)$, the better the approximation of the integral with the mean value is.

We see that the points x that will count the most to compute the integral are those with higher values of $\pi(x)$ (where the points of the Markov chain concentrate the more). In our case $\pi(m, \vec{r}, \vec{r'})$ is maximal for $\vec{r'}$ close to $ma\vec{e_x}$. Therefore the Markov chain will have with high probability a lot of points in the neighbouring of such values of $\vec{r'}$. This algorithm thus enables to focus on the points where the integrand becomes very big or even diverges. Such regions are much better explored than with a classic Monte-Carlo algorithm, where the random variables X_i are uniform over the whole space of integration.

Our goal is therfore to generate a Markov chain whose invariant probability measure is π, and the means of the values of $F(.)$ along the trajectory will give us an approximation of the correction to the energy.

Construction of the Markov chain :
Let $W_{x\longrightarrow y}$ be the probability of transition from x to y :

$$W_{x\longrightarrow y} = P(X_{n+1} = y|X_n = x) \tag{2.93}$$

if $y \neq x$.
If $x = y$: $W_{x\longrightarrow x} = 1 - \sum_{y\neq x} W_{x\longrightarrow y}$.

We decompose $W_{x\longrightarrow y}$ as :

$$W_{x\longrightarrow y} = T_{x\longrightarrow y} A_{x\longrightarrow y} \tag{2.94}$$

where $A_{x\longrightarrow y}$ is the acceptation rate and $T_{x\longrightarrow y}$ the transition rate.

The transition matrix $T_{x\longrightarrow y}$ over the space of possible states E has to be irreductible and to satisfy :

$$\forall (x,y) \in E^2, T_{x\longrightarrow y} > 0 \Rightarrow T_{y\longrightarrow x} > 0 \tag{2.95}$$

As an acceptation rate, we can use :

$$A_{x\longrightarrow y} = h(\frac{\pi(y)T_{y\longrightarrow x}}{\pi(x)T_{x\longrightarrow y}}) \tag{2.96}$$

where h :$]0;+\infty[\longrightarrow]0,1]$ is increasing and such that $h(u) = uh(\frac{1}{u})$. For instance, $h(u) = inf(1,u)$ or $h(u) = \frac{u}{1+u}$ are possible functions. **We choose $h(u) = inf(1,u)$ in the following calculations**. We also take a symetric transition rate : $T_{y\longrightarrow x} = T_{x\longrightarrow y}$, to simplify the previous expression.

The algorithm is the following :
Given X_n, we first choose Y according to the transition law $T_{X_n\longrightarrow Y}$.
We then choose a uniform random number U_{n+1} in $[0,1]$:
If $U_{n+1} < A_{X_n\longrightarrow Y}$, then $X_{n+1} = Y$.
Otherwise : $X_{n+1} = X_n$.

The state Y is accepted with probability $A_{X_n\longrightarrow Y}$, hence the name of "acceptation rate".

The theorem of Metropolis implies that the transition matrix $W_{x\longrightarrow y}$ is irreductible and reversible for the measure π :

$$\forall (x,y) \in E^2, \pi(y)W_{y\longrightarrow x} = \pi(x)W_{x\longrightarrow y} \tag{2.97}$$

Therefore $\pi(.)$ is its unique invariant measure.

As a transition rate, I choose :

$$T_{x\longrightarrow y} = P(X_{n+1} = y = (m', \vec{r_1}, \vec{r_1'})|X_n = x = (m, \vec{r}, \vec{r'})) \tag{2.98}$$

such that :
- given $m = X_n[1]$, $l' = X_{n+1}[1]$ equals $m+1$ with probability $\frac{1}{2}$ and $m-1$ with probability $\frac{1}{2}$
- given $\vec{r}$, $\vec{r_1}$ is choosen uniformly in a cube centered in $\vec{r}$ and of tunable side length θ.
- given $\vec{r'}$, $\vec{r_1'}$ is choosen uniformly in a cube centered in $\vec{r'}$ and of tunable side length θ.

Thus we have $T_{x\longrightarrow y} = T_{y\longrightarrow x}$.

For a one-dimensional lattice, the equation 2.86 can be rewritten in the following way, if we take gaussian functions as localised orbitals ($\psi_l(r) = \chi(r - la)$ where $\chi(.)$ is the wave function of an atomic orbital) :

$$e^2 K \sum_{m=1}^{N} \int\int \frac{(N_e - \delta_{k_n}^{occ} - \sum_{j\neq n, jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n-k_j)ma})}{\sqrt{(x_1-x_2)^2 + (y_1-y_2)^2 + (z_1-z_2)^2}} \frac{e^{-2(\frac{x_1^2+y_1^2+z_1^2}{\delta^2})} e^{-2(\frac{(x_2-ma)^2+y_2^2+z_2^2}{\delta^2})}}{N} d\vec{r_1} d\vec{r_2} \quad (2.99)$$

where K is a constant coming from the integration on the angular part of the atomic orbital wave function. So far we take a constant angular function to simplify the calculations.

Other type of functions, like lorentzians, are possible and also satisfy the **non-overlapping assumption** we used. After changing the origins of the two space integrations :

$$\frac{\Delta(E_{k_n})}{e^2} = a^5 K \sum_{m=1}^{N} \int\int \frac{(N_e - \delta_{k_n}^{occ} - \sum_{j\neq n, jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n-k_j)ma})}{\sqrt{(x_1-x_2-m)^2 + (y_1-y_2)^2 + (z_1-z_2)^2}} \frac{e^{-2(\frac{x_1^2+y_1^2+z_1^2}{(\frac{\delta}{a})^2})} e^{-2(\frac{x_2^2+y_2^2+z_2^2}{(\frac{\delta}{a})^2})}}{N} d\vec{r_1} d\vec{r_2} \quad (2.100)$$

where K is a constant with the good dimension (as e^2 is an energy times a length, the product Ka^5 is the inverse of a length.

In a two-dimensional lattice, we have a similar expression for $\frac{\Delta(E_{(k_n)_x,(k_n)_y})}{e^2}$:

$$a^5 K' \sum_{l_1,p_1} \sum_{l_2,p_2} \int\int \frac{(N_e - \delta_{k_n}^{occ} - \sum_{j\neq n, jocc.} \delta_{\sigma_j,\sigma_n} e^{i(\vec{k_n}-\vec{k_j})(\vec{R_{l_1,p_1}}-\vec{R_{l_2,p_2}})})}{\sqrt{(x_1-x_2+l_2-l_1)^2 + (y_1-y_2+p_2-p_1)^2 + (z_1-z_2)^2}} \frac{e^{-2(\frac{x_1^2+y_1^2+z_1^2}{(\frac{\delta}{a})^2})} e^{-2(\frac{x_2^2+y_2^2+z_2^2}{(\frac{\delta}{a})^2})}}{N^4} d\vec{r_1} d\vec{r_2} \quad (2.101)$$

However after numerous tests, I noted that this algorithm was converging very slowly. Other problem : even with 1000000 random selections (1000000 points in the Markov chain), the estimation of the integral doesn't seem to converge... How to know the number of random selections to do ?

We decided to use a simpler method, which worked far better in the case we chose gaussian localised orbitals $\psi_m(.)$.

Second method, using spherical coordinates and gaussian random variables

We want to compute :

$$\Delta(E_{k_n}) = \frac{e^2}{N} \sum_{m=1}^{N} I_{0,m} \Theta_{0,m}^n \quad (2.102)$$

(we showed that we had the right to chose any value of l : here we take 0)

As $\Theta_{0,m}^n$ is easy to compute, we will first focus on $I_{0,m}$, which requires stochastic methods to be estimated :

$$I_{0,m} = \int\int d\vec{r} d\vec{r'} \frac{|\psi_0(\vec{r'})|^2 |\psi_m(\vec{r})|^2}{|\vec{r} - \vec{r'}|} = \int\int d\vec{r} d\vec{r'} \frac{|\chi(\vec{r'})|^2 |\chi(\vec{r} - ma\vec{e_x})|^2}{|\vec{r} - \vec{r'}|} \quad (2.103)$$

where $\chi(.)$ is the atomic orbital wave-function of the site of the lattice located at the origin of the coordinates. After changing of variables :

$$I_{0,m} = \int\int d\vec{u} d\vec{u'} \frac{|\chi(\vec{u'})|^2 |\chi(\vec{u})|^2}{|\vec{u} - \vec{u'} + ma\vec{e_x}|} \quad (2.104)$$

The dimension of $I_{0,m}$ is the inverse of a length, L^{-1}, because $d\vec{u}|\chi(\vec{u})|^2$ is a probability, a number without physical dimension.

As $\Theta_{0,m}^n$ is also of dimension 1, $\Delta(E_{k_n})$ has the dimension of $e^2 I_{0,m} = \frac{q_e^2}{4\pi\epsilon_0 L}$, which is an energy.

Let's first assume that $\chi(.)$ has no angular dependence :

$$\chi(\vec{\rho}) = K \frac{1}{\sqrt{4\pi}} e^{-\frac{(\frac{\rho}{a})^2}{2(\frac{d}{a})^2}} \quad (2.105)$$

We switch to spherical coordinates :

$$\vec{u} = \begin{pmatrix} \rho_1 sin(\theta_1)cos(\phi_1) \\ \rho_1 sin(\theta_1)sin(\phi_1) \\ \rho_1 cos(\theta_1) \end{pmatrix}, \vec{u'} = \begin{pmatrix} \rho_2 sin(\theta_2)cos(\phi_2) \\ \rho_2 sin(\theta_2)sin(\phi_2) \\ \rho_2 cos(\theta_2) \end{pmatrix} \tag{2.106}$$

we obtain for the integrand :

$$\frac{\frac{K^4}{(4\pi)^2} e^{-\frac{(\frac{\rho_1}{a})^2}{(\frac{d}{a})^2}} e^{-\frac{(\frac{\rho_2}{a})^2}{(\frac{d}{a})^2}} \rho_1^2 \rho_2^2 sin(\theta_1)sin(\theta_2) d\rho_1 d\rho_2 d\theta_1 d\theta_2 d\phi_1 d\phi_2}{\sqrt{(\rho_1 sin(\theta_1)cos(\phi_1) - \rho_2 sin(\theta_2)cos(\phi_2) - ma)^2 + (\rho_1 sin(\theta_1)sin(\phi_1) - \rho_2 sin(\theta_2)sin(\phi_2))^2 + (\rho_1 cos(\theta_1) - \rho_2 cos(\theta_2))^2)}} \tag{2.107}$$

which gives, by expanding the denominator and setting $\rho_1' = \frac{\rho_1}{a}$, $\rho_2' = \frac{\rho_2}{a}$:

$$\frac{1}{(4\pi)^2} \frac{K^4 a^5 e^{-\frac{\rho_1'^2}{(\frac{d}{a})^2}} e^{-\frac{\rho_2'^2}{(\frac{d}{a})^2}} \rho_1'^2 \rho_2'^2 sin(\theta_1)sin(\theta_2) d\rho_1' d\rho_2' d\theta_1 d\theta_2 d\phi_1 d\phi_2}{\sqrt{\rho_1'^2 + \rho_2'^2 - 2\rho_1'\rho_2'(sin(\theta_1)\sin(\theta_2)cos(\phi_1 - \phi_2) + cos(\theta_1)cos(\theta_2)) + 2m(\rho_2' sin(\theta_2)cos(\phi_2) - \rho_1' sin(\theta_1)cos(\phi_1)) + m^2}} \tag{2.108}$$

The idea is to use the fact that the radial part of the wave functions is gaussian, as we know how to generate random normal variables. We are going to select randomly ρ_1' and ρ_2' according to the density of probability $f(\rho) = \frac{1}{\sqrt{\pi(\frac{d}{a})^2}} e^{-\frac{\rho^2}{(\frac{d}{a})^2}}$; a gaussian random variable with means 0 and standard deviation $\frac{d}{\sqrt{2}a}$. θ_1 and θ_2 will be selected uniformly between 0 and π according to the distribution $g(\theta) = \frac{1}{\pi}$, and ϕ_1, ϕ_2 also uniformly in the space of integration, with density of probability $h(\phi) = \frac{1}{2\pi}$.

Let denote $F_m(\rho_1', \rho_2', \theta_1, \theta_2, \phi_1, \phi_2)$ the following function :

$$\frac{\rho_1'^2 \rho_2'^2 sin(\theta_1)sin(\theta_2)}{\sqrt{\rho_1'^2 + \rho_2'^2 - 2\rho_1'\rho_2'(sin(\theta_1)\sin(\theta_2)cos(\phi_1 - \phi_2) + cos(\theta_1)cos(\theta_2)) + 2m(\rho_2' sin(\theta_2)cos(\phi_2) - \rho_1' sin(\theta_1)cos(\phi_1)) + m^2}} \tag{2.109}$$

Given all these notations, we now have :

$$I_{0,m} = \frac{K^4 a^5}{(4\pi)^2} \pi (\frac{d}{a})^2 \pi^2 (2\pi)^2 \int\int F_m(\rho_1', \rho_2', \theta_1, \theta_2, \phi_1, \phi_2) f(\rho_1') d\rho_1' f(\rho_2') d\rho_2' g(\theta_1) d\theta_1 g(\theta_2) d\theta_2 h(\phi_1) d\phi_1 h(\phi_2) d\phi_2 \tag{2.110}$$

Let x be the joint variable : $x = (\rho_1', \rho_2', \theta_1, \theta_2, \phi_1, \phi_2)$. As all these variables will be selected independently, the density of probability of x is :

$$\mu(x) d^6x = f(\rho_1') f(\rho_2') g(\theta_1) g(\theta_2) h(\phi_1) h(\phi_2) d\rho_1' d\rho_2' d\theta_1 d\theta_2 d\phi_1 d\phi_2 \tag{2.111}$$

Therefore

$$I_{0,m} = \frac{K^4 a^5 \pi^3}{4} (\frac{d}{a})^2 \int F_m(x) \mu(x) d^6x \tag{2.112}$$

Let's compute K thanks to the normalisation condition :

$$\int |\chi(\vec{r})|^2 d\vec{r} = 1 \tag{2.113}$$

$$\Rightarrow \frac{K^2}{4\pi} (\int_0^\infty r^2 e^{-\frac{(\frac{r}{a})^2}{(\frac{d}{a})^2}} dr)(\int_0^\pi sin(\theta) d\theta)(\int_0^{2\pi} d\phi) = 1 \tag{2.114}$$

$$\Rightarrow K^2 a^3 \int_0^\infty u^2 e^{-\frac{u^2}{(\frac{d}{a})^2}} = K^2 a^3 \frac{\sqrt{\pi}}{2} (\frac{d}{a})^3 \tag{2.115}$$

Therefore the value of K is :

$$K = \frac{\sqrt{2}}{\pi^{\frac{1}{4}}} \frac{1}{d^{\frac{3}{2}}} \tag{2.116}$$

The equation 2.112 becomes :

$$I_{0,m} = \frac{\pi^2}{d} (\frac{a}{d})^3 \int F_m(x) \mu(x) d^6x \tag{2.117}$$

We find that $I_{0,m}$ has indeed the dimension of the inverse of a length, as all variables in the vector x have no physical dimension. Let call

$$E_\mu(F_m) = \int F_m(x)\mu(x)d^6x \tag{2.118}$$

the expectation value of F_m for the distribution of probability $\mu(.)$.

