

Numerical calculation of the band structure using the Central Equation

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Abstract: The aim of this work is to create a tool to calculate the electronic band structure of any type of crystal. Firstly, I will recover the band structure for the text-book models: the empty lattice model and the tightly bound electrons model, and then I will compute the band structure for a more realistic particular case of a body centered cubic crystal, trying to reproduce the electronic band structure of sodium. This program is developed with the free software *Octave*.

I. INTRODUCTION

The starting point of this work is the central equation, which is the Schrödinger equation defined for the electrons of a crystal with a periodic structure. In this section I will present a very introductory description of the formalism that gives rise to calculations in crystalline solids.

A. Crystals and reciprocal lattice

Crystals have the particularity that their structure is based on a repetition of a basic block. The existence of this periodicity is the base for developing techniques to describe their behavior.

The direct lattice is defined from the vectors \mathbf{a}_1 , \mathbf{a}_2 and \mathbf{a}_3 . The primitive vectors, give the position of any atom of the crystal by making linear combinations of them.

To describe many of physics phenomena belonging of periodical structure, we use the **reciprocal lattice**, that is described as follows:

$$\begin{aligned} \mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} & \mathbf{b}_2 &= 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \\ \mathbf{b}_3 &= 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \end{aligned} \quad (1)$$

Taking the primitive vectors of the reciprocal lattice, we can write any vector of the lattice by making a lineal combination of them:

$$\mathbf{G} = h \cdot \mathbf{b}_1 + k \cdot \mathbf{b}_2 + l \cdot \mathbf{b}_3 \quad (2)$$

Dimensions are length inverse, but as they are multiplied by the factor 2π in their definition, their units correspond to wave vector units. So, reciprocal space can be considered like wave vector space.

B. Bloch's theorem and central equation

Bloch's theorem sets that wave functions of electrons are independent and must have into account solid periodicity. Bloch's functions are described as a periodic function modulated by a plane wave of wave vector \mathbf{k} that gives the phase variation when we change from one primitive cell to another. Because of their periodicity, they can be written as a superposition of plane waves:

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{k}-\mathbf{G}} e^{i(\mathbf{k}-\mathbf{G}) \cdot \mathbf{r}} \quad (3)$$

Schrödinger's equation of electrons inside a crystal lattice depends on too much variables. The Hamiltonian of the particles of the solid have the interaction between ions and electrons and both kinetic energy terms too. To solve it, it's necessary to make various approximations that allows one to define interactions with the rest of crystal as an effective potential. This allows to write Schrödinger equation for one electron in its usually form:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \phi(\mathbf{r}) = E\phi(\mathbf{r}) \quad (4)$$

If we suppose a perfect crystal, then ionic nuclei will be distributed in a periodic and regular way, therefore it's reasonable to suppose that the potential will have the underlying periodicity of the crystal, or said in other words, the periodicity of the Bravais lattice.

$$V(\mathbf{r} + \mathbf{R}) = V(\mathbf{r}) \quad (5)$$

This potential can be developed as a Fourier series as follows:

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (6)$$

I will focus on the details of the potential in a next section.

Replacing this potential in Schrödinger equation and choosing the correct form of wave functions, the result is a system of linear equations called **central equation** and forms the basis for the calculus of the electronic states:

$$\left[\frac{\hbar^2 |\mathbf{k} - \mathbf{G}|^2}{2m} - E_{\mathbf{k}} \right] C_{\mathbf{k}-\mathbf{G}} + \sum_{\mathbf{G}''} V_{\mathbf{G}''-\mathbf{G}} C_{\mathbf{k}-\mathbf{G}''} = 0 \quad (7)$$

Where we have an equation for each vector \mathbf{G} in the reciprocal lattice and the summation goes for all \mathbf{G} vectors as well.

C. Brillouin's zone

Both the energy and the wave functions are periodic functions with the periodicity of the reciprocal lattice:

$$E(\mathbf{k} + \mathbf{G}) = E(\mathbf{k}) \quad (8)$$

Therefore it is possible to describe all the states of electrons considering the states in the primitive cell of the reciprocal lattice. This primitive cell is called **First Brillouin's zone** and it's very useful to calculate energy bands because calculations are greatly simplified.

