Study the Complexity of the Tight Binding approach

D. Anouar Akacha*

(*) Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS),
UMR 7504 du CNRS, 23 rue du Loess, 67034 Strasbourg, France, EU

The aim of this work is to explain in a decent way the most used method to evaluate electronic structure proprieties of any compounds. Mainly within the frame work of this topic we targeted the semiconductors (Si and Ge) and Carbon for the sake of diversity. The latter method is refers to Tight Binding approach. Furthermore, We introduced the theoretical formalism in more simplified way, where we focus to break down the complexity of the problem. We were also interested to evaluate the Density of state using the Linear Tetrahedron Method.

Keywords: Electronic Structure, semiconductors, Tight Binding, Density of state, Linear Tetrahedron Method.

I. INTRODUCTION

The motivation for the present work is to show that no matter the complexity of the compounds we are interested in, it can be subdivide into more simple steps, in order to give an insight understanding of the materials. So far, the ability to exploit the optical and electrical proprieties of materials stand as the key for a crucial optimizing process, therefore a better performance can be achieved.

In the following we will introduce the approach of Tight Binding step by step from the simple problem of the linear atomic chain into the band structure of semiconductors materials(daily life examples).

II. FORMALISM

Basically, Tight Binding method consist of an upgrade of the free electron model, where we aim to construct our crystal (specific arrangement of atoms) by plugging the potential created by the equal-spaced individual species of the compound to the Hamiltonian $\hat{H} = \hat{P} + \hat{V}$ [1]. The effect of this modification turn the electrons tightly bounding with more restriction when it comes to describe the transport behavior.

Moreover, the wave function $|\Psi>$ needed to deal with such Hamiltonian is constructed using Blöch theorem and the Linear Combination of Atomic Orbital (LCAO) principal, and it is given as following:

$$|\Psi> = \frac{1}{\sqrt{N}} \sum_n \exp[i\vec{K}\vec{R}_n] \times |\varphi_n(r, \theta, \phi)> \quad (1)$$

Note that $|\varphi_n(r, \theta, \phi)>$ describe the Linear Atomic Orbital (it include a radial and angular parts). In the future we will abbreviate it by referring to the name of the corresponding Orbital.

Now the road is paved towards us and we just need to evaluate the matrix elements [2]:

$$H_{ij} = <\Psi_i|\hat{H}|\Psi_j> \quad (2)$$

Note that in the vicinity of the Tight Binding approach the potential is the one who is dominant [3], and fortunately, We will not bother our self to discuss the orthogonality of the wave-function, and this is due to Löwdin recipe [2]. Moreover, we have the propriety of the basis set of each atoms $<\varphi_j|\varphi_i> = \delta_{ji}$.

III. BUILDING UP THE HAMILTONIAN

For the case of Semiconductors we will use the two type of orbital atomic s and p. And by considering two kind of atoms per cell, our Hamiltonian can be written within the basis $\{|\varphi_i^A>, |\varphi_j^B>\}$ in block matrix form as [3]:

$$H = \begin{pmatrix} E_A & S_{A,B} \\ S_{A,B}^\dagger & E_B \end{pmatrix} \quad (3)$$

Where The diagonal block are the in-site energies matrix and the off diagonal describe the interaction between the corresponding atomic orbital on different sites. The latter interaction is referred to the electron transport propriety in the bulk, conventionally it is named the hopping parameters. In our frame work we will work with 8 by 8 Matrices, because the basis $\{s^A, \{p^A\}\} \times \{s^B, \{p^B\}\}$, and as rule of thumb $Dim(H) = N_{atoms}(per\ cell) \times N_{orbitals}(per\ site)$.

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[1] $\hat{P}$ is the kinetic energy, and $\hat{V}$ is the potential due to the crystal (Assumed to be periodic).

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[2] The sub-index i and j are referring to the atomic orbital on each jth and i^{th} sites respectively.