The global correction can be rewritten as :

$$\Delta(E_{k_n}) = \frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\Theta^n_{0,m} = \pi^2(\frac{a}{d})^3\frac{q_e^2}{4\pi\epsilon_0 d}\frac{1}{N}\sum_{m=1}^{N} E_\mu(F_m)\Theta^n_{0,m} \tag{2.119}$$

The factor $\frac{q_e^2}{4\pi\epsilon_0 d}$, which is the Coulomb interaction energy for two electrons located at d one from each other, gives the order of magnitude of the terms. A very important thing is that once the integrals $I_{0,m}$ are estimated with very little deviation from their real values, we can use them for each computation of $\Delta(E_{k_n})$, having only to compute $(\Theta^n_{0,m})_{m=1..N}$ for each correction. **Therefore we only need to compute** $(I_{0,m})_{m=1..N}$ **once**.

$E_f(F_m)$ is estimated simply, by generating M times independent random variables $X_i = ((\rho_1')_i, (\rho_2')_i, (\theta_1)_i, (\theta_2)_i, (\phi_1)_i, (\phi_2)_i)$, each following the density of probability previously mentioned. Each vector X_i of random variables follows $x \longmapsto l(x)$ as density of probability, therefore :

$$\frac{1}{M}\sum_{i=1}^{M} F_m(X_i) \longrightarrow_{M\longrightarrow+\infty} E_\mu(F_m) = \int F_m(x)\mu(x)d^6x \tag{2.120}$$

For most of the integrals $I_{0,m}$, $M = 10000$ random selections are sufficient to esimate $I_{0,m}$ with less than 1% error.

Given that $\Theta^n_{0,m}$ is made up of two separate terms :

$$\Theta^n_{0,m} = (N_e - \delta^{occ}_{k_n} - \sum_{j\neq n, jocc.} \delta_{\sigma_j,\sigma_n} e^{i(k_n-k_j)ma}) \tag{2.121}$$

we can see the contribution to the correction of the energy only due to the term of Fock without self-interaction ; by setting $\Theta^n_{0,m} = -\sum_{j\neq n,jocc.}\delta_{\sigma_j,\sigma_n}e^{i(k_n-k_j)ma}$ in the code. We will call $\Delta(E_{k_n})^{Fockw.s.i.}$ the corresponding correction.

The correction due to Hartree's term, and Fock-self-interaction term (if there is one) only depends on n in the term $\delta^{occ}_{k_n}$:

$$\Delta(E_{k_n}) = (N_e - \delta^{occ}_{k_n})\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m} = (N_e - \delta^{occ}_{k_n})\pi^2(\frac{a}{d})^3\frac{q_e^2}{4\pi\epsilon_0 d}\frac{1}{N}\sum_{m=1}^{N} E_\mu(F_m) \tag{2.122}$$

Therefore if $N_e \gg 1$, the dependence on n of the correction $\Delta(E_{k_n})$ will become negligible, and **Hartree's effect will be to translate the energy spectrum** (computed with the Fock term) **by a constant**.
For small values of electrons in the system, Hartree's term will make a significant difference between the occupied states (such that $\delta^{occ}_{k_n} = 1$) and the empty states (such that $\delta^{occ}_{k_n} = 0$).

Correction of the energy spectrum due to the term of Fock only :
The simulations show that the correction due to Fock's term :

$$\Delta(E_{k_n})^{Fockw.s.i.} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\sum_{j\neq n,jocc.}\delta_{\sigma_j,\sigma_n}\cos((k_n-k_j)ma) \tag{2.123}$$

$$= -\pi^2(\frac{a}{d})^3\frac{q_e^2}{4\pi\epsilon_0 d}\frac{1}{N}\sum_{m=1}^{N} E_\mu(F_m)\sum_{j\neq n,jocc.}\delta_{\sigma_j,\sigma_n}\cos((k_n-k_j)ma) \leq 0 \tag{2.124}$$

is always negative.

The following grahics show the results obtained with the method which has just been described . N is the number of atoms in the lattice, while NB is the total number of electrons in the system : $NB \leq 2N$. We assume that the energy levels are filled in a non-magnetic way, from the lowest energy level, each level having two electrons with opposite spins. For instance if there are 10 electrons in the system (NB=10), there will be 5 occupied states. We will see later that for numerous values of NB, there will be different ways to fill the lowest energy levels with NB electrons, and therefore different initial states, ending uo with different corrections.
nb is the number of random selections done to compute each value of $I_{0,m}$, for $m \in [1, N]$.

In blue, the energy profile computed in the tight-binding approximation :

$$E(k_n) = E_0 - t_0 - 2tcos(k_n a) \tag{2.125}$$

with $E_0 = 13eV$, $t_0 = 0.5eV$, $t = 2eV$ and $a = 10^{-10}m$, and $k_n = \frac{2\pi}{Na}m$, $m \in [-\lfloor\frac{N}{2}\rfloor, \lfloor\frac{N}{2}\rfloor]$.

In green, the energy spectrum corrected by Fock's term :

$$E(k_n)_{corrige} = E(k_n) + \Delta(E_{k_n})^{Fockw.s.i.} \tag{2.126}$$

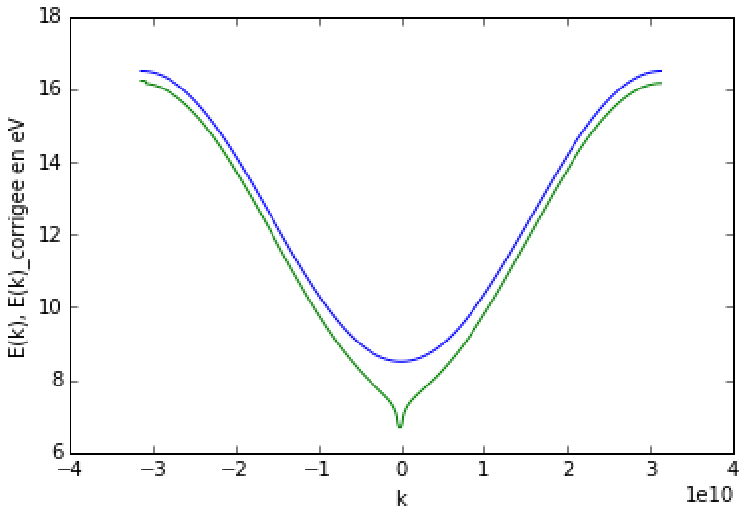

Figure 2.10: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=10 ($k_F = 0.03.10^{10}m^{-1}$) and nb=10000

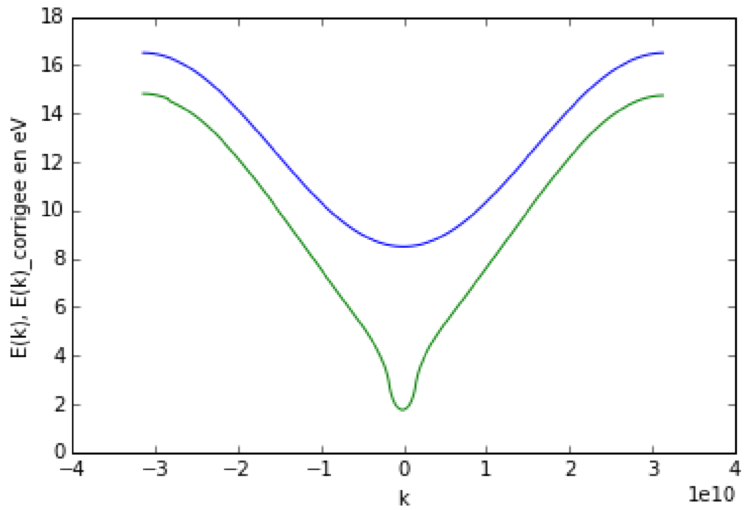

Figure 2.11: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=50 ($k_F = 0.16.10^{10}m^{-1}$) and nb=10000

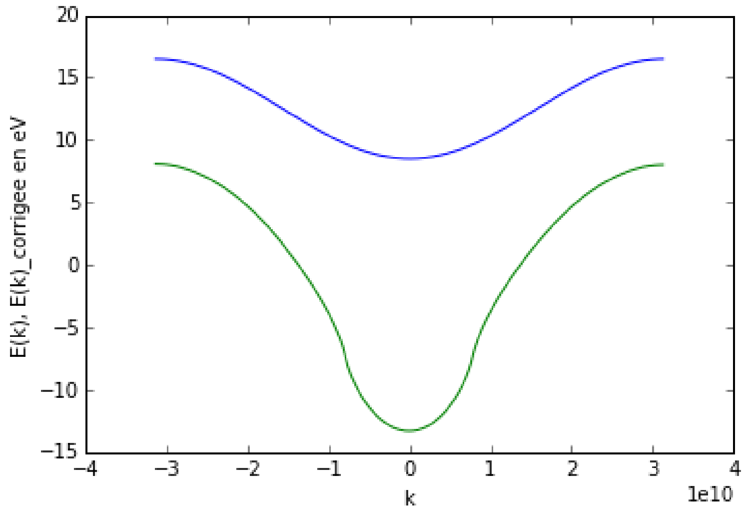

Figure 2.12: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=250 ($k_F = 0.79.10^{10}m^{-1}$) and nb=10000

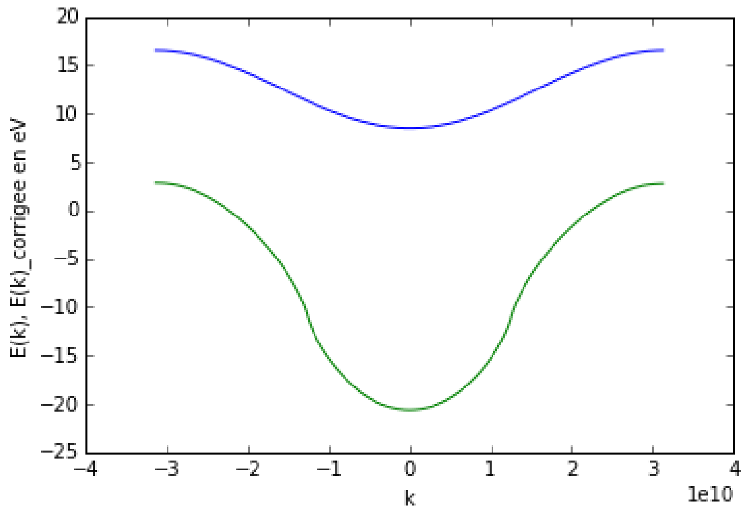

Figure 2.13: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=400 ($k_F = 1.26.10^{10}m^{-1}$) and nb=10000

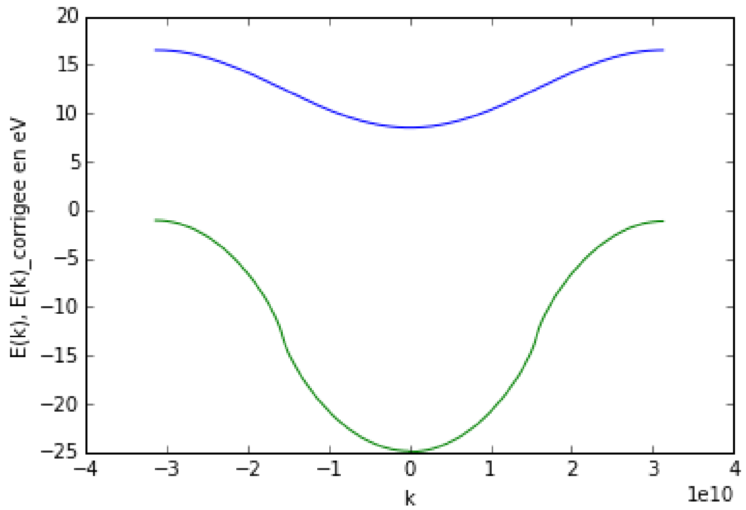

Figure 2.14: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=500 ($k_F = 1.57.10^{10}m^{-1}$, half-filling) and nb=10000

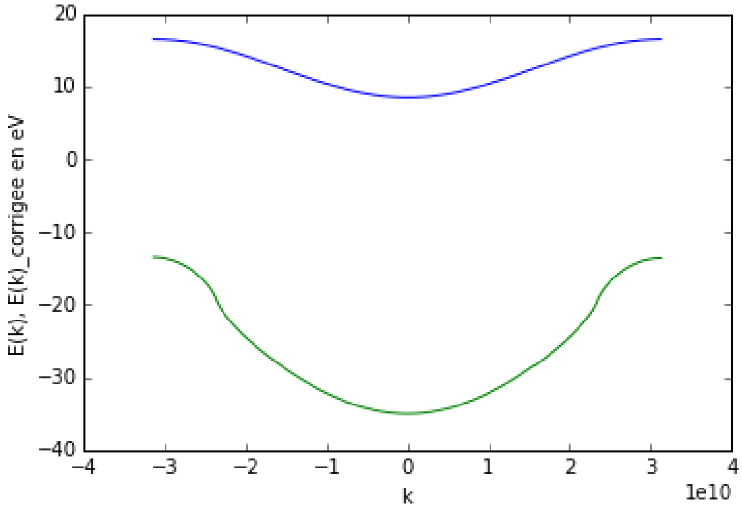

Figure 2.15: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=750 ($k_F = 2.4.10^{10}m^{-1}$) and nb=10000

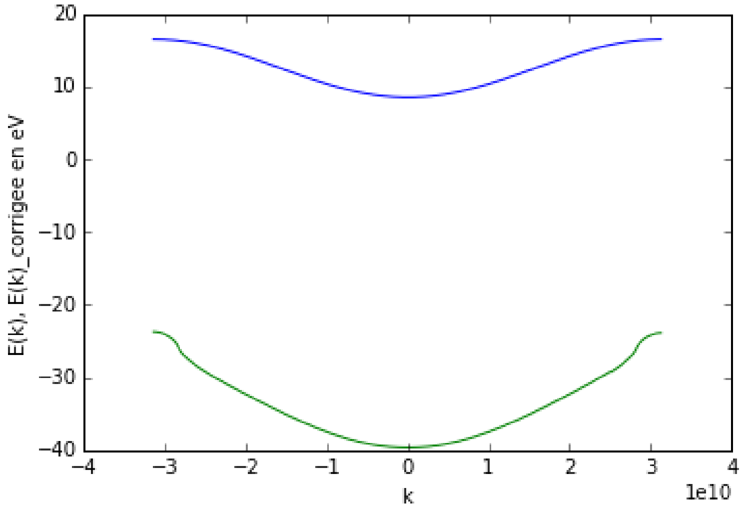

Figure 2.16: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=900 ($k_F = 2.8.10^{10}m^{-1}$) and nb=10000

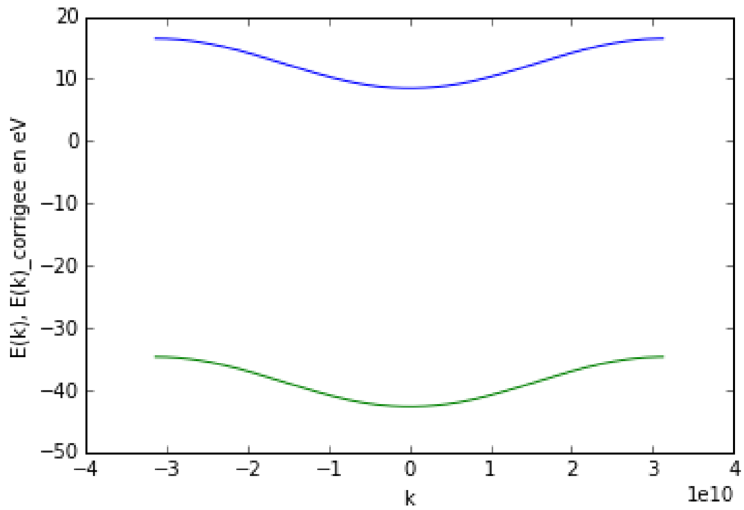

Figure 2.17: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=1000 ($k_F = \frac{\pi}{a} = 3.14.10^{10}m^{-1}$) and nb=10000

Analysis of the results :

We see that for N given, the correction becomes bigger and bigger when the number of electrons in the system NB increases (the correction to the energy, in green, goes lower and lower when NB increases compared to the previous energy spectrum, in blue).