II. APPROACH TO THE PROBLEM

Development of the problem is based on design a program able to calculate the electronic band structure for a solid using the mathematical tool *Octave*, that is the free equivalent to *Matlab*. It uses a high level language and it's oriented to matrix calculations, so it's an useful tool for the calculations that I am pretending to perform.

A. Study frame

There are 14 Bravais lattices in three dimensions. The program can make calculations of the band structure for the three cubic Bravais lattices namely:

- Simple cubic (SC)
- Face centered cubic (FCC)
- Body centered cubic (BCC)

The definition of the lattice in the program structure is carried out through the definition of the vectors \mathbf{k} and \mathbf{G} , that will be different depending on the lattice studied. It was the first step I made at the beginning of program.

It is impossible to represent the bands of a real 3D solid, therefore usually some stablished directions in the reciprocal space are chosen. There are some characteristic points inside the first Brillouin zone, that have to do with their symmetry and these will mark the direction of \mathbf{k} vectors.

In Fig. 1, graphical representations of the first Brillouin zones of each lattice, as well as the characteristic points are shown:

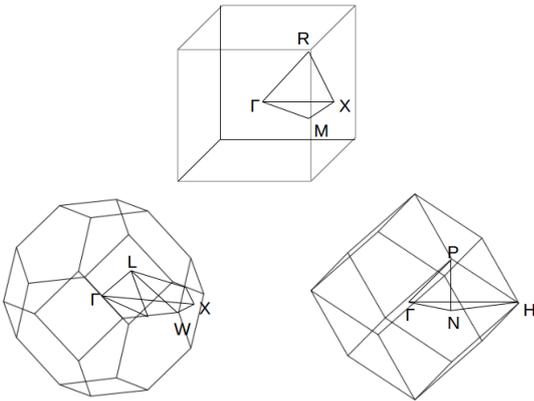


FIG. 1: Diagram of the first Brillouin zone for the three cubic lattices (SC, FCC and BCC) with the characteristic points of each **GRAZ University of Technology**: <http://lamp.tu-graz.ac.at/~hadley/ss1/bzones/>

Of all critical points, I use the following:

SC	FCC	BCC
$\Gamma=[0,0,0]$	$\Gamma=[0,0,0]$	$\Gamma=[0,0,0]$
$X=[0,\frac{1}{2},0]$	$X=[0,\frac{1}{2},\frac{1}{2}]$	$H=[0,0,1]$
$M=[\frac{1}{2},\frac{1}{2},0]$	$W=[\frac{1}{2},1,0]$	$P=[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$
$R=[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$	$L=[\frac{1}{2},\frac{1}{2},\frac{1}{2}]$	$N=[\frac{1}{2},\frac{1}{2},0]$

They're all expressed in units of $\frac{2\pi}{a}$, so they must be multiplied by this factor to obtain units of wave vector. Once characteristic points are defined, directions are created by making a vector that goes from one to the next. The program will run along each of these directions by considering n discret \mathbf{k} values between each pair of characteristic points.

The primitive vectors of the reciprocal lattice for each lattice must be defined, since it is from these the vectors that \mathbf{G} are computed.

For each lattice, and expressed in $\frac{2\pi}{a}$ units too, primitive vectors are:

- Simple cubic

$$\mathbf{b}_1 = (1, 0, 0) ; \quad \mathbf{b}_2 = (0, 1, 0) ; \quad \mathbf{b}_3 = (0, 0, 1)$$

- Face centered cubic

$$\mathbf{b}_1 = (-1, 1, 1) ; \quad \mathbf{b}_2 = (1, -1, 1) ; \quad \mathbf{b}_3 = (1, 1, -1)$$

- Body centered cubic

$$\mathbf{b}_1 = (0, 1, 1) ; \quad \mathbf{b}_2 = (1, 0, 1) ; \quad \mathbf{b}_3 = (1, 1, 0)$$

B. The potential

Interaction of an electron with the lattice can be expressed as an effective potential created by the nuclei and other electrons. Below is a picture to show intuitively the shape of the potential that I consider, in addition to the resulting formula:

$$V(\mathbf{r}) = - \sum_{\mathbf{R}} \left| \frac{C}{\mathbf{r} - \mathbf{R}} \right| \quad (9)$$