[3] $<\Psi_i|\hat{H}|\Psi_j> \approx <\Psi_i|\hat{V}|\Psi_j>$

After setting up the matrix we search for the eigenvalues straight forward by diagonalize the Hamiltonian for which the block matrix are given by the following:

$$E_\alpha = \begin{pmatrix} E_S^\alpha & 0 & 0 & 0 \\ 0 & E_{Px}^\alpha & 0 & 0 \\ 0 & 0 & E_{Py}^\alpha & 0 \\ 0 & 0 & 0 & E_{Pz}^\alpha \end{pmatrix} \; ; \; S_{AB} = \begin{pmatrix} A<S|V|S>_B \times g_0 & A<S|V|P_x>_B \times g_1 & A<S|V|P_y>_B \times g_2 & A<S|V|P_z>_B \times g_3 \\ A<P_x|V|S>_B \times g_1 & A<P_x|V|P_x>_B \times g_0 & A<P_x|V|P_y>_B \times g_3 & A<P_x|V|P_z>_B \times g_2 \\ A<P_y|V|S>_B \times g_2 & A<P_y|V|P_x>_B \times g_3 & A<P_y|V|P_y>_B \times g_0 & A<P_y|V|P_z>_B \times g_1 \\ A<P_z|V|S>_B \times g_3 & A<P_z|V|P_x>_B \times g_2 & A<P_z|V|P_y>_B \times g_1 & A<P_z|V|P_z>_B \times g_0 \end{pmatrix} \quad (4)$$

Where α being A or B, and the g_i's [4] functions that popped up due to the exponential factor originated from the Blöch Theorem, are holding the information that describe how the current atomic orbital interacting with the nearest neighbors(see Appendix[X]).

IV. BAND STRUCTURE

In this section we shall present two basic example. The first one is the linear atomic chain, then we move to the Graphene.
The following figure represent the dispersion relationship of the energy and the wave vector for 1D mono-atomic system with cell parameter of **a** and an s state on each site.
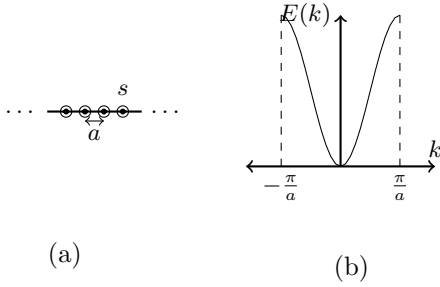

(a)

(b)

FIG. 1: (a): 1D LAC Model, (b): the corresponding Band structure.

Moreover, working on an augmented 3D space make us in the simplest model of a crystal with just two s and p states per site will be more further step a head to describe the bulk material (Fig.2). Despite the fact that the latter one, does not provide better vision for the 3D case, We can deduce for instance the effective mass, and for example it is found to be $\hbar^2/(2V_{ss\sigma})$ for the s band at the $\Gamma(0,0,0)$ point[5],and beside that we observe an important band gap which is not so bad for our simple model.

[4] $g_i = \sum_n sign \times \exp[i\overrightarrow{K}\overrightarrow{R}_n]$
$sign = \begin{cases} 1 & \text{For positive overlap between the O.A} \\ -1 & \text{else} \end{cases}$
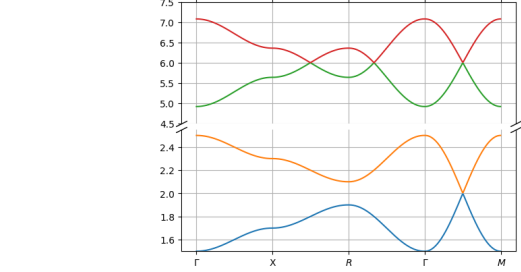[5] The cell parameter is taken to be 1 $a.u.$

FIG. 2: Band Structure of 3D mono-atomic bulk simple cubic with an s and p_z states on each sites ($E_s = 6eV, E_p = 2eV, V_{ss\sigma} = 0.3eV, V_{pp\sigma} = 0.3eV, V_{pp\pi} = 0.05eV$ and V_{ss} not considered [3]).

When it comes to Tight Binding method it is almost mandatory to mention the Graphene and to discuss it's bands structure behaviors. A simple 2D description is the one given by the following expression:

$$E_\pm(k) = \frac{E_p \pm \gamma|\sum \exp(-i\overrightarrow{K}\overrightarrow{R})|}{1 \mp \sigma|\sum \exp(-i\overrightarrow{K}\overrightarrow{R})|} \quad (5)$$

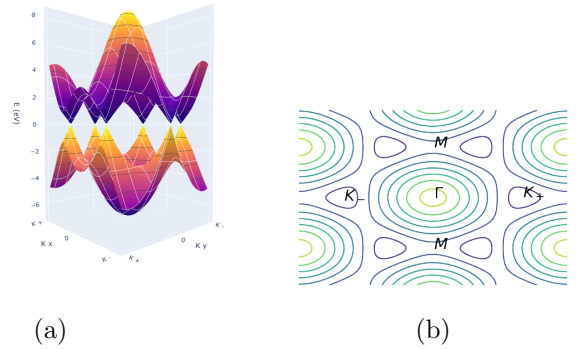Where γ and σ stand for the hopping and the overlap parameters respectively.