On the contrary, at NB fixed, when the number of atoms in the lattice increases, the correction due to the term of Fock decreases, as the following graphs show :

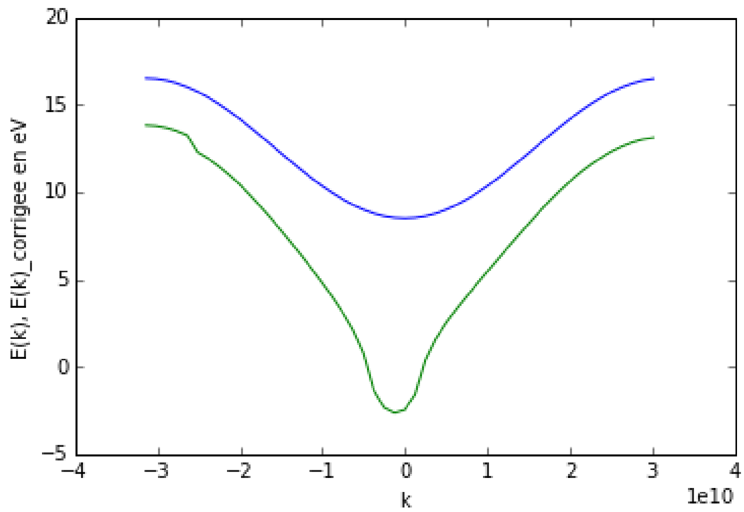

Figure 2.18: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=50, NB=10 ($k_F = 0.3.10^{10}m^{-1}$) and nb=10000

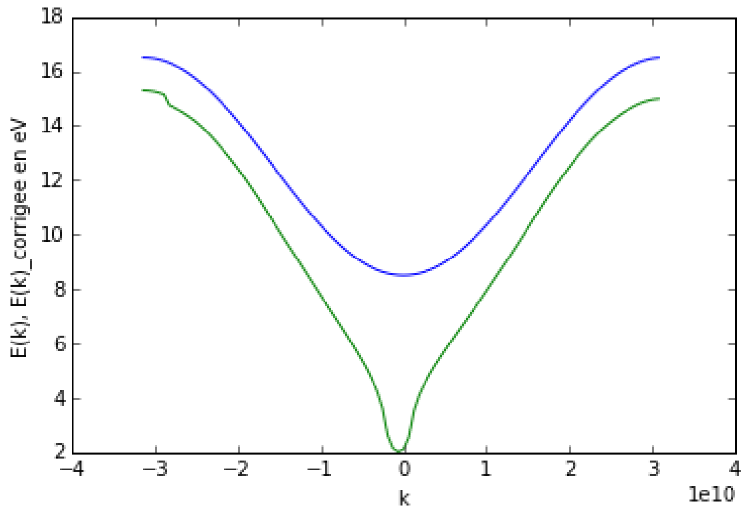

Figure 2.19: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=100, NB=10 ($k_F = 0.15.10^{10} m^{-1}$) and nb=10000

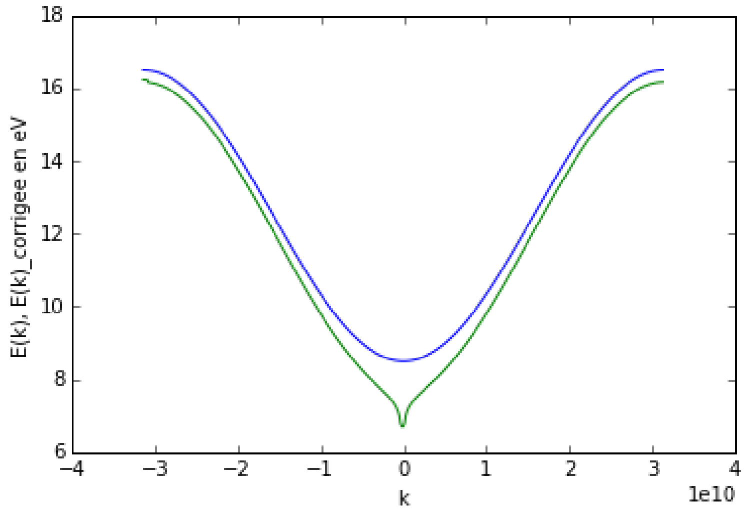

Figure 2.20: Energy computed for the one-dimensionnal lattice corrected by Fock's term, for N=500, NB=10 ($k_F = 0.03.10^{10} m^{-1}$) and nb=10000

The shape of the correction of the energy due to Fock's term for the one-dimensionnal lattice is very similar to that obtained for free electrons.

First, the correction of the energy due to the term of Fock is bigger for k close to 0 than in the edges of the band, which is also the case for free electrons, as we have seen in the graph 2.1.

Then, **the bandwidth $E(k_F) - E(k = 0)$ increases** when when take into account Hartree-Fock's term, similarly to the case of free electrons :

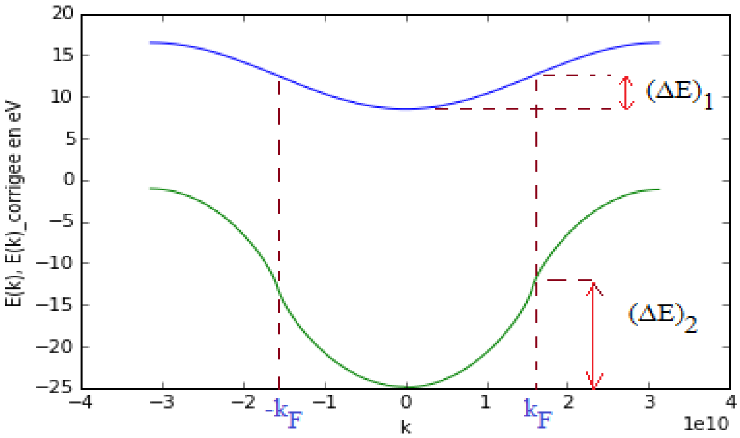

Figure 2.21: Increase of the bandwidth of the energy spectrum for the one-dimensionnal lattice by taking into account Fock's term (Half-filling : N=500, NB=500, $k_F = 1.57.10^{10}m^{-1}$)

$(\Delta E)_1$ is the bandwidth estimated in the tight-binding approximation, while $(\Delta E)_2$ is the bandwidth estimated in the corrected energy spectrum, after taking Coulomb interactions and Pauli principle into account. We see that $(\Delta E)_2 > (\Delta E)_1$, **which is the case for all values of the total number of electrons in the system NB**. We can understand this effect thanks to the big correction of the energy at $k = 0$, which "plumbs down" the corrected energy spectrum. For very low fillings ($NB \leq q50$), this effect is clear and sharp, as it can be seen in the previous graphs.

The modulous of the Fermi vector is given by : $k_F = \frac{2\pi}{Na} p_F$, where $p_F = \frac{N^{occ}}{2} = \frac{NB}{4}$ is the number of occupied states corresponding to a positive quasi-momemtum k. Therefore :

$$k_F = \frac{\pi}{a} \frac{NB}{2N} \tag{2.127}$$

Moreover, **the Fermi velocity is not defined**, because like for free electrons, $k \longmapsto (\frac{dE_{corr.}}{dk})(k)$ is discontinuous at $k = k_F$ and $k = -k_F$. In the case of free electrons, the derivative of the energy goes logarithmically towards $+\infty$, which leads formally to an infinite Fermi velocity. It seems to be also the case for the one-dimensionnal lattice, as we clearly see a sudden change of concavity at $k = k_F$. Let's plot this derivative :

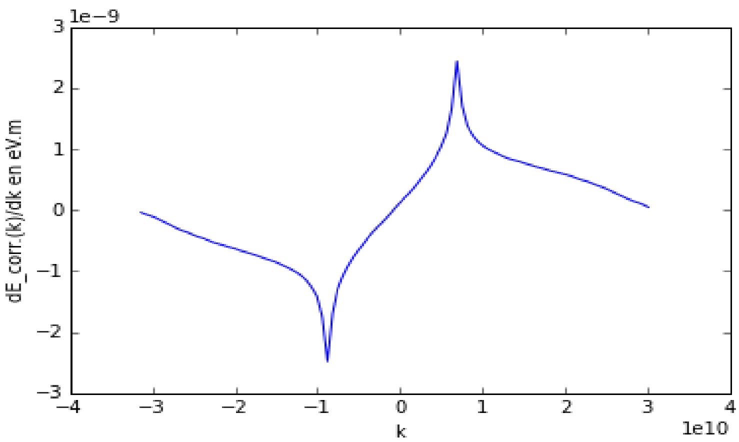

Figure 2.22: Derivative of the energy corrected by Hartree-Fock's term for $N = 100$ and $NB = 50$

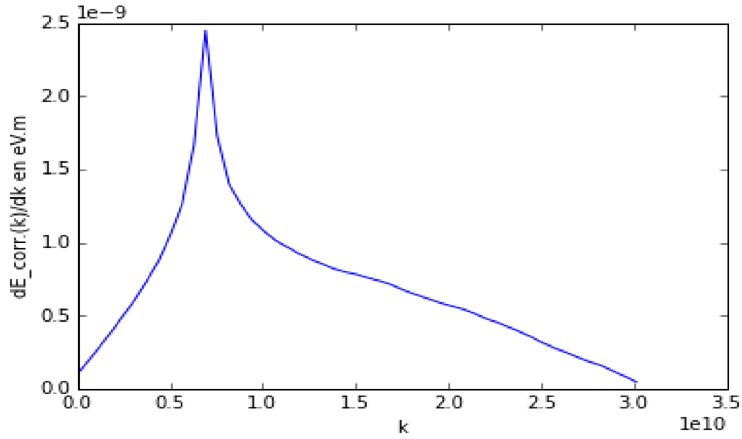

Figure 2.23: Zoom 1 on the derivative of the energy corrected by Hartree-Fock's term for $N = 100$ and $NB = 50$

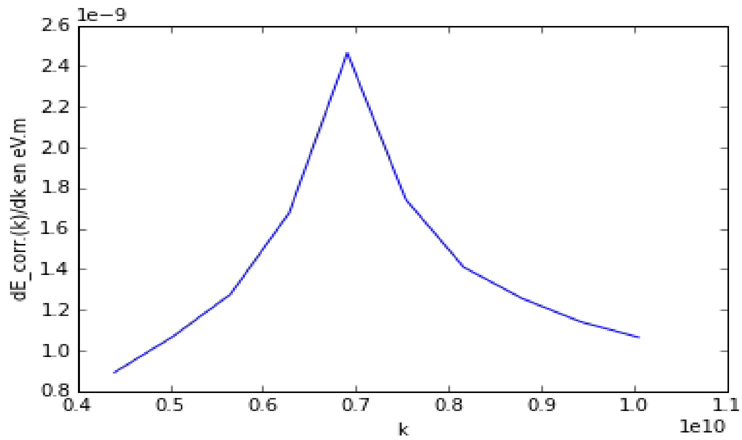

Figure 2.24: Zoom 2 on the derivative of the energy corrected by Hartree-Fock's term for $N = 100$ and $NB = 50$

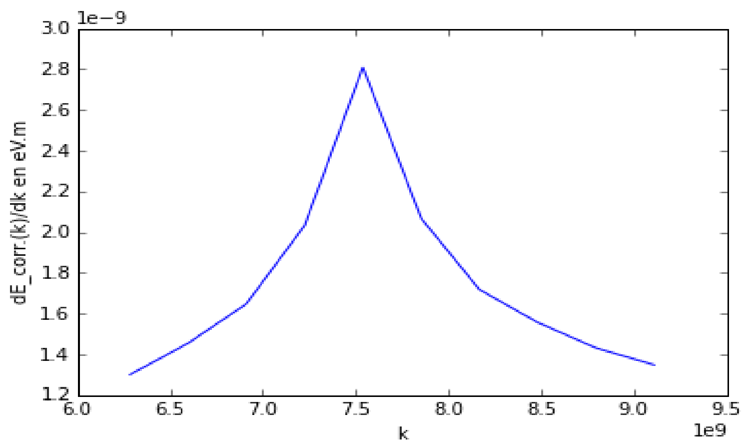

Figure 2.25: Zoom on the derivative of the energy corrected by Hartree-Fock's term for $N = 200$ and $NB = 100$

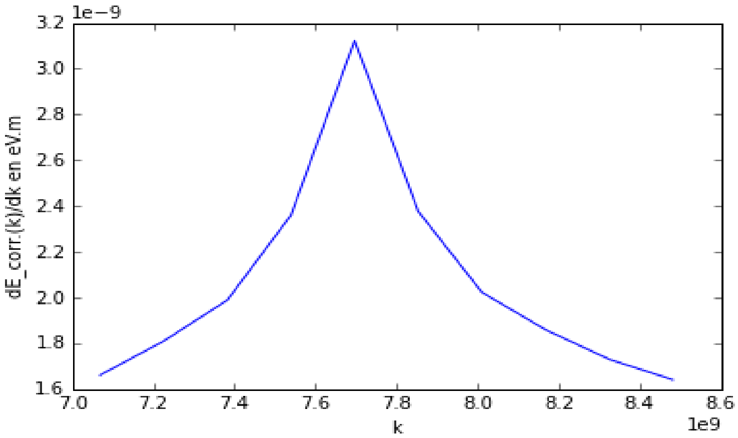

Figure 2.26: Zoom on the derivative of the energy corrected by Hartree-Fock's term for $N = 400$ and $NB = 200$

We can see the peak slowly rising when we increase N and the number of electrons NB in the system, keeping the same proportion (so that k_F is constant).

