Electronic Properties in Single-Orbital Crystalline System Using Tight-Binding Approximation

Qusiy H. Al-Galiby* and Sarah Shabeeb Dakhil
Department of Physics, College of Education, University of Al-Qadisiyah, Iraq.
*E-mail: qusiy.algaliby@qu.edu.iq and qusiyalgaliby@gmail.com

Abstract. Using quantum theory (QT) combined with Tight-binding Approximation (TBA), we studied the electronic properties for single-orbital one dimensional, two-dimensional and diatomic crystalline chain to get simply qualitative understanding of electronic structure calculation in the periodic systems. Density of states (DOS) is one of the electrical properties that we try to understand within the band structures that lead to be able to know the mechanism of transport in the materials. The band structure and density of state (DOS) for both cases were calculated by using FORTRAN code. The calculation of DOS for ordered and disordered systems were performed via a numerical decimation method.

1. Introduction
Understanding of electronic structure for materials have supported qualitatively the efforts to control on properties of these materials such as electron transport and band gap [1]. Those have motivated recently the idea of using single electronic molecules in a wide range of applications in the field of molecular electronics devices [2-9]. As a part of electronic chip, designing a periodic electronic transmission medium is needed, in which an electron pass freely through it into a single molecule (scattering region) [10-13]. The crystalline conductor materials represent a periodic infinite system and act as an electrodes, where electrons transmit without any scattering with a perfect waveguides [14-16].

The goal is to understand the electronic properties for nanogap crystalline system by simplifying this system to the crystalline atomic chain, where every single orbital atom is identical and one electron placed into this orbital. In what follow, we shall demonstrate the perfect crystal, which is an infinite atomic chain in one and two dimensional crystalline chain as shown in Figures 1 and 2.

2. Theoretical approaches
We use quantum theory to describe the evolution of the physical characterization of a system in only position. The time independent Schrodinger equation includes the Hamiltonian operator which characterizes the total energy of any given wave function. In what follow, we suggest the following Tight-binding models:
2.1. Simple problem—one dimensional infinite chain

In Figure 1, we introduce one-dimensional perfect chain hydrogen atoms with simple tight-binding description to get qualitative understanding of electronic structure calculation in periodic systems, where \( \varepsilon_o \) and \( \beta \) are the site and hopping energies respectively. First, we start with the time independent Schrodinger equation to recognize the physical characterisation for this model:

\[
\mathbf{H} |\psi\rangle = E |\psi\rangle
\]

(1)

where \( \mathbf{H} \) is the Hamiltonian that characterizes the total energy of any given wave function. The \( |\psi\rangle \) can be represented as an infinite column of eigenvector containing all the wave function amplitudes \( |\psi_m|^2 = \psi^\ast \psi \), which mentions to the probability of finding the electron on site \( m \). Whereas \( E \) is the real eigenvalues.

\[
|\psi\rangle = \begin{pmatrix} -\infty \\ \vdots \\ \psi_{m-2} \\ \psi_{m-1} \\ \psi_m \\ \psi_{m+1} \\ \psi_{m+2} \\ \vdots \\ \infty \end{pmatrix}
\]

(2)

To generate a Hamiltonian for the system such as in Figure 1, we use the tight-binding approach, in which of simplify only the case of the nearest neighbor interactions. The Schrodinger equation includes the Hamiltonian \( \mathbf{H} \) as attempt to describe the properties of the quantum strip for the perfect chain that is of infinite length in the dimension of current flow, where the units are linked together in the periodic direction (such as in \( z \) direction). This model represents a structure that involves large number of mesoscopic solid state atoms. This is exactly applied in study of realistic super cell in one, two and three dimensional crystalline systems like ribbon or sheet of the graphene and bulk of the gold as shown in Figures 2a and 2b.
Figure 2. The models of optimized geometries for two dimensional graphene sheet (the left) and three dimensional nanogap gold (the right).