(a)

(b)

FIG. 3: (a): 2D Energy dispersion of the Graphene ($\gamma = 1.7eV$ & $\sigma = 0.13$), (b): top view of the iso-energy contour ($\gamma = 3eV$ & $\sigma = 0.13$), for the parameters see [1].

The most interesting behavior of the Graphene is hap-

pen to be around the K's valleys where the carriers appears as they where without a mass.

V. RESULTS FOR C, SI AND GE - BAND STRUCTURE-

In this stage we present The band structure according to famous paper of Chadi and Cohen [2]. As we mentioned earlier for each compound that we are interested in it suffice to introduce as a minimum the family of the p orbitals beside the s one, which yield to an 8 by 8 matrix to be diagonalized according to our interest in this paper.
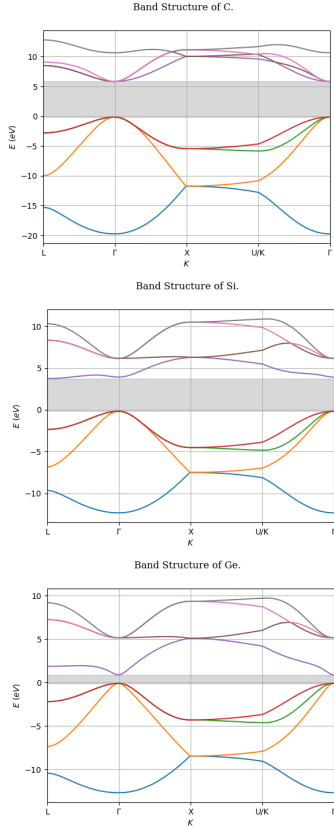

FIG. 4: Band structure of C, Si and Ge from top to bottom respectively.

The figures above shows different band gap in descending order from C to Ge (the width of the shaded area):

TABLE I: Calculated Band gap using Tight Binding Method.

Elements	C	Si	Ge
Band Gap (eV)	6.0	3.92	0.99

The mentioned values are highly influenced by any slightly change in the fitted parameters, and according to *Chadi and Cohen* the main in site energy for the s orbital and the p one, can be chosen as the following [2]:

TABLE II: Calculated Band gap using Tight Binding Method.

Elements	C	Si	Ge
$E_p - E_s$ (eV)	7.4	7.20	8.41

Without neglecting the fact that the results are well behaved, we can not turn our back to the reality that our result does not describe which kind of the Band Gap (i.e Direct or indirect) we are dealing with. So far a more suitable solution for this situation is to add more orbital that are higher energetically, in our case we joined $\{s_A^*, s_B^*\}$ to the old set of basis.
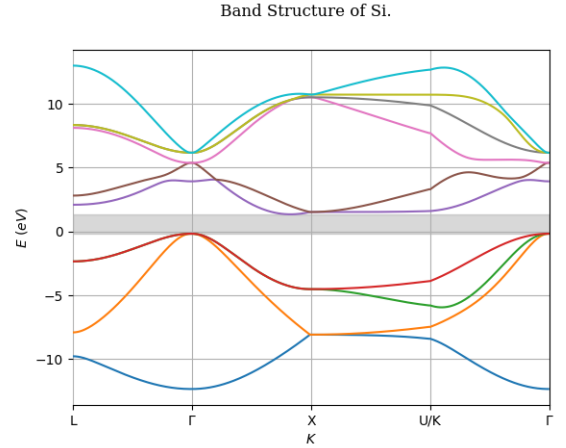

FIG. 5: Bands Structure of Silicon after the inclusion of higher atomic orbital ($s*$).

In addition to the new advantage, we were able also to get more accurate, where we estimate a new Band Gap for the Silicon: 1.52 eV.
Getting to now our band structure is the first step to exploit the characteristics of our compound. In the following, we will describe briefly, one of the most used method to evaluate the density of state.