Spin-polarized energy correction :
In theory, there are different possible ways of filling up the energy levels, for a given number of electrons NB, which can lead to different correction spectra. We will illustrate this important fact with the simple case of 8 electrons in the system. Of course, when the number of electrons in the system becomes huge, the following situations won't be physical... (at the thermodynamic limit, there isn't any reason to break the symmetry of the filling : in a non-magnetic solid, electrons with spins up and down will see the same chemical potential).
We start from an initial state which is a Slater determinant of single-electron states computed in the tight binding approximation, each of these occupied states having an energy $E_0 - t_0 - 2tcos(k_n a)$, where k_n is the corresponding quasi-momemtum. **Our approach is a perturbative approach** : we assume that the correction to the energy $E(k_n)$ of a single-electron state due to Fock's term is small enough to be estimated by the means value $< \psi_{k_n}|H^{Fock}|\psi_{k_n} >$ of the perturbation in the eigen state ψ_{k_n} computed in the tight-binding approximation. We haven't taken into account the possible variation $\delta\psi$ of the state itself so far.

In fact, the single-electron state to be considered is (k_n, σ_n). Indeed, because of Pauli principle, computing the correction to the energy implies to compare the spin σ_n to the spins σ_j of all other electrons in the occupied states k_j (except the state k_n itself in case it is occupied). Electrons contribute to the correction of the energy only for spins σ_j parallel to σ_n.

Let's take an example that gives a spin-polarized energy correction, that is to say

$$\Delta(E_{k_n,\sigma_n=\uparrow}) \neq \Delta(E_{k_n,\sigma_n=\downarrow}) \tag{2.128}$$

for some values of k_n. We consider 8 electrons in the system : we know that 6 of these electrons are in the three lowest energy levels, but we don't know the precise states of the other two electrons, as there are two states at the Fermi energy.

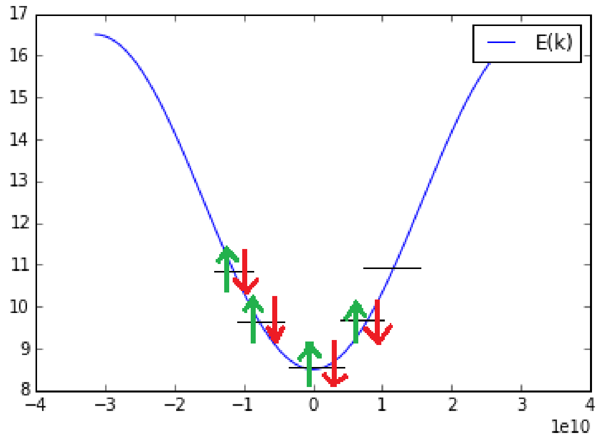

Figure 2.27: $NB = 8$ electrons, situation 1

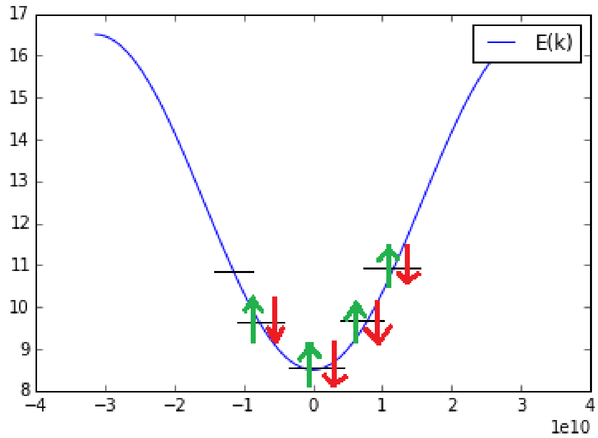

Figure 2.28: $NB = 8$ electrons, situation 2

These two first situations don't lead to a spin-polarized energy correction :

$$\forall k_n, \Delta(E_{k_n,\sigma_n=\uparrow}) = \Delta(E_{k_n,\sigma_n=\downarrow}) \tag{2.129}$$

Indeed, each occupied state contains two electrons with opposite spins so that $\{j \neq n, jocc.|\delta_{\sigma_n=\uparrow,\sigma_j} = 1\} = \{j \neq n, jocc.|\delta_{\sigma_n=\downarrow,\sigma_j} = 1\}$ for all n, which leads to the same correction for both states of spin.

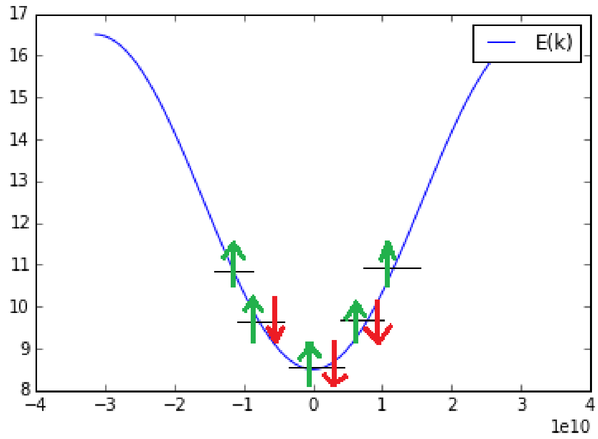

Figure 2.29: $NB = 8$ electrons, situation 3

For the situation above, there is a dependence of the correction of the energy on spin. Let's analyse it in further detail in this simple example. The three full states are $k_{-1} = -\frac{2\pi}{Na}$, $k_0 = 0$ and $k_1 = \frac{2\pi}{Na}$. The two states at the Fermi energy, each with one electron with spin up, are associated to the quasi-momemta $k_{-2} = -\frac{4\pi}{Na}$ and $k_2 = \frac{4\pi}{Na}$.

For any state k_n different from k_2 and k_{-2}, the corrections are different for the states $(k_n, \sigma_n =\uparrow)$ and $(k_n, \sigma_n =\downarrow)$:

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\uparrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n-k_j)ma) + \cos((k_n - \frac{4\pi}{Na})ma) + \cos((k_n + \frac{4\pi}{Na})ma)] \tag{2.130}$$

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m} \sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n-k_j)ma) \tag{2.131}$$

as there are no electrons with spin $\downarrow$ in the states k_{-2} and k_2.

This magnetic filling thus leads to a difference of energy :

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\uparrow} - \Delta E_{k_n=\frac{2\pi}{Na}n,\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\cos((k_n - \frac{4\pi}{Na})ma) + \cos((k_n + \frac{4\pi}{Na})ma)] = -2\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\cos(\frac{2\pi n}{N}m)\cos(\frac{4\pi}{N}m \tag{2.132}$$

For the two states k_{-2} and k_2, there is no difference of the correction due to the spin :

$$\Delta E_{\frac{4\pi}{Na},\uparrow} = \Delta E_{\frac{4\pi}{Na},\downarrow}, \Delta E_{-\frac{4\pi}{Na},\uparrow} = \Delta E_{-\frac{4\pi}{Na},\downarrow} \tag{2.133}$$

(notice that $(k_2 = \frac{4\pi}{Na}, \downarrow)$ and $(k_{-2} = \frac{-4\pi}{Na}, \downarrow)$ are empty states)

The polarized correction to the band structure computed with Python for some similar filling at the energy level gives the following :

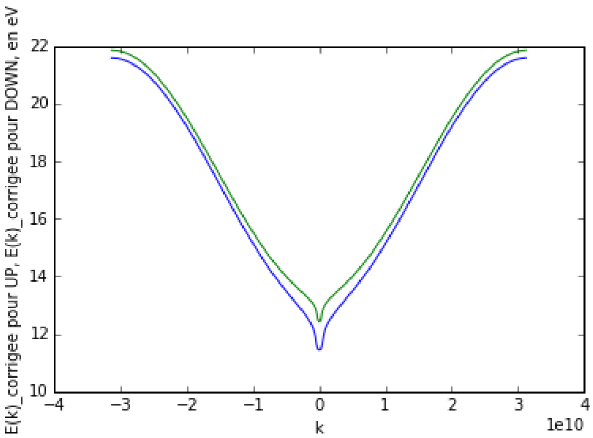

Figure 2.30: Spin-polarized correction to the energy computed with Hartree-Fock for $N = 300$ and $NB = 8$

In green, the band corresponding to the spins DOWN. In blue, to the the spins UP.

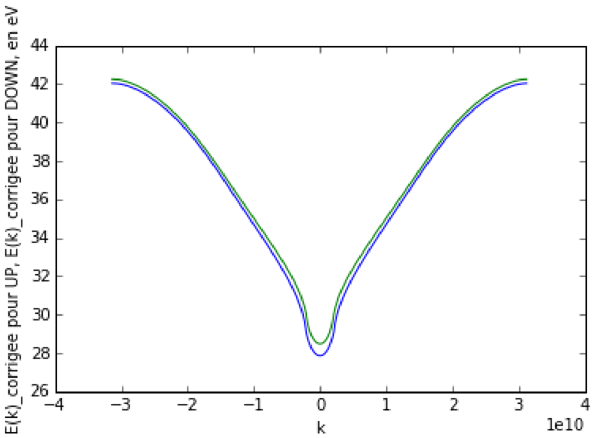

Figure 2.31: Spin-polarized correction to the energy computed with Hartree-Fock for $N = 300$ and $NB = 40$

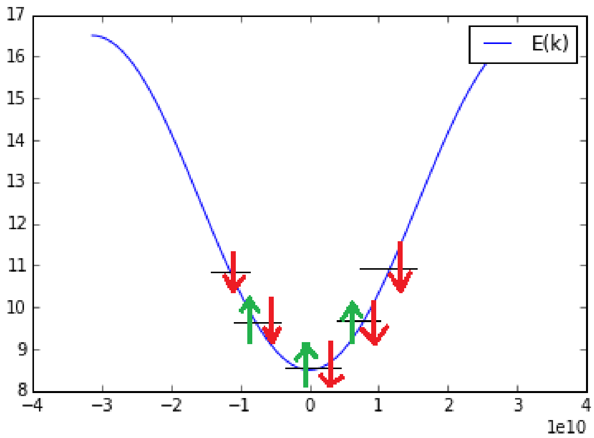

Figure 2.32: $NB = 8$ electrons, situation 4

For the situation 4, we have for $n \neq 2$ and $n \neq -2$:

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\uparrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m} \sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n - k_j)ma) \tag{2.134}$$

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n - k_j)ma) + \cos((k_n - \frac{4\pi}{Na})ma) + \cos((k_n + \frac{4\pi}{Na})ma)] \tag{2.135}$$

This magnetic situation lifts the degeneracy of spin by the energy :

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\uparrow} - \Delta E_{k_n=\frac{2\pi}{Na}n,\downarrow} = +\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\cos((k_n - \frac{4\pi}{Na})ma) + \cos((k_n + \frac{4\pi}{Na})ma)] = 2\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\cos(\frac{2\pi n}{N}m)\cos(\frac{4\pi}{N}m) \tag{2.136}$$

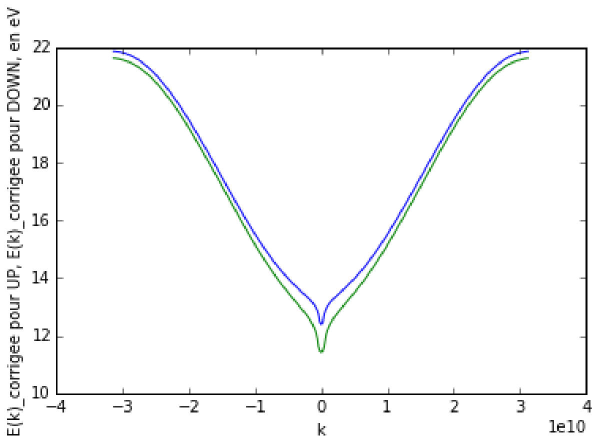

Figure 2.33: Spin-polarized correction to the energy computed with Hartree-Fock for $N = 300$ and $NB = 8$

In green, the band corresponding to the spins DOWN. In blue, to the the spins UP.

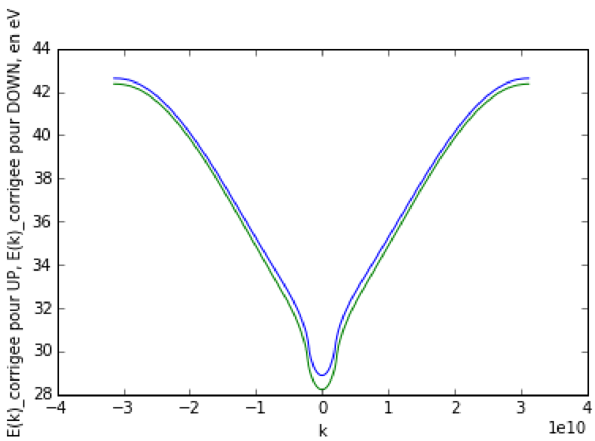

Figure 2.34: Spin-polarized correction to the energy computed with Hartree-Fock for $N = 300$ and $NB = 40$

The effect becomes weaker and weaker for bigger values of NB, when the number of electrons in the system increases, as the following graph shows :

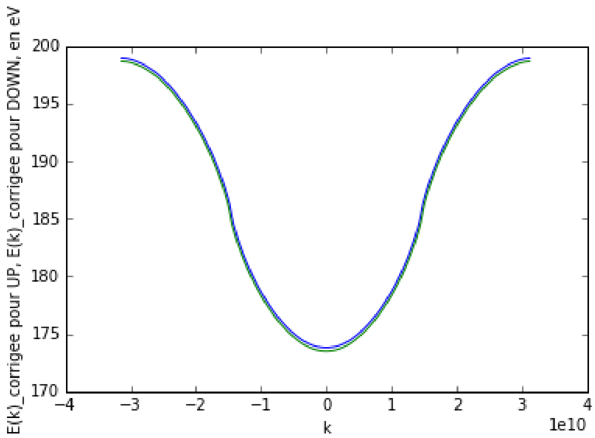

Figure 2.35: Spin-polarized correction to the energy computed with Hartree-Fock for $N = 300$ and $NB = 280$

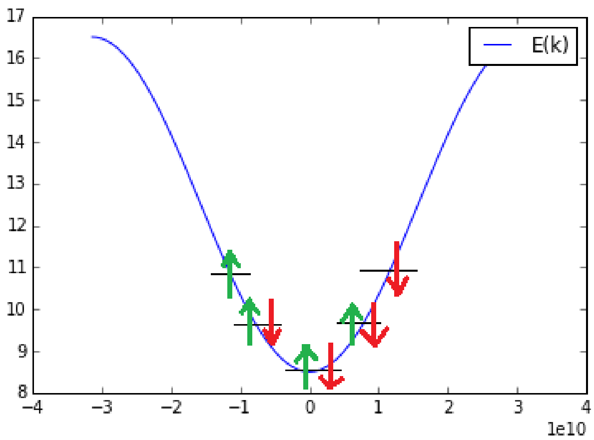

Figure 2.36: $NB = 8$ electrons, situation 5

For this last possible situation, every level of energy becomes spin-polarized. For $n \neq 2$ and $n \neq -2$:

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\uparrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n-k_j)ma) + \cos((k_n+\frac{4\pi}{Na})ma)] \tag{2.137}$$

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n-k_j)ma) + \cos((k_n-\frac{4\pi}{Na})ma)] \tag{2.138}$$

which leads to :

$$\Delta E_{k_n=\frac{2\pi}{Na}n,\uparrow} - \Delta E_{k_n=\frac{2\pi}{Na}n,\downarrow} = +\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\cos((k_n-\frac{4\pi}{Na})ma) - \cos((k_n+\frac{4\pi}{Na})ma)] = 2\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\sin(\frac{2\pi n}{N}m)\sin(\frac{4\pi}{N}m) \tag{2.139}$$

This time,

$$\Delta E_{k_2=\frac{4\pi}{Na},\uparrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n-k_j)ma) + \cos((k_n+\frac{4\pi}{Na})ma)] \tag{2.140}$$

$$\Delta E_{k_2=\frac{4\pi}{Na},\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\sum_{j\in\{-1,0,1\},j\neq n} \cos((k_n-k_j)ma) \tag{2.141}$$

because k_{-2} is occupied, bbut only with an electron with spin $\uparrow$.