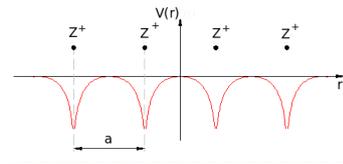


FIG. 2: Particle in a one dimensional lattice. [Wikipedia]

As mentioned in the introduction, the potential can be expressed as a Fourier series whose coefficients $V_{\mathbf{G}}$ must to be computed. The coefficients are obtained from the Eq. 10:

$$V_{\mathbf{G}} = \frac{1}{V_C} \int_{cell} d\mathbf{r} V(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r}) \quad (10)$$

Making appropriate calculations, the result of taking $V(\mathbf{r})$ as in Eq. 10 is:

$$V_{\mathbf{G}} = - \frac{\beta}{a\pi} \frac{C}{h^2 + k^2 + l^2} \quad (11)$$

If I suppose that interaction is only between electrons and atomic nucleus, then the potential will be Coulombian. Taking the integral of $V_{\mathbf{G}}$ and adding the term of the Coulomb potential the result is

$$V_{\mathbf{G}} = -\frac{\beta q^2}{a^2 \pi \epsilon_0} \frac{1}{h^2 + k^2 + l^2} \quad (12)$$

Making that assumption, I have not taken into account the interaction between electrons, so I know that probably this potential will be too strong because I have not considered screening produced by the other electrons around the atomic nucleus. In order to consider that, I add a constant A to the potential that I will tune to get the expected results:

$$V_{\mathbf{G}} = -\frac{\beta q^2}{a^2 \pi \epsilon_0} \frac{A}{h^2 + k^2 + l^2} \quad (13)$$

C. Representation units

All results shown in next sections are expressed in reduced units. To show general results, energies are expressed in E_0 units. E_0 is defined by considering the result for the empty lattice model to be:

$$\begin{aligned} E &= \frac{\hbar^2 |\mathbf{k} - \mathbf{G}|^2}{2m} = \frac{\hbar^2 (2\pi)^2}{2a^2 m} |(\xi_x, \xi_y, \xi_z) - (h, k, l)|^2 = \\ &= E_0 [(\xi_x - h)^2 + (\xi_y - k)^2 + (\xi_z - l)^2] \Rightarrow \boxed{E_0 = \frac{\hbar^2 (2\pi)^2}{2a^2 m}} \end{aligned} \quad (14)$$

Thus, all energy values showed from now will be relative values of E_0 :

$$\tilde{E} = \frac{E}{E_0} \quad (15)$$

To express the potential with the same units, I divide its value by E_0 too. Proceeding this way, the term of the potential is expressed as:

$$\tilde{V}_{\mathbf{G}} = \frac{V_{\mathbf{G}}}{E_0} = \frac{V_{\mathbf{G}}}{\frac{\hbar^2 (2\pi)^2}{2m_e a^2}} = \frac{0.383 \cdot a^2 \cdot \beta \cdot A}{h^2 + k^2 + l^2} \quad (16)$$

I take $a = 1 \text{ \AA}$ due crystal lattices have their interatomic distance of that order. So, for a particular lattice, it has to be multiplied by its interatomic distance in \AA squared.

D. Core Program's design

Writing the central equation in matricial form, the problem to solve is reduced to the following set of linear equations:

$$\begin{pmatrix} \Delta - E_{\mathbf{k}_i} & V_{\mathbf{G}'_1 - \mathbf{G}_1} & \dots & V_{\mathbf{G}'_N - \mathbf{G}_1} \\ V_{\mathbf{G}'_1 - \mathbf{G}_2} & \Delta - E_{\mathbf{k}_i} & \dots & V_{\mathbf{G}'_N - \mathbf{G}_2} \\ \vdots & \vdots & \ddots & \vdots \\ V_{\mathbf{G}'_1 - \mathbf{G}_N} & V_{\mathbf{G}'_2 - \mathbf{G}_N} & \dots & \Delta - E_{\mathbf{k}_i} \end{pmatrix} \begin{pmatrix} C_{\mathbf{k}_i - \mathbf{G}_1} \\ C_{\mathbf{k}_i - \mathbf{G}_2} \\ \vdots \\ C_{\mathbf{k}_i - \mathbf{G}_N} \end{pmatrix} = 0$$

with

$$\Delta = \frac{\hbar^2}{2m} |\mathbf{k}_i - \mathbf{G}|^2 + V_0 \quad \text{if } \mathbf{G} = \mathbf{G}$$