By substituting the Hamiltonian $H$ and the wave function $|\psi\rangle$ (2) over a range of sites $m$ into Schrodinger equation (1), we obtain an infinite of linear equations and end to produce the most general equation for one dimensional crystalline chain for row $m$ of $H$:

$$
\begin{pmatrix}
\varepsilon_0 & -\beta & 0 & 0 & 0 & \cdots \\
-\gamma & \varepsilon_0 & -\beta & 0 & 0 & \cdots \\
0 & -\gamma & \varepsilon_0 & -\beta & 0 & \cdots \\
0 & 0 & -\gamma & \varepsilon_0 & -\beta & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
\psi_{m-2} \\
\psi_{m-1} \\
\psi_m \\
\psi_{m+1} \\
\psi_{m+2} \\
\vdots
\end{pmatrix} = E
\begin{pmatrix}
\psi_{m-2} \\
\psi_{m-1} \\
\psi_m \\
\psi_{m+1} \\
\psi_{m+2} \\
\vdots
\end{pmatrix}
$$

(3)

By substituting the Hamiltonian $H$ and the wave function $|\psi\rangle$ (2) over a range of sites $m$ into Schrodinger equation (1), we obtain an infinite of linear equations and end to produce the most general equation for one dimensional crystalline chain for row $m$ of $H$:

$$
\varepsilon_0 \psi_m - \beta \psi_{m-1} - \beta \psi_{m+1} = E \psi_m
$$

(4)

The equation (3.2) is satisfied for all $m$ go to $\pm \infty$, and we can write (4) as :

$$
\psi_{m+1} = \left(\frac{\varepsilon_0 - E}{\gamma}\right) \psi_m - \psi_{m-1}
$$

(5)

This is called Recurrent Relation.

To calculate the dispersion relation for this system $E$, we use Block’s theorem and by substituting $\psi_m = A e^{i k m}$ into equation (4) we get:

$$
E(k) = \varepsilon_0 - 2 \beta \cos k
$$

(6)

Where

$$
k = \frac{n \pi}{N + 1}
$$

(7)

The spectrum of an infinite system is continuous. Where $E$ as a function of $k$, and the bandwidth is directly proportional to the hopping integral, where $BW = 4 \beta$.

2.2. Density of states (DOS)

Density of state is one of the physical quantities that is of great interest in Condensed Matter Physics [1, 4], that is described by analytical and numerical methods. Using differential equations (6) and (7) with (k) and (n) respectively, we calculate the analytical Formula for DOS:
\[ D(E) = \frac{dn}{dE} = \frac{dn}{dk} \frac{dk}{dE} = \frac{1}{\pi} \frac{1}{\sqrt{4\beta^2 - (\varepsilon_0 - E)^2}} \]  
\[ D(E) = \frac{dn}{dE} = \frac{1}{\pi} \frac{1}{\sqrt{4\beta^2 - (\varepsilon_0 - E)^2}} \]  

Where \( dn \) is the number of eigenvalues in an interval of \( k \). \( D(E) \) is the density of state which is defined that the number of eigenvalues per unit energy, this is only correct if the energy lies within the energy band:

\[ \varepsilon_0 - 2\beta < E < \varepsilon_0 + 2\beta \]

But when the energy lies outside these ranges then the energy band will be zero and then the DOS will be zero as well.