Therefore

$$\Delta E_{k_2=\frac{4\pi}{Na},\uparrow} - \Delta E_{k_2=\frac{4\pi}{Na},\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\cos((k_n+\frac{4\pi}{Na})ma) \tag{2.142}$$

$(k_n = \frac{4\pi}{Na}, \uparrow)$ is an empty state, while $(k_n = \frac{4\pi}{Na}, \downarrow)$ is occupied.

Similarly,

$$\Delta E_{k_{-2}=-\frac{4\pi}{Na},\uparrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\sum_{j\in\{-1,0,1\},j\neq n}\cos((k_n-k_j)ma) \tag{2.143}$$

and

$$\Delta E_{k_{-2}=-\frac{4\pi}{Na},\downarrow} = -\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}[\sum_{j\in\{-1,0,1\},j\neq n}\cos((k_n-k_j)ma) + \cos((k_n-\frac{4\pi}{Na})ma)] \tag{2.144}$$

Therefore

$$\Delta E_{k_{-2}=-\frac{4\pi}{Na},\uparrow} - \Delta E_{k_{-2}=-\frac{4\pi}{Na},\downarrow} = +\frac{e^2}{N}\sum_{m=1}^{N} I_{0,m}\cos((k_n-\frac{4\pi}{Na})ma) \tag{2.145}$$

$(k_{-2} = -\frac{4\pi}{Na}, \uparrow)$ is an occupied state, while $(k_{-2} = -\frac{4\pi}{Na}, \downarrow)$ is empty.

In that case, this "magnetic" filling at the Fermi level shifts the two bands (one for spins UP, one for spins DOWN) horizontally, and not vertically anymore :

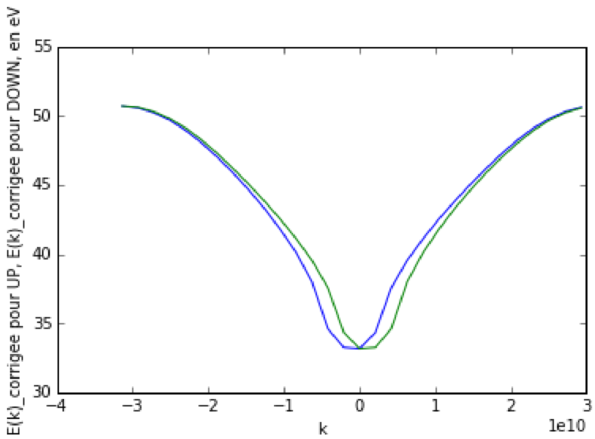

Figure 2.37: Spin-polarized correction to the energy computed with Hartree-Fock for $N = 30$ and $NB = 8$

How to upgrade these results :

1. We have shown that for a fixed value of NB, there can be numerous possible initial states, some of them leadind to spin-polarized corrections. **If NB is odd, this will necessarily be the case** (as there will be a level of energy with only one spin)! What should be computed in that case is the correction of the energy spectrum for electrons with spin $\uparrow$, namely $k \longmapsto \Delta(E_{k,\uparrow})$, and the correction for electrons with spin $\downarrow$: $k \longmapsto \Delta(E_{k,\downarrow})$.

2. We must compare quantitatively the bandwidth increase in the corrected band. Let's denote $\Delta L_{occ}^{corrige}$ the bandwidth of the occupied states, computed with the corrected energy band, $\Delta L_{vide}^{corrige}$ the bandwidth of the empty states, computed with the corrected energy band, ΔL_{occ} the bandwidth of the occupied states, computed with the original energy spectrum, ΔL_{vide} the bandwidth of the occupied states, computed with the original energy band. We obtain the following evolution, for 10 computations of these bandwidths :

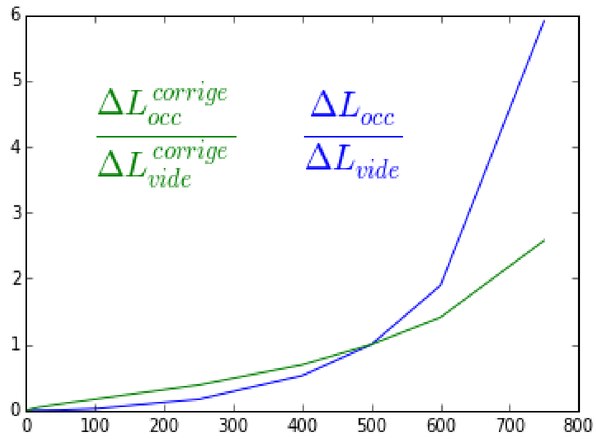

Figure 2.38: Comparison of the relative bandwidth of empty and occupied states in the corrected and non-corrected case

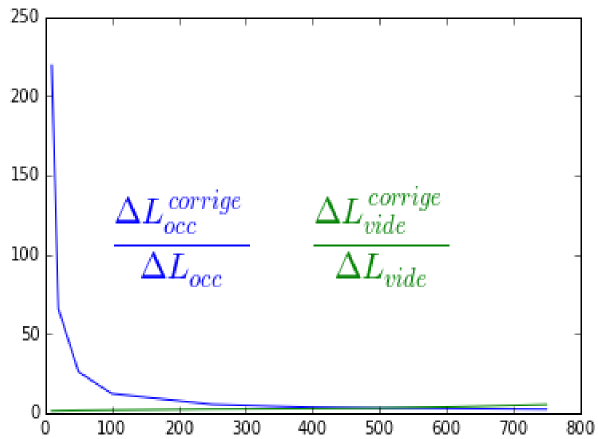

Figure 2.39: Comparison of the relative bandwidth of empty and occupied states in the corrected and non-corrected case

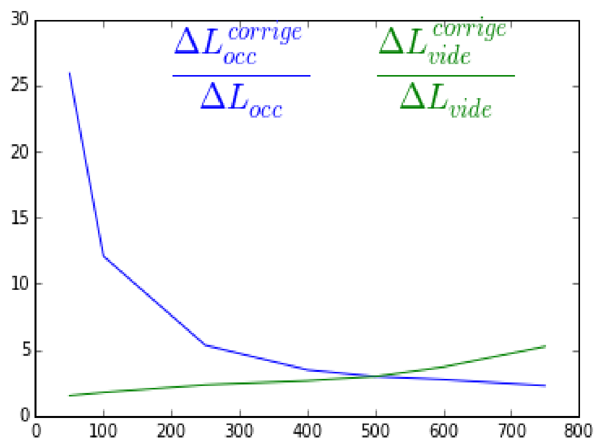

Figure 2.40: Comparison of the relative bandwidth of empty and occupied states in the corrected and non-corrected case

Conclusion The bandwidth is much larger for small fillings in the corrected energy band, which is coherent when we look at the plots : Hartree-Fock's term plumps the band down between $-k_F$ and k_F, in a brutal way (that's why there is a discontinuity of the slope at k_F). It makes the bandwith for very small fillings much bigger than in the non-corrected case. Then, when NB increases, the trend diminishes and there is a revearsal of this trend at the half-filling.

3. My Python program works to estimate the corrections both for one-dimensionnal and two-dimensionnal lattices. However we must compare the bandwidth we obtain with **the coupling** t between two neighbouring atoms. This coupling also depends on which type of localised atomic orbital we choose.

$$t =< \psi_l|V_{l+1}|\psi_{l+1} >= \sum_{i=1, i\neq l}^{N} < \psi_l|V_{at}(\vec{r} - \vec{R}_i)|\psi_{l+1} > \tag{2.146}$$

Idea: density n(r) <-> $V_{at}(r)$ <-> t. Hohenberg-Kohn theorem? Ways to estimate $V_{at}(r)$ iteratively ?

4.We saw that the correction of the energy computed thanks to the Fock's term seemed to become much larger than the energy itself when the number of electrons in the system increases. We must therefore check the validity of the perturbative approach, by analysing the variations of the eigen vectors $\delta\phi$. This validity is not correlated to the correction computed, and may remain valid for big values of corrections, as it is the case here.
When there are so many electrons in the system, it becomes necessary to take **screening** into account, by replacing Coulomb potential with a Yukawa potential with an adequate screening length.

Correction of the energy spectrum due to both terms of Hartree and Fock : The following corrections computed with Python are continuous, which is a physical result.

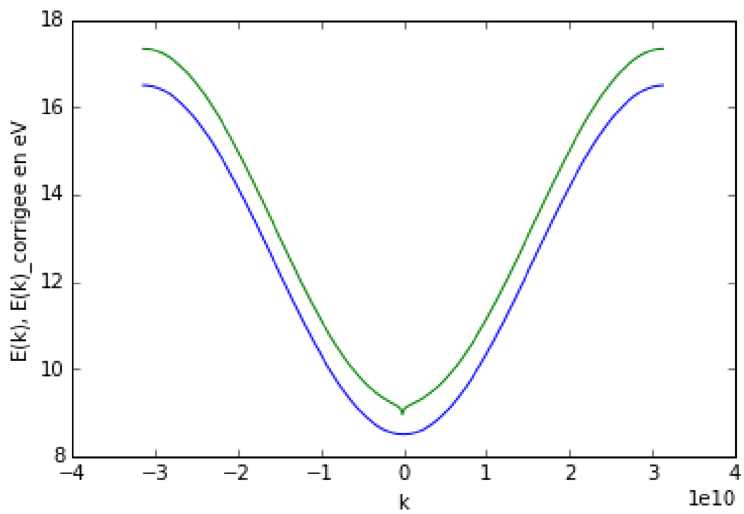

Figure 2.41: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=2 ($k_F = 0.006.10^{10}m^{-1}$) and nb=10000

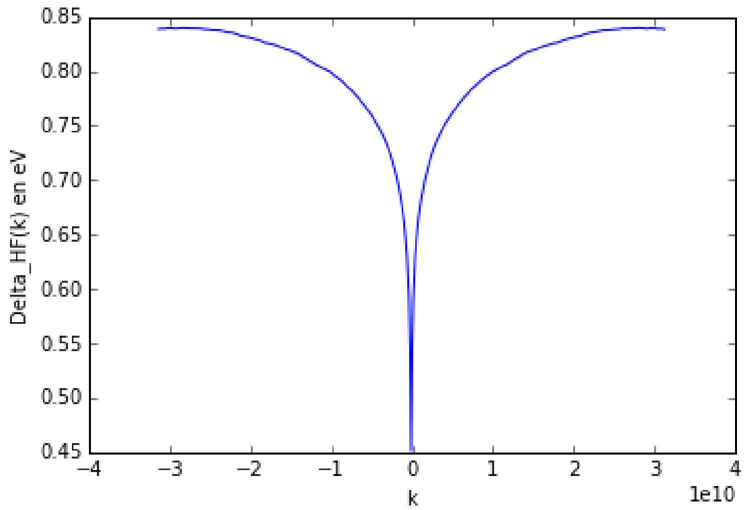

Figure 2.42: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=2 ($k_F = 0.006.10^{10}m^{-1}$) and nb=10000

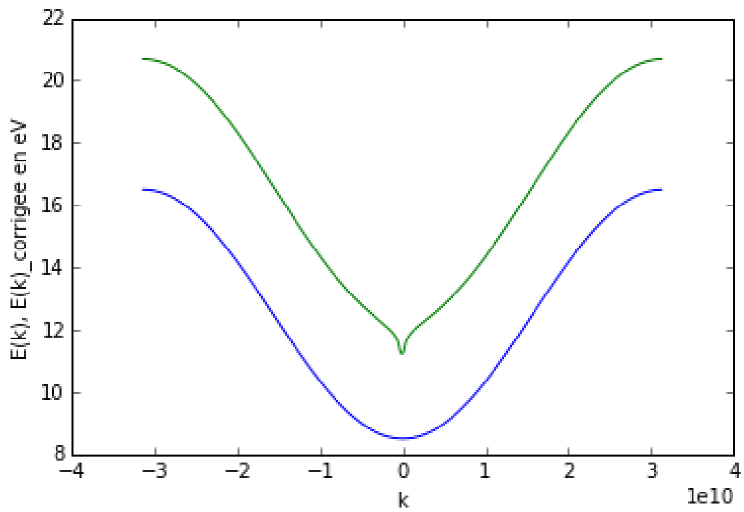

Figure 2.43: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=10 ($k_F = 0.03.10^{10}m^{-1}$) and nb=10000

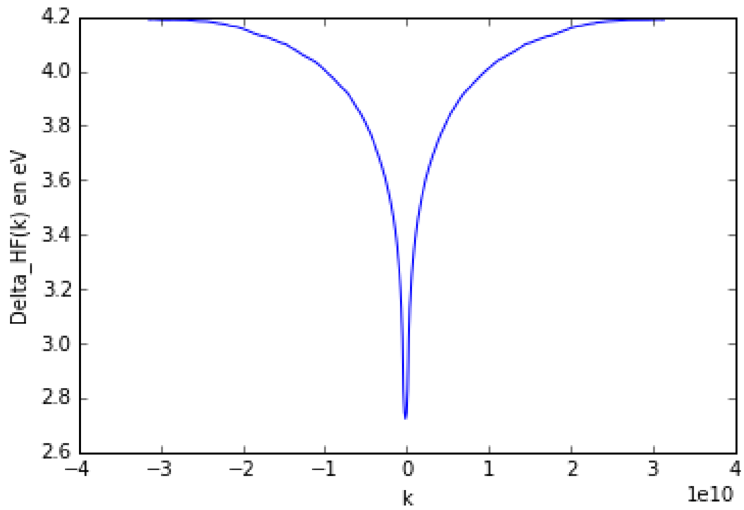

Figure 2.44: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=10 ($k_F = 0.03.10^{10}m^{-1}$) and nb=10000

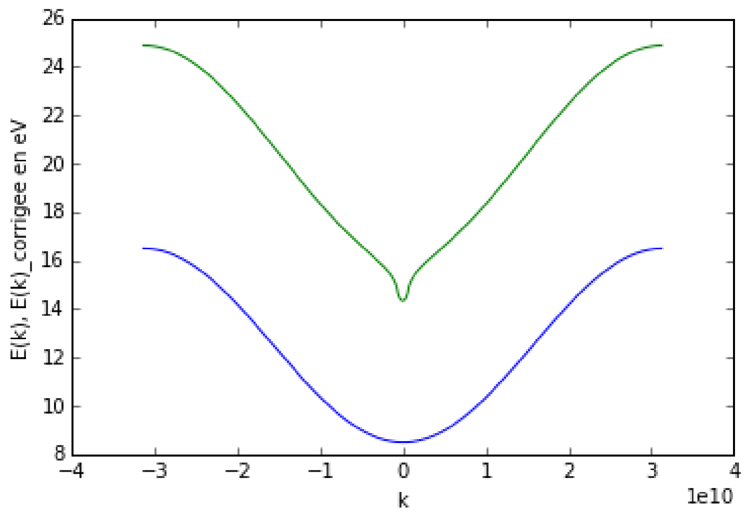

Figure 2.45: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=20 ($k_F = 0.06.10^{10}m^{-1}$) and nb=10000