From central equation, program's core is a matrix from which I'll obtain the energy eigenvalues, that will be the energy of each band for each \mathbf{k} . The form that acquires this matrix when it's implemented at the program is:

$$\begin{pmatrix} \frac{\hbar^2}{2m} |\mathbf{k}_i - \mathbf{G}_1|^2 + V_0 & V_{\mathbf{G}'_1 - \mathbf{G}_1} & \dots & V_{\mathbf{G}'_N - \mathbf{G}_1} \\ V_{\mathbf{G}'_1 - \mathbf{G}_2} & \frac{\hbar^2}{2m} |\mathbf{k}_i - \mathbf{G}_2|^2 + V_0 & \dots & V_{\mathbf{G}'_N - \mathbf{G}_2} \\ \vdots & \vdots & \ddots & \vdots \\ V_{\mathbf{G}'_1 - \mathbf{G}_N} & V_{\mathbf{G}'_2 - \mathbf{G}_N} & \dots & \frac{\hbar^2}{2m} |\mathbf{k}_i - \mathbf{G}_N|^2 + V_0 \end{pmatrix}$$

I call this matrix \mathbf{M} and is defined for each \mathbf{k} belonging to the first Brillouin zone. It will tour a number of vectors \mathbf{G} previously defined that makes that the size of \mathbf{M} to be finite. That number of vectors that are considered at Eq. 3 will determine the quality of the solution found. To see this effect I define a parameter, that I call G_{MAX} , as the maximum modulus of the \mathbf{G} vectors. Program builds a big number of vectors \mathbf{G} by making linear combinations of primitive vectors for each lattice, but only those shorter or equal to G_{MAX} will be considered in \mathbf{M} .

Thus, for each value of \mathbf{k} , the program build a new matrix and calculate the corresponding eigenvalues. Proceeding this way I save memory because it creates a new array for each value of \mathbf{k} . *Octave* has a function to calculate the eigenvalues of a given matrix. In order to represent the results, they must be sorted in increasing order. *Octave* has a function to do it called *sort* [4].

Calculation time depends strongly on the size of \mathbf{M} , that as I've said, is determined by G_{MAX} . To see how increases the size of \mathbf{M} ($N \times N$), where N is equal to the number of vectors \mathbf{G} with its modulus less or equal than G_{MAX} , Fig. 3 the dependence of N on G_{MAX} for the three lattices considered.

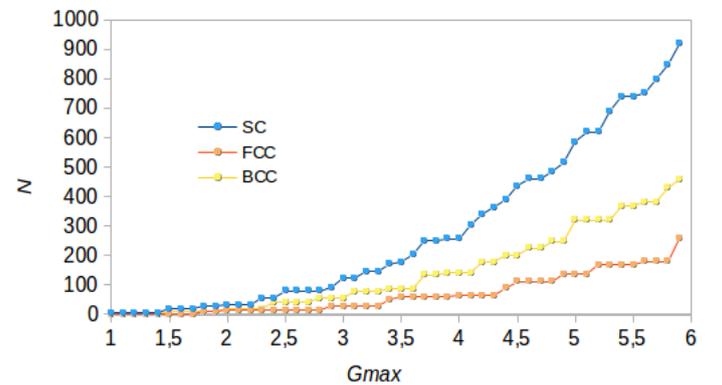


FIG. 3: N as a function of G_{MAX}

From the last figure it is evident that the complexity of the problem grows very fast with G_{MAX} . Therefore, I choose

a value of G_{MAX} computation time must be taken into account. Fig. 4 shows the computation time increases with G_{MAX} for different values of the discretization parameter n :

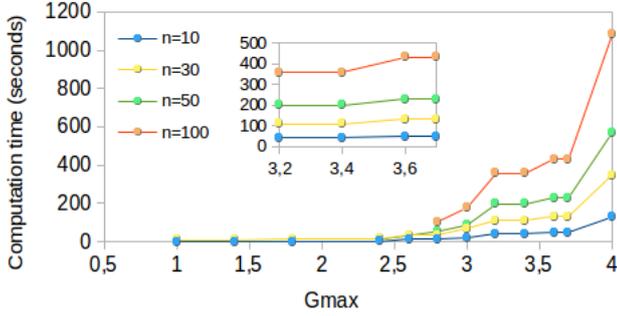


FIG. 4: Computation time in seconds as a function of G_{MAX} for different discretization parameter n for a BCC lattice

To obtain quantifiable values of the effect of changing G_{MAX} on the quality of the solution, I choose a particular point in the reciprocal space to see how the potential modifies the energy. In a BCC lattice, the second band has the minimum at the critical point N, as is shown on Fig. 9. The potential opens a *bandgap* whose width is the parameter I will try to determine.