VI. LINEAR TETRAHEDRON METHOD

In solid state physics to evaluate most physical quantities it is mandatory to pass throw the next famous integral[4]:

$$I = \int \frac{dS}{|\overrightarrow{\nabla}\mathcal{E}(k)|} \qquad (6)$$

And for the sake of simplicity we assume that our system undergo very low temperature (T = 0 K) [6], which

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[6] Fermi distribution is a unitary within an energy less than the Fermi level.

lead to more simplification of the density of state. A further explanation, of the idea behind the LTM is to bring the problem to Brillouin Zone, and in order to evaluate the quantity I we like two break the Brillouin zone into small irreducible Tetrahedron. Furthermore, in the case of Cubic system we get six Tetrahedrons(for more details about LTM see Appendix XI). Thus we can write:

$$D(\mathcal{E}) \propto \frac{V_T}{V_B} \sum_i^6 \int_{V_{T_i}} \frac{dS}{|\overrightarrow{\nabla}\mathcal{E}(k)|} \qquad (7)$$

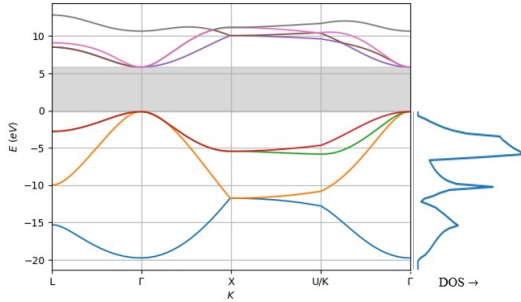The next figure stand as a proof for the validity of the LTM.

FIG. 6: Band structure of C with the corresponding density of state in the vicinity of valence bands.

This is also in good agreements with *Chadi and Cohen* paper[2].

VII.   DISCUSSION

It appears that for better emulation of the compound we need more Atomic Orbital to describe it behaviours, which lead to higher dimension of the Hamiltonian to be diagonalized, therefore, an intensive computation calculus is needed.

This point leave us with a choice of time cost over precision, this remark is well descried for the case of DOS calculation where we want to see the effect of the resolution of the Tetrahedrons mesh grid(i.e: The process of dividing the tetrahedron volume to more small one), so the following Figure compare between the mesh grid of 35 vs the first 100 Tetrahedrons for Ge. Note that the 35 Tetrahedrons were extracted from [5], and for the other 100 Tetrahedrons we just truncate our data to 100 for the sake of comparison.
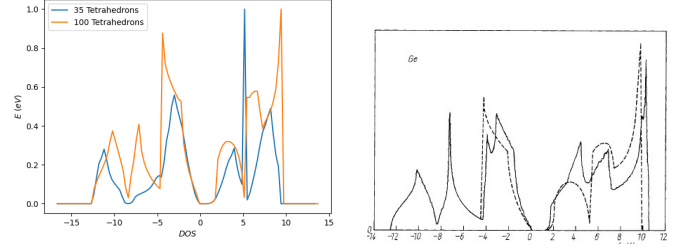

FIG. 7: The density of states (in arbitrary units and normalized) of Ge (a): Comparison between 35 and 100 Tetrahedron accuracy, along (b): The DOS from *Chadi and Cohen* work [2] with and without second-nearestneighbor interaction (- - - Nearest-neighbor interaction, ___ second-nearest-neighbor interaction).

VIII.   CONCLUSION

In this work we shows how we can go from one dimensional system and keeping upgrade it until we achieve sufficient amount of modifications, that helped to describe in more realistic way our compound. As a results, Tight Binding Method is a fundamental brick in the Theory of electronic structure. And the more we take care of small details, the more accuracy we get.

IX.   ACKNOWLEDGEMENTS

X. APPENDIX.I

Calculating $_A<P_x|V|S>_B\equiv<\Psi_A^{P_x}|V|\Psi_B^S>$:

$$_A<P_x|V|S>_B=\frac{1}{N}\sum_j^N e^{-i\overrightarrow{k}\overrightarrow{R_{Aj}}}\sum_j^N e^{i\overrightarrow{k}\overrightarrow{R_{Bj}}}<\varphi_A^{P_x}|V|\varphi_B^S>$$

Now we will fix our origin at site A ($\overrightarrow{R_{Aj}}=\overrightarrow{0}$) therefore:

$$_A<P_x|V|S>_B=\sum_j^N e^{i\overrightarrow{k}\overrightarrow{R_j}}<\varphi_A^{P_x}|V|\varphi_B^S>$$

As we are interested to study the physics of the first neighbors and due to the structure of the crystal we are interested in (Diamond structure), therefore four neighboring atoms siting at: $R_1 = a/4(1,1,1); R_2 = a/4(-1,-1,1); R_3 = a/4(-1,1,-1); and R_4 = a/4(1,-1,-1)$ will be the main character that act on the g's function.