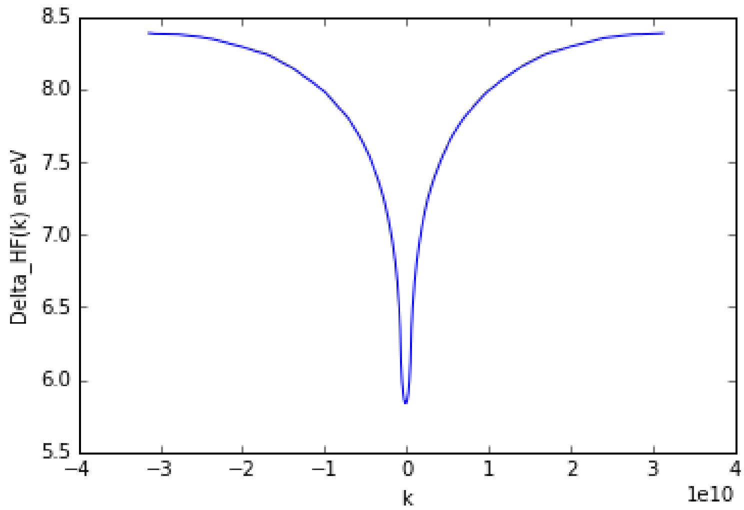

Figure 2.46: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=20 ($k_F = 0.06.10^{10}m^{-1}$) and nb=10000

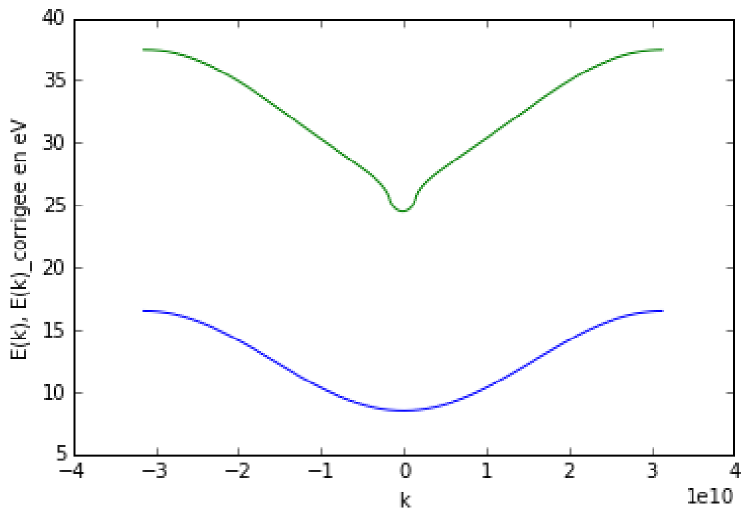

Figure 2.47: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=50 ($k_F = 0.16.10^{10}m^{-1}$) and nb=10000

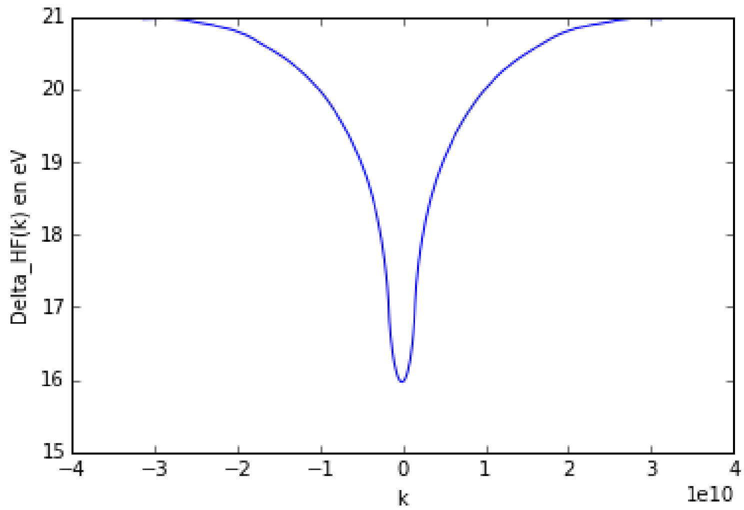

Figure 2.48: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=50 ($k_F = 0.16.10^{10}m^{-1}$) and nb=10000

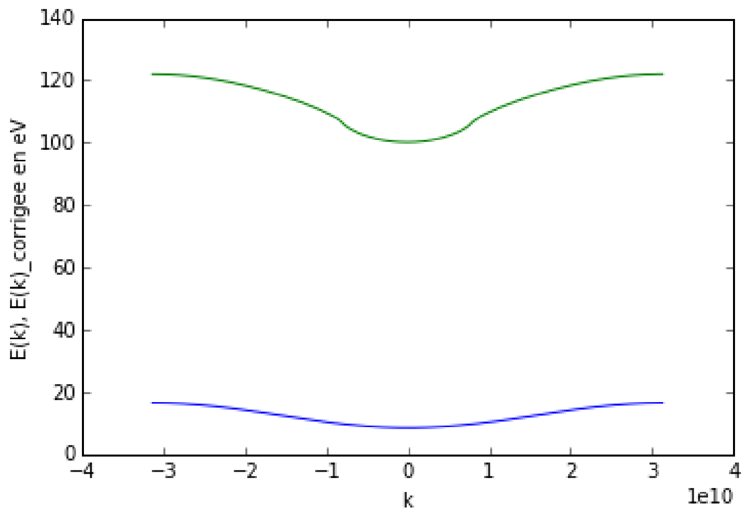

Figure 2.49: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=250 ($k_F = 0.79.10^{10}m^{-1}$) and nb=10000

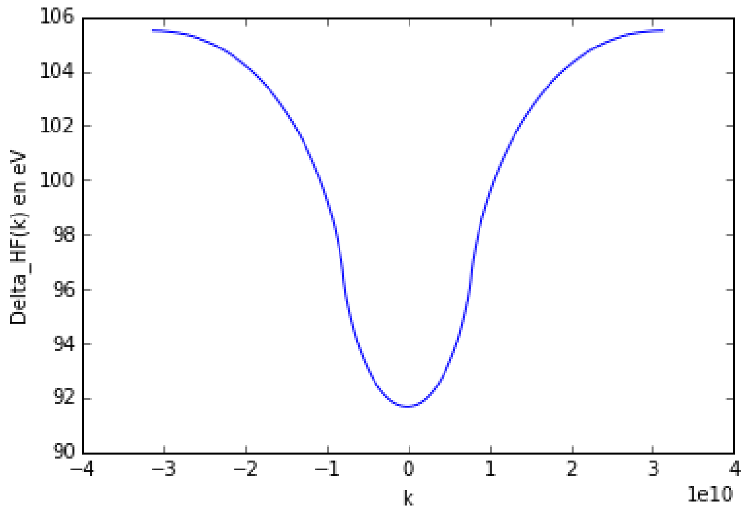

Figure 2.50: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=250 ($k_F = 0.79.10^{10}m^{-1}$) and nb=10000

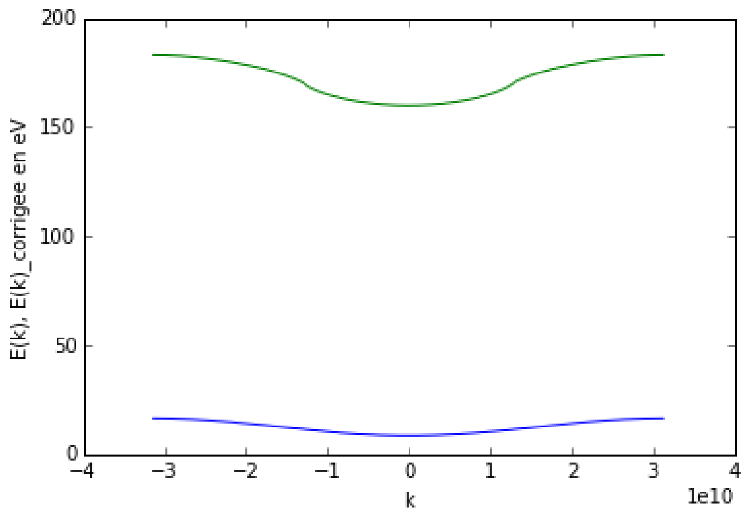

Figure 2.51: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=400 ($k_F = 1.26.10^{10}m^{-1}$) and nb=10000

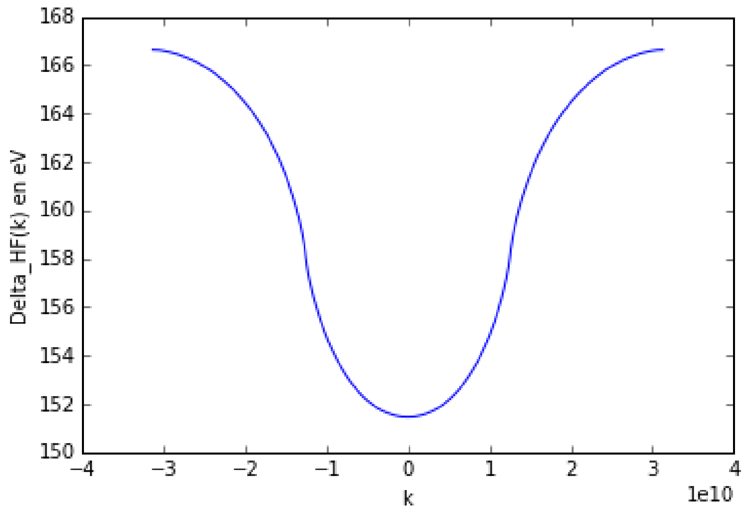

Figure 2.52: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=400 ($k_F = 1.26.10^{10} m^{-1}$) and nb=10000

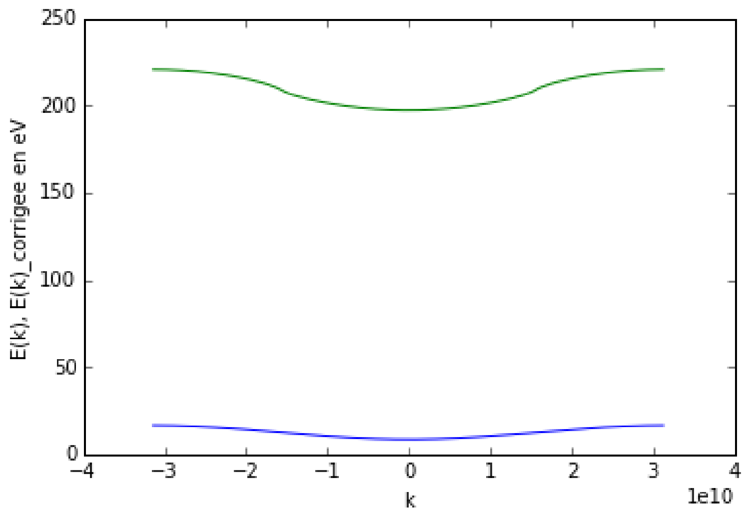

Figure 2.53: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=500 ($k_F = 1.57.10^{10} m^{-1}$) and nb=10000

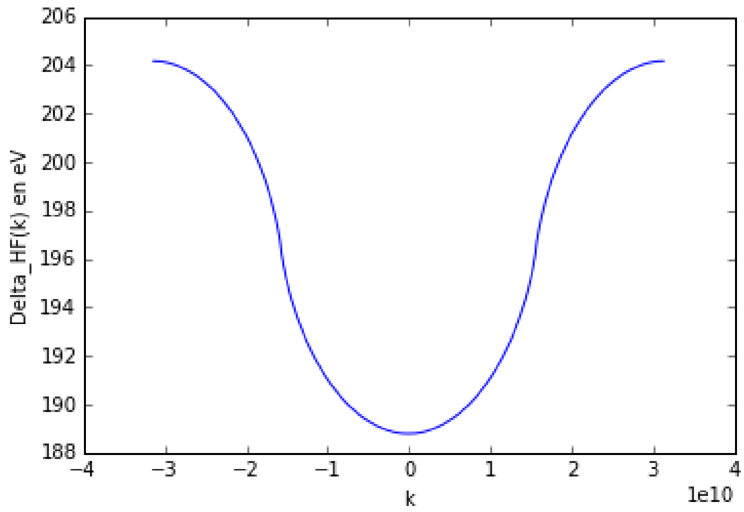

Figure 2.54: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=500 ($k_F = 1.57.10^{10}m^{-1}$) and nb=10000

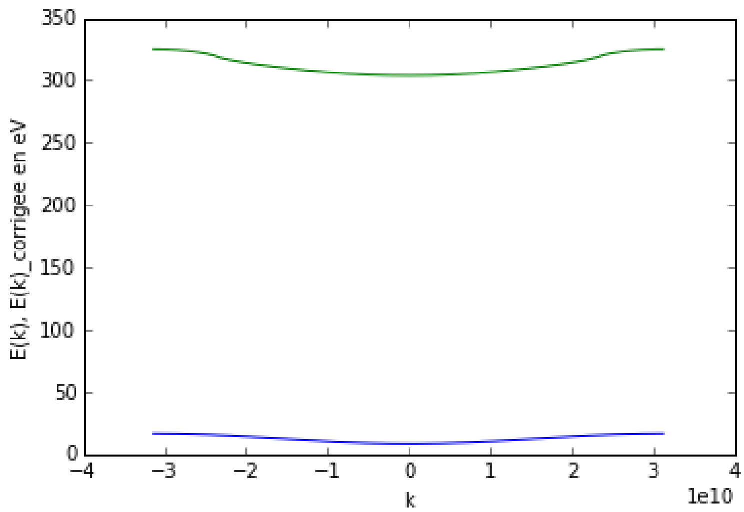

Figure 2.55: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=750 ($k_F = 2.4.10^{10}m^{-1}$) and nb=10000

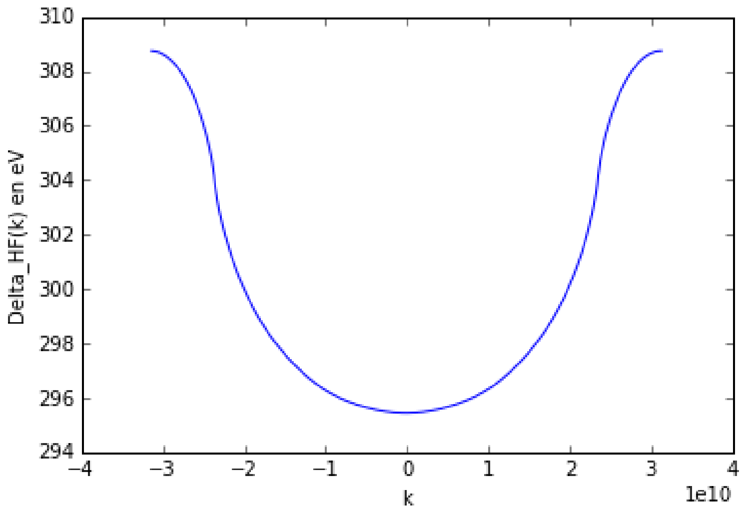

Figure 2.56: Correction of the energy by **Hartree-Fock's term** computed for the one-dimensionnal lattice , for N=500, NB=750 ($k_F = 2.4.10^{10}m^{-1}$) and nb=10000