For this calculation, I take $A=0.0365$, to study the quality of the solution found. I'll explain later why I choose this value.

Fig. 5 shows how varies the energy difference between first and second bands at N for increasing values of G_{MAX} :

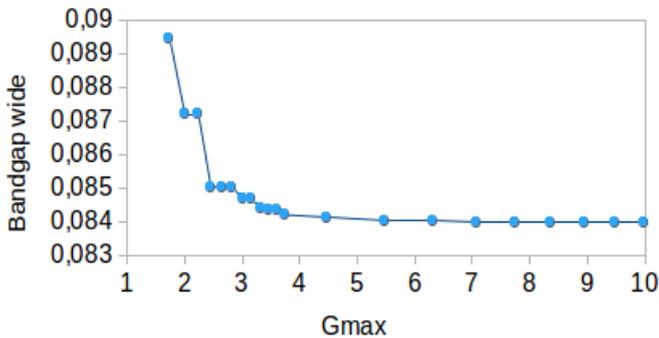


FIG. 5: Bandgap between first and second bands of BCC lattice at critical point N. Y axis shows bandgap energy in terms of E_0

As it can be seen, bandgap's energy quickly tends to a finit value $0.08397 \cdot E_0$. Taking this number as a final result, I calculated percentatge error for $G_{MAX} < 10$ (Fig. 6).

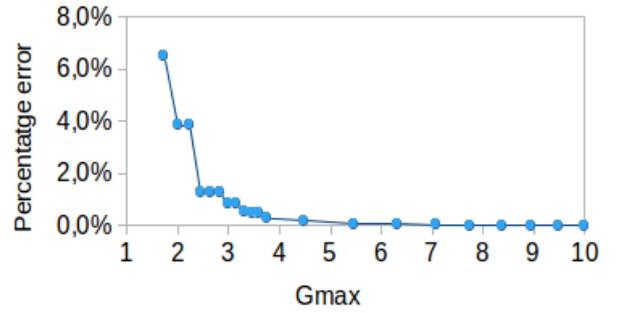


FIG. 6: Percentatge error of bandgap's energy taking $0.08397 E_0$ as the correct result as function of G_{MAX} for a BCC lattice

Taking $G_{MAX} = 3.7$, percentatge error is only 0,27 % and taking $G_{MAX} = 3.2$ error is 0.83 %. It's a very small error and represents, for a discretization parameter n between 10 and 50, a computation time of about 3 minutes approximately. It can be seen at the inset of Fig. 4.

III. RESULTS

A. Text-book models

To see if program works fine, I made calculations for two cases well known. Fig. 7 shows the result for simple cubic lattice when potential is equal to zero. It shows how the energy bands look for each direction taken in the crystal. Vertical lines marks the characteristic points. This model is known as the Empty Lattice Model:

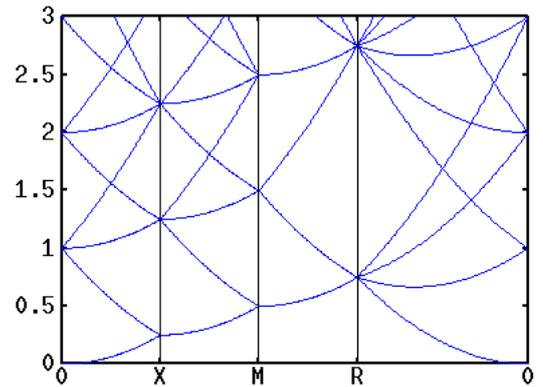


FIG. 7: Band structure for the empty lattice model in a SC lattice. Vertical axis corresponds to \bar{E} , depending on \mathbf{k} for critical points ($G_{MAX}=2.8$)

There are two sets of results in Fig. 7. One, plotted in red that is the analytical result for this model, and another in blue solved with the program using zero potential. They're completely superposed, so the model works perfectly.