$$_A<P_x|V|S>_B=\left(e^{i\overrightarrow{k}\overrightarrow{R_1}}-e^{i\overrightarrow{k}\overrightarrow{R_2}}-e^{i\overrightarrow{k}\overrightarrow{R_3}}+e^{i\overrightarrow{k}\overrightarrow{R_4}}\right)<\varphi_A^{P_x}|V|\varphi_B^S>$$

Which can be writing as:

$$_A<P_x|V|S>_B=V_{sp\sigma}\times g_1$$

Where:

$$\begin{cases} V_{ss\sigma}=<\varphi_A^{P_x}|V|\varphi_B^S> \\ g_1=e^{i\overrightarrow{k}\overrightarrow{R_1}}-e^{i\overrightarrow{k}\overrightarrow{R_2}}-e^{i\overrightarrow{k}\overrightarrow{R_3}}+e^{i\overrightarrow{k}\overrightarrow{R_4}} \end{cases}$$

Note: The calculus is the same, and once we take care of the sign ($\pm$) that comes from the interaction between the atomic orbital, the full Hamiltonian is just a matter of tedious work.

XI. APPENDIX.II

Why the term of **Linear**?

A better way to answer this question is a better visualization of our situation, and we need to understand how the LTM work. The following Figure [8] depict a cross section of Fermi sphere with our irreducible Tetrahedron.

It is obvious that we interpolate the intersection into plan (3D), thus gives us the ability to rewrite the energies as:

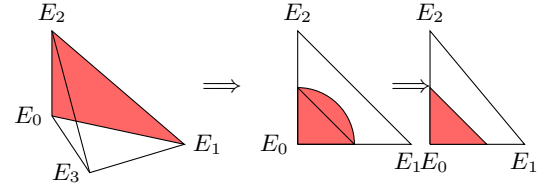$$\mathcal{E}-\mathcal{E}_i=\mathcal{E}_i-\mathcal{E}_0+b.k_i$$

FIG. 8: Visualization of the Linear approach of LTM.

Where b is a bias given by : $\sum_i(\mathcal{E}-\mathcal{E}_0).r_i$, and k is the wave vector labeling the corners of the Tetrahedron which related to r by: $k_j.r_i=\delta_{ij}$. Note that it is equivalent to label by energies or wave vectors. and we should sort the eigenvalues in ascending order. So far we get the following cases:

$$D(\mathcal{E})\propto\frac{V_T}{V_B}\begin{cases} 3\frac{(\mathcal{E}-E_0)^2}{E_{10}\times E_{20}\times E_{30}} & E_0<\mathcal{E}<E_1 \\ \frac{1}{E_{20}\times E_{30}}[3\times E_{10}+6(\mathcal{E}-E_1) & E_1<\mathcal{E}<E_2 \\ -3\frac{(E_{20}+E_{31})\times(\mathcal{E}-E_1)^2}{(E_{21}\times E_{31})}] \\ 3\frac{E_3-(\mathcal{E})^2}{E_{30}\times E_{31}\times E_{32}} & E_2<\mathcal{E}<E_3 \end{cases}$$

Where $E_{ij}=E_i-E_j$ and if $\mathcal{E}<E_0$ or $\mathcal{E}>E_3$ then $D(\mathcal{E})=0$.

[1] Pierre E Allain and Jean-Noel Fuchs. Klein tunneling in graphene: optics with massless electrons. *The European Physical Journal B*, 83(3):301–317, 2011.

[2] DJ Chadi and Marvin L Cohen. Tight-binding calculations of the valence bands of diamond and zincblende crystals. 1974.

[3] Debdeep Jena. *Quantum Physics of Semiconductor Materials and Devices*. Oxford University Press, 2022.

[4] G Lehmann and M Taut. On the numerical calculation of the density of states and related properties. *physica status solidi (b)*, 54(2):469–477, 1972.

[5] AH MacDonald, SH Vosko, and PT Coleridge. Extensions of the tetrahedron method for evaluating spectral properties of solids. *Journal of Physics C: Solid State Physics*, 12(15):2991, 1979.

[6] P Vogl, Harold P Hjalmarson, and John D Dow. A semi-empirical tight-binding theory of the electronic structure of semiconductors. *Journal of physics and chemistry of solids*, 44(5):365–378, 1983.