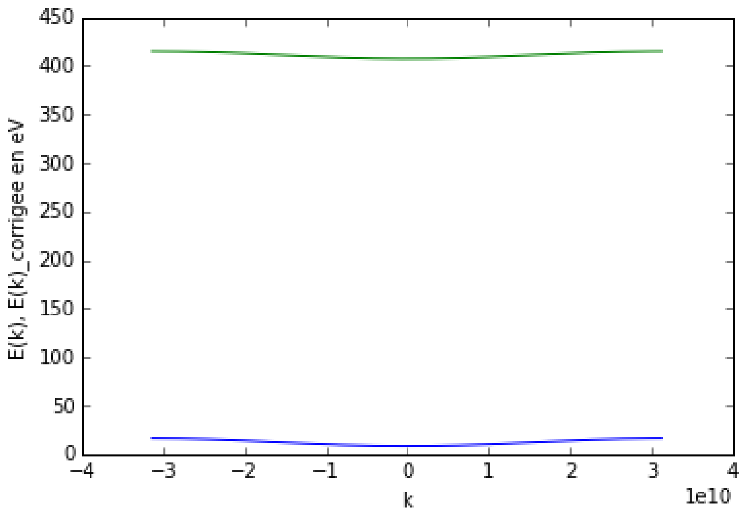

Figure 2.57: Energy computed for the one-dimensionnal lattice corrected by **Hartree-Fock's term**, for N=500, NB=1000 ($k_F = \frac{\pi}{a} = 3.14.10^{10}m^{-1}$) and nb=10000

2.2 Two-dimensionnal lattice

In two dimensions, it is nearly the same. The correction is :

$$\Delta(E_{(k_n)_x,(k_n)_y}) = \frac{e^2}{N^4} \sum_{l_1,p_1} \sum_{l_2,p_2} I_{l_1,p_1,l_2,p_2} \Theta^n_{l_1,p_1,l_2,p_2} \tag{2.147}$$

We proove the invariance by translation like in 1D, therefore :

$$\Delta(E_{(k_n)_x,(k_n)_y}) = \frac{e^2}{N^2} \sum_{l_1,p_1} I_{l_1,p_1,0,0} \Theta^n_{l_1,p_1,0,0} \tag{2.148}$$

where

$$I_{l_1,p_1,0,0} = \frac{K^4 a^5}{(4\pi)^2} \pi (\frac{d}{a})^2 \pi^2 (2\pi)^2 \int\int F_{l_1,p_1}(\rho_1', \rho_2', \theta_1, \theta_2, \phi_1, \phi_2) f(\rho_1') d\rho_1' f(\rho_2') d\rho_2' g(\theta_1) d\theta_1 g(\theta_2) d\theta_2 h(\phi_1) d\phi_1 h(\phi_2) d\phi_2 \tag{2.149}$$

$F_{l_1,p_1}(\rho_1', \rho_2', \theta_1, \theta_2, \phi_1, \phi_2)$ is the generalisation of the function $F_m(.)$ that we used in one dimension :

$$\frac{\rho_1'^2 \rho_2'^2 sin(\theta_1) sin(\theta_2)}{\sqrt{(\rho_1' sin(\theta_1) cos(\phi_1) - \rho_2' sin(\theta_2) cos(\phi_2) - l_1)^2 + (\rho_1' sin(\theta_1) sin(\phi_1) - \rho_2' sin(\theta_2) sin(\phi_2) - p_1)^2 + (\rho_1' cos(\theta_1) - \rho_2' cos(\theta_2))^2}} \tag{2.150}$$

With the same notations as for the one-dimensionnal case, the correction can be rewritten as :

$$\Delta(E_{(k_n)_x,(k_n)_y}) = \frac{e^2}{N^2} \sum_{l_1,p_1} I_{l_1,p_1,0,0} \Theta^n_{l_1,p_1,0,0} = \pi^2 (\frac{a}{d})^3 \frac{q_e^2}{4\pi\epsilon_0 d} \frac{1}{N^2} \sum_{l_1,p_1} E_\mu(F_{l_1,p_1}) \Theta^n_{l_1,p_1,0,0} \tag{2.151}$$

where

$$\Theta^n_{l_1,p_1,0,0} = N_e - \delta_{occ}^{(k_n)_x,(k_n)_y} - \sum_{j \neq n, jocc.} \delta_{\sigma_j,\sigma_n} cos[((k_n)_x - (k_j)_x) l_1 a + ((k_n)_y - (k_j)_y) p_1 a] \tag{2.152}$$

$$= N_e - \delta_{occ}^{\vec{k_n}} - \sum_{j \neq n, jocc.} \delta_{\sigma_j,\sigma_n} cos((\vec{k_n} - \vec{k_j}).(l_1 a \vec{e_x} + p_1 a \vec{e_y})) \tag{2.153}$$

The following graphs are some first results of the correction of the energy computed in the tight-binding approximation, in two dimensions. The lattice is a square of size N which repeats periodically. There are N^2 possible states, and $2N^2$ electrons at most in the system.

We denote α_1 the number of differents values of $(k_n)_x$ for all occupied states, and α_2 the number of differents values of $(k_n)_y$ ($\alpha_1 \leq N$ and $\alpha_2 \leq N$). There are $\alpha_1\alpha_2$ occupied states, and $2\alpha_1\alpha_2$ in the system. The occupied states are such that :

$$(k_n)_x = -\frac{\pi}{a} + i_1 \frac{2\pi}{Na}, i_1 \in [\frac{N-\alpha_1}{2}, \frac{N+\alpha_1}{2}] \tag{2.154}$$

and

$$(k_n)_y = -\frac{\pi}{a} + i_1 \frac{2\pi}{Na}, i_1 \in [\frac{N-\alpha_2}{2}, \frac{N+\alpha_2}{2}] \tag{2.155}$$

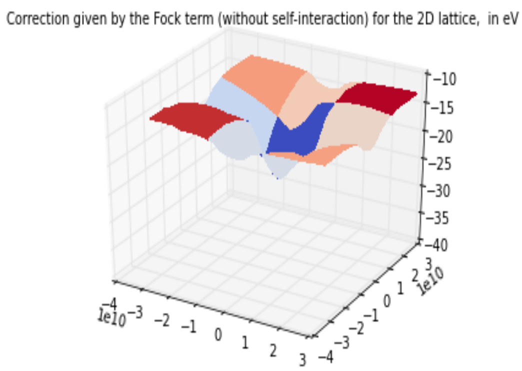

Figure 2.58: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 5$, $\alpha_2 = 5$, NB=50 and nb=1000

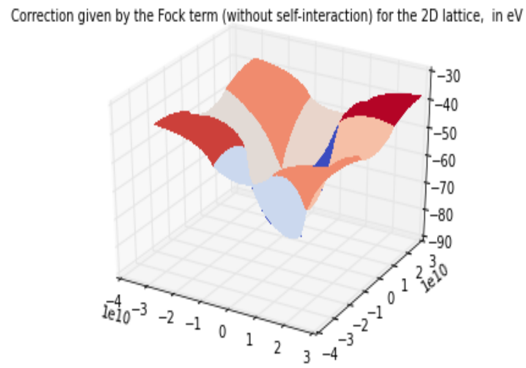

Figure 2.59: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 10$, $\alpha_2 = 10$, NB=100 and nb=1000

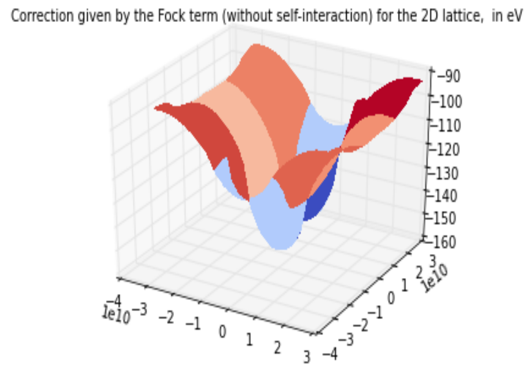

Figure 2.60: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 10$, $\alpha_2 = 20$, NB=400 and nb=1000

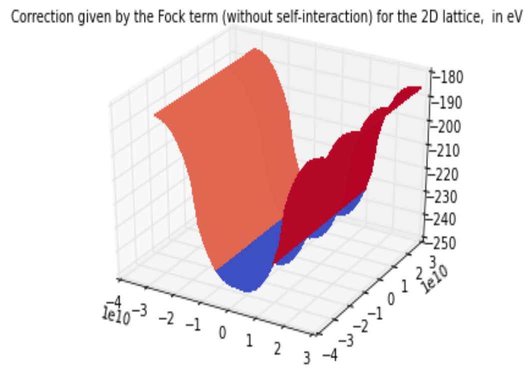

Figure 2.61: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 10$, $\alpha_2 = 30$, NB=600 and nb=1000

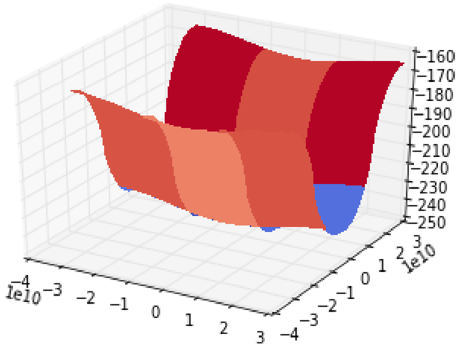

Figure 2.62: Energy for the two-dimensionnal lattice corrected by **Fock's term** (sum of the energy computed in tight-binding and the correction), for N=30, $\alpha_1 = 10$, $\alpha_2 = 30$, NB=600 and nb=1000

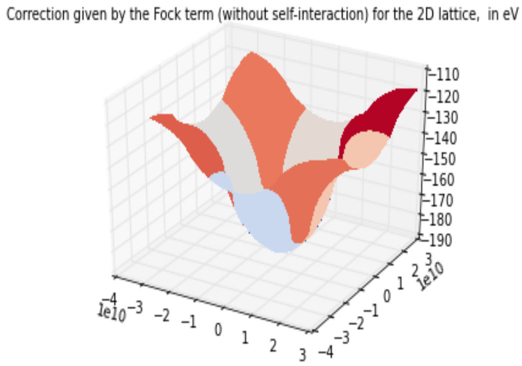

Figure 2.63: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 15$, $\alpha_2 = 15$, NB=450 and nb=1000

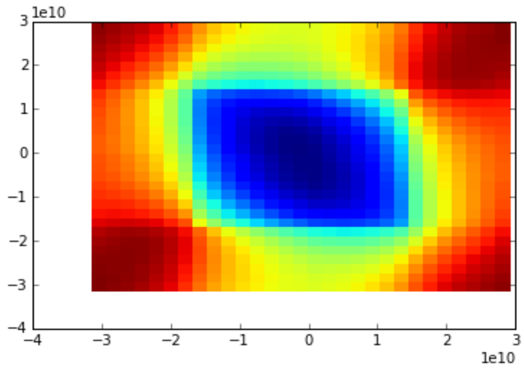

Figure 2.64: Projection of the correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 15$, $\alpha_2 = 15$, NB=450 and nb=1000

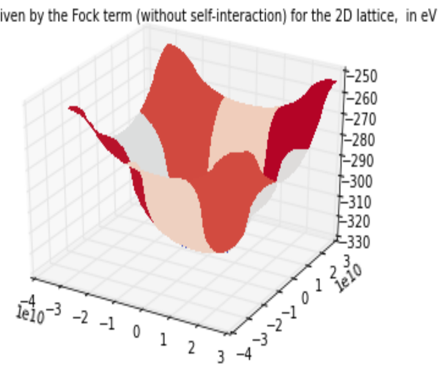

Figure 2.65: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 20$, $\alpha_2 = 20$, NB=800 and nb=1000

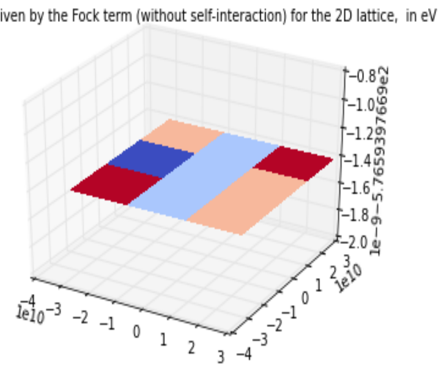

Figure 2.66: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=30, $\alpha_1 = 30$, $\alpha_2 = 30$, NB=1800 and nb=1000

The correction is constant when all the states are occupied.