After having verified the behavior for the empty lattice model, the next step is to check whether the program is functioning correctly when studying the case of strongly bound electrons. To see it, I considered $A=1000$ in the expression of the potential terms. Result is showed in Fig. 8.

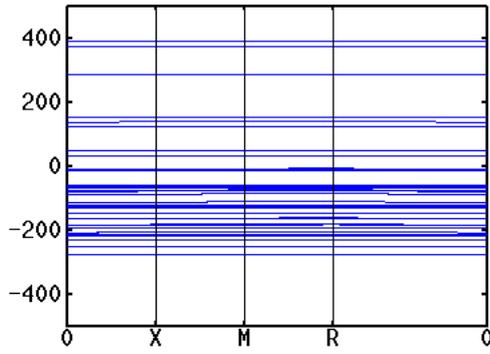


FIG. 8: Band structure for tightly bound electrons model in a SC lattice. It shows \tilde{E} depending on \mathbf{k} for critical points ($G_{MAX}=2.8$)

The result is consistent with the expected. In this case, the strong interaction causes the energy bands to be flat. As it can be seen in the plot, there are negative energy values indicating the binding energy of the electron.

After having checked that program works well with the standard models, I make the study for a particular case.

B. Particular case: Sodium

I will try to emulate the behavior of a known material as, for example, sodium. It has a BCC structure and its interatomic distance is 4.29 Å. Fig. 9 shows sodium band structure (Graph extracted from [3]):

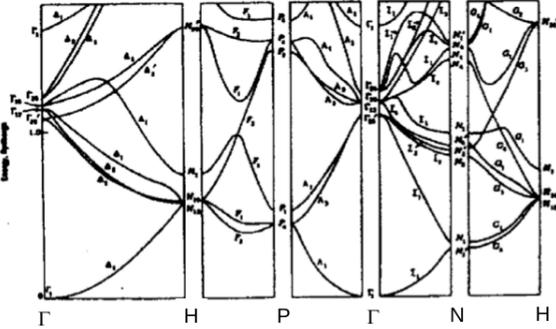


FIG. 9: Band structure for sodium extracted from [3]

Taking this figure as a reference, I gave different values to A to obtain a similar plot with the program. The value with which I observed more similarity was $A=0.0365$. Fig.

10 shows the band structure computed with this value. The final potential form is:

$$\tilde{V}_{\mathbf{G}} = \frac{0.383 \cdot \beta \cdot 0.0365}{h^2 + k^2 + l^2} = \frac{0.12}{h^2 + k^2 + l^2} \quad (17)$$

IV. CONCLUSIONS

I have developed a program able to compute perfectly the band structure for the three cubic lattices of Bravais for the empty lattice model. For the tightly bound electrons models,

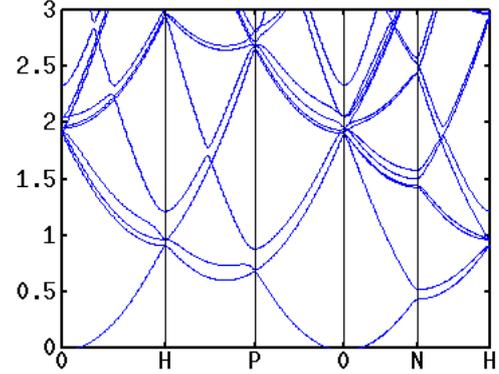


FIG. 10: Band structure computed with $A=0.0365$ and $G_{MAX}=2.8$

it shows the expected results. It's also able to reproduce the band structure for a particular material by fine tuning the parameters of the potential as well.

Program would be able to solve the band structure for different lattices by making small modifications. The changes will only imply the definition of primitive vectors and the characteristic points of the lattice studied.

In view of the results found, it is evident the power of the program, which is able to calculate the energy of the first bands with an error less than 1%, and with a maximum resolution that can be obtained with in the calculation times of 3 minutes approximately.

Acknowledgments

I want to thank my tutor Joan Manel Hernández their willingness and their invaluable help that has helped me to keep learning.

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