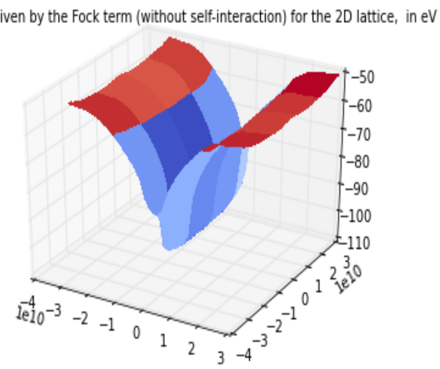

Figure 2.67: Correction to the energy due to **Fock's term** computed for the two-dimensionnal lattice, for N=40, $\alpha_1 = 5$, $\alpha_2 = 35$, NB=350 and nb=1000

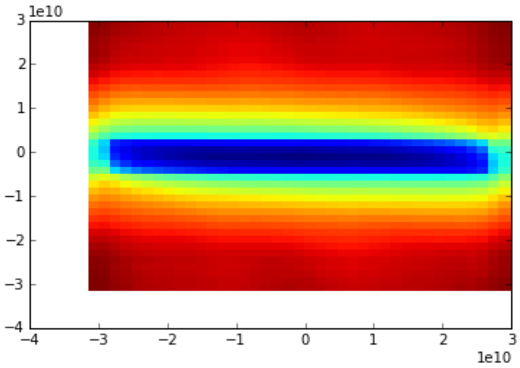

Figure 2.68: Projection of the correction to the energy due to **Fock's term**, computed for the two-dimensionnal lattice, for N=40, $\alpha_1 = 5$, $\alpha_2 = 35$, NB=350 and nb=1000

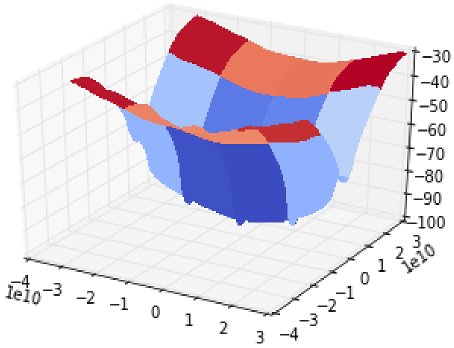

Figure 2.69: Energy for the two-dimensionnal lattice corrected by **Fock's term**, for N=40, $\alpha_1 = 5$, $\alpha_2 = 35$, NB=350 and nb=1000

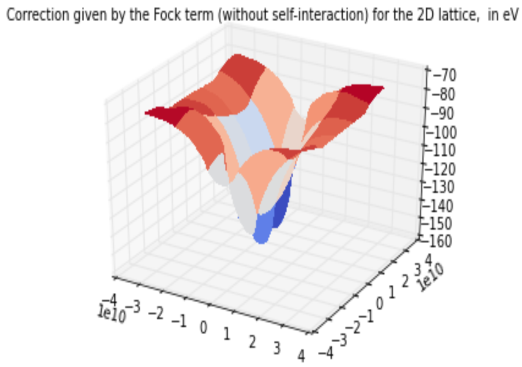

Figure 2.70: Energy for the two-dimensionnal lattice corrected by **Fock's term**, for N=50, $\alpha_1 = 10$, $\alpha_2 = 30$, NB=600 and nb=1000

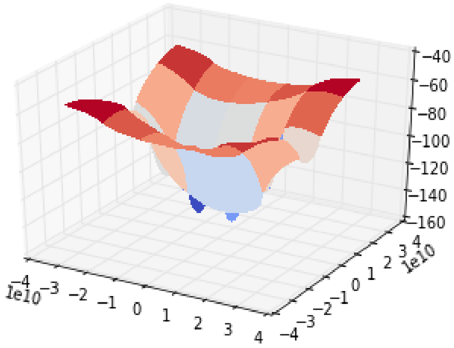

Figure 2.71: Energy for the two-dimensionnal lattice corrected by **Fock's term** (sum of the energy computed in tight-binding and the correction), for N=50, $\alpha_1 = 10$, $\alpha_2 = 30$, NB=600 and nb=1000

Multiorbital case Let χ_1 and χ_2 be the two possible orbitals of a localized wave function. The calculations are tough, but we are tempted to generalize the expression of the correction in the following way :

$$\Delta E_{k_n,\sigma_n,\chi_1} = \frac{e^2}{N}\sum_{m=1}^{N}[I_{0,m}(N^e - \delta^{occ}_{k_n,\sigma_n,\chi_1}) - \sum_{j\neq n, k_j occ.} \delta_{\sigma_n,\sigma_j}(I^{1,1}_{0,m}\delta^{occ}_{k_j,\sigma_j,\chi_1} + I^{1,2}_{0,m}\delta^{occ}_{k_j,\sigma_j,\chi_2}) - I^{1,2}_{0,0}\delta^{occ}_{k_n,\sigma_n,\chi_2}] \tag{2.156}$$

There are inter and intra atomic exchange terms, which ends up with a spin-polarizes and orbital-polarized energy correction !

2.3 How screening modulates the Hartree-Fock effect previously computed

We saw that the correction of the energy computed thanks to the Fock's term was becoming much larger than the energy itself when the number of electrons in the system increases. **The perturbative approach therefore is no longer valid** (which may explain why the correction of Fock becomes much greater than the usual order of magnitude of the energy itself). Besides, when there are so many electrons in the system, it becomes necessary to take screening into account.

Annex 1 : Density of states calulations for the two dimensional lattice

$$N_<^{2D}(E) = \int\int dm_1 dm_2 = \frac{(Na)^2}{(2\pi)^2}\int\int_{\{\vec{k}\in 1.B.Z.|E_{\vec{k}}\leq E\}} dk_x dk_y \tag{2.157}$$

$$= \frac{N^2}{(2\pi)^2}\int\int_{\{\begin{pmatrix}x\\y\end{pmatrix}\in[-\pi,\pi[^2|cos(x)+cos(y)\geq\alpha(E)\}} dxdy \tag{2.158}$$

where $\alpha(E) = \frac{E_0-t_0-E}{2t} \in [-2,2]$.

$$N_<^{2D}(E) = (\frac{N}{2\pi})^2\int_{-\pi}^{\pi}(\int_{\{z|cos(z)\geq\alpha(E)-cos(y)\}} dz)dy \tag{2.159}$$

$$N_<^{2D}(E) = (\frac{N}{2\pi})^2\int_{-\pi}^{\pi}(2\pi 1_{\alpha(E)+1\leq cos(y)} + 2Arccos(\alpha(E)-cos(y))1_{\alpha(E)-1\leq cos(y)\leq\alpha(E)+1})dy \tag{2.160}$$

$$\alpha(E)\leq 0 \Rightarrow N_<^{2D}(E) = (\frac{N}{\pi})^2[4\pi Arccos(\alpha(E)+1) + 2*2\int_{Arccos(\alpha(E)+1)}^{\pi} Arccos(\alpha(E)-cos(y))dy] \tag{2.161}$$

because $y \longmapsto Arccos(\alpha(E)-cos(y))$ is an even function.

$$\alpha(E)\geq 0 \Rightarrow N_<^{2D}(E) = \frac{N^2}{(2\pi)^2}2\int_{-Arccos(\alpha(E)-1)}^{Arccos(\alpha(E)-1)} Arccos(\alpha(E)-cos(y))dy \tag{2.162}$$

Thanks to a change of variable $z = cos(y)$, we finally obtain that :

$$E\geq E_0-t_0 \Rightarrow \alpha(E)\leq 0 \Rightarrow N_<^{2D}(E) = \frac{N^2}{\pi^2}(\pi Arccos(\alpha(E)+1)+\int_{-1}^{\alpha(E)+1}\frac{Arccos(\alpha(E)-z)}{\sqrt{1-z^2}}dz) \tag{2.163}$$

$$E\leq E_0-t_0 \Rightarrow \alpha(E)\geq 0 \Rightarrow N_<^{2D}(E) = \frac{N^2}{2\pi^2}\int_{\alpha(E)-1}^{1}\frac{Arccos(\alpha(E)-z)}{\sqrt{1-z^2}}dz \tag{2.164}$$

Annex 2 : Density of states calulations for the three dimensional lattice

$$N_{3D}(E) = (\frac{N}{2\pi})^3 \int_{-\pi}^{\pi} I_x dx \tag{2.165}$$

$$\alpha(E) - cos(x) \geq 2 \longrightarrow I_x = 0 \tag{2.166}$$

$$\alpha(E) - cos(x) \leq -2 \longrightarrow I_x = (2\pi)^2 \tag{2.167}$$

$$\alpha(E) - cos(x) \in [-2,2] \Rightarrow I_x = \int\int_{cos(y)+cos(z)\geq\alpha(E+2tcos(x))} dydz = (\frac{2\pi}{N})^2 N_<^{2D}(E+2tcos(x)) \tag{2.168}$$

To sum up these three distinctions :

$$N_<^{3D}(E) = (\frac{N}{2\pi})^3 [\int_{-\pi}^{\pi} (2\pi)^2 1_{cos(x)\geq\alpha(E)+2} dx + \int_{-\pi}^{\pi} (\frac{2\pi}{N})^2 N_<^{2D}(E+2tcos(x)) 1_{-2\leq\alpha(E)-cos(x)\leq 2} dx] \tag{2.169}$$

$$\alpha(E) \geq -1 \Rightarrow \int_{-\pi}^{\pi} 1_{cos(x)\geq\alpha(E)+2} dx = 0 \tag{2.170}$$

$$\alpha(E) \leq -1 \Rightarrow \alpha(E)+2 \in [-1,1] \Rightarrow \int_{-\pi}^{\pi} 1_{cos(x)\geq cos(Arccos(\alpha(E)+2))} dx = 2Arccos(\alpha(E)+2) \tag{2.171}$$

Therefore

$$N_<^{3D}(E) = 2\frac{N^3}{2\pi} 1_{\alpha(E)\leq -1} Arccos(\alpha(E)+2) + \frac{N}{2\pi} \int_{-\pi}^{\pi} N_<^{2D}(E+2tcos(x)) 1_{-2\leq\alpha(E)-cos(x)\leq 2} dx \tag{2.172}$$

Let's precise the second term denoted by $T(E)$:

$$\alpha(E) \in [-1,1] \Rightarrow \forall x \in [-\pi,\pi], 1_{-2\leq\alpha(E)-cos(x)\leq 2} = 1 \tag{2.173}$$

$$\alpha(E) \leq -1 \Rightarrow \forall x \in [-\pi,\pi], 1_{-2\leq\alpha(E)-cos(x)\leq 2} =_{-2\leq\alpha(E)-cos(x)} = 1_{cos(x)\leq cos(Arccos(\alpha(E)+2))} \tag{2.174}$$

$$\alpha(E) \geq 1 \Rightarrow \forall x \in [-\pi,\pi], 1_{-2\leq\alpha(E)-cos(x)\leq 2} = 1_{\alpha(E)\leq cos(x)+2} = 1_{cos(Arccos(\alpha(E)-2))\leq cos(x)} \tag{2.175}$$

which gives for this second term :

$$\alpha(E) \in [-1,1] \Rightarrow T(E) = \frac{N}{2\pi} \int_{-\pi}^{\pi} N_<^{2D}(E+2tcos(x)) dx \tag{2.176}$$

$$\alpha(E) \leq -1 \Rightarrow T(E) = \frac{N}{2\pi} 2 \int_{Arccos(\alpha(E)+2)}^{\pi} N_<^{2D}(E+2tcos(x)) dx \tag{2.177}$$

$$\alpha(E) \geq 1 \Rightarrow T(E) = \frac{N}{2\pi} \int_{-Arccos(\alpha(E)-2)}^{Arccos(\alpha(E)-2)} N_<^{2D}(E+2tcos(x)) dx \tag{2.178}$$

Therefore

$$\alpha(E) \leq -1 \Rightarrow N_<^{3D}(E) = \frac{N^3}{\pi} Arccos(\alpha(E)+2) + \frac{N}{\pi} \int_{Arccos(\alpha(E)+2)}^{\pi} N_<^{2D}(E+2tcos(x)) dx \tag{2.179}$$

$$\alpha(E) \in [-1,1] \Rightarrow N_<^{3D}(E) = \frac{N}{\pi} \int_0^{\pi} N_<^{2D}(E+2tcos(x)) dx \tag{2.180}$$

$$= \frac{N}{\pi} (\int_0^{Arccos(\alpha(E))} N_<^{2D}(E+2tcos(x)) dx + \int_{Arccos(\alpha(E))}^{\pi} N_<^{2D}(E+2tcos(x)) dx) \tag{2.181}$$

$$\alpha(E) \geq 1 \Rightarrow N_<^{3D}(E) = \frac{N}{\pi} \int_0^{Arccos(\alpha(E)-2)} N_<^{2D}(E+2tcos(x)) dx \tag{2.182}$$

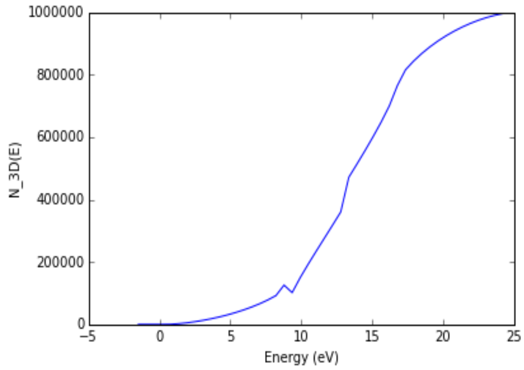

Figure 2.72: Number of energy states in a three dimensional lattice

Annex 3 : Exact formula for density of states in a three dimensionnal lattice

$\forall E \geq E_0 - t_0 + 2t$,

$$D^{3D}(E) = \frac{N}{\pi} \int_{Arccos(\frac{E_0 - t_0 + 4t - E}{2t})}^{\pi} D^{2D}(E + 2tcos(x))dx \tag{2.183}$$

$\forall E \leq E_0 - t_0 - 2t$

$$D^{3D}(E) = \frac{N}{\pi} \int_0^{Arccos(\frac{E_0 - t_0 - 4t - E}{2t})} D^{2D}(E + 2tcos(x))dx \tag{2.184}$$

For $E \in]E_0 - t_0 - 2t, E_0 - t_0 + 2t[$, if we take formally the derivative of :

$$\int_0^{Arccos(\alpha(E))^-} N_<^{2D}(E + 2tcos(x))dx; \int_{Arccos(\alpha(E))^+}^{\pi} N_<^{2D}(E + 2tcos(x))dx \tag{2.185}$$

we obtain :

$$D^{3D}(E) = \frac{N}{\pi}[\int_0^{Arccos(\frac{E_0 - t_0 - E}{2t})} D^{2D}(E + 2tcos(x))dx + \int_{Arccos(\frac{E_0 - t_0 - E}{2t})}^{\pi} D^{2D}(E + 2tcos(x))dx] \tag{2.186}$$

$$+ \frac{N}{2\pi t} \frac{lim_{E \longrightarrow (E_0 - t_0))^+} N_<^{2D}(E) - lim_{E \longrightarrow (E_0 - t_0))^-} N_<^{2D}(E)}{\sqrt{1 - \alpha(E)^2}} \tag{2.187}$$

The problem is that $N_<^{2D}(E + 2tcos(x))$ is not continuous at $x = Arccos(\alpha(E))$ because $N_<^{2D}(.)$ is not continuous at $E_0 - t_0$. We cut the integral because D^{2D} goes towards $+\infty$ at $E_0 - t_0$.

Formally, we obtain :

$$E \in]E_0 - t_0 - 2t, E_0 - t_0 + 2t[\Rightarrow D^{3D}(E) = \frac{N}{\pi} \int_0^{\pi} D^{2D}(E + 2tcos(x))dx + \frac{N}{2\pi t} \frac{lim_{E \longrightarrow (E_0 - t_0))^-} N_<^{2D}(E)}{\sqrt{1 - \alpha(E)^2}} \tag{2.188}$$

having used the expression 1.13 for the limits of $N^{2D}(E)$.

The previous expressions of $D^{3D}(E)$ give the following trend :

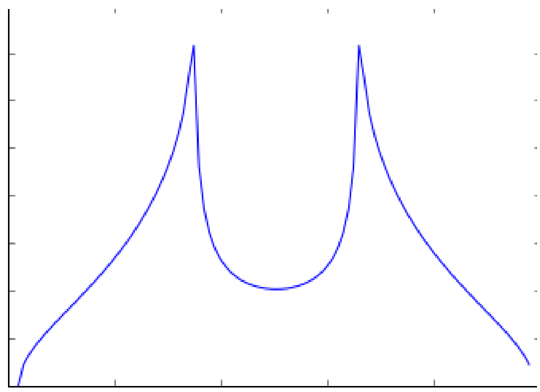

Figure 2.73: Density of states in a three dimensional lattice

The analytical expressions we found, related to the density of states for a two dimensionnal lattice, seem correct for $E < E_0 - t_0 - 2t$ and $E > E_0 - t_0 + 2t$, but not in-between.
This time, contrary to the one and two dimensionnal lattice, the density is continuous.