The density of state is proportional to the number of atoms, and also it is always going to proportional to \( \frac{dk}{dE} \)

\[ D(E) \propto \frac{1}{\pi} \frac{1}{\sqrt{4\beta^2 - (\varepsilon_0 - E)^2}} \]  

\[ 9 \]

2.2.1 Decimation method

To understand the electronic properties such as density of state, we use a numerical decimation technique [10]. This numerical method shows how to simplify a large complicated Hamiltonian (ordered or disordered system) to compute the electronic properties like density of state DOS.

\[ \begin{pmatrix} H_{10} & H_{11} & H_{12} & \cdots & H_{1N} \\ H_{10} & H_{20} & H_{21} & \cdots & H_{2N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H_{10} & H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \]

\[ H_{ij} = \begin{pmatrix} H_{ij} & \cdots & \cdots & H_{iN} \\ \vdots & \ddots & \vdots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ H_{1i} & \cdots & \cdots & H_{NN} \end{pmatrix} \]

\[ H_{ij} \sim H_{ij} + \begin{pmatrix} H_{in} \end{pmatrix} \]

The equation 11 represents the general formula to eliminate a limited system for \( N \) atoms such as in Figure 3. The new Hamiltonian \( H_{ij} \) depends on the number of eigenvalues \( E \) and the wave
vectors $\varphi_j$ and $\varphi_i$ do not effect. The critical point is, all properties of this lattice are preserved when we make a mathematical transformation.

2.3 Band structure for two dimensional single orbital chains

We demonstrate two dimensional square lattice for the crystalline system as shown in Figure 4, where each atom has been labelled on X and Y coordinates where $l$ and $j$ has assumed as a pair coordinates of the position for atoms.

![Figure 4](image_url)

**Figure 4.** illustrates two dimensional square lattice for the crystalline system.

That means we have got atom numbers $(l,j)$, $(l+1,j)$, $(l-1,j)$, $(l,j+1)$, and $(l,j-1)$ respectively. The slope is $\frac{dE}{dk} = 0$, that means DOS goes to the infinite in the edges for energy band of crystals which are $E_{\text{max}} = \varepsilon_o + 2\gamma$ and $E_{\text{min}} = \varepsilon_o - 2\gamma$ this is called a Van Hove singularity in the DOS, which is often referred to as critical points of the Brillouin zone [4]. According to equation (12), we get the general solution of Schrodinger equation for periodic system, which is satisfied on all atoms that located to $j$ and $l$.

$$\varepsilon_o \psi_{l,j} - \gamma \psi_{l+1,j} - \gamma \psi_{l-1,j} - \gamma \psi_{l,j+1} - \gamma \psi_{l,j-1} = E \psi_{l,j} \quad (12)$$

That is the Schrodinger equation in two dimension (2-D), and each atom has got four neighbours, and then the final formula to compute the band structure for (2-D) lattice for single orbital is given by:

$$E = \varepsilon_o - 2\gamma (\cos k_x + \cos k_y) \quad (13)$$

2.4 One Dimensional (1-D) Diatomic Crystalline chain

The band structure for diatomic chain has been introduced as shown in Figure 5. The situation for this system is in which all of atoms we connected to each other and each unit cell in this lattice involves two atoms are $\varepsilon_a$ and $\varepsilon_b$ leading to two independent chain.
Figure 5. shows the band structure for diatomic chain.

We derived the analytical formula for band structure of diatomic chain by using Block’s theorem and Schrödinger equation and the final formula that we got is given by:

\[ E_{\pm}(k) = \varepsilon_a + \varepsilon_b - 2(\gamma_a - \gamma_b) \cos k - 2(\gamma_a - \gamma_b) \cos \frac{k}{2} \sqrt{\left(\varepsilon_a - \varepsilon_b - 2(\gamma_a - \gamma_b) \cos k\right)^2 + \beta_1^2 + \beta_2^2 + 2a(\beta_1 + \beta_2) \cos k + 2\beta_1 \beta_2 \cos 2k} \]  

(14)

3. Results and discussion

We used FORTRAN and MATLAB codes to calculate the electronic properties for the suggested models. We summarize the electronic properties calculations and the results show the density of states calculation in different ways. In Figure 6 there is some correspondence between analytical (equation 8) and a numerical method for crystalline system, where Van-Hove singularity feature appears in both cases and also life shift tails of distribution for density of states graphs extend on both sides when the system is disordered and that depends on the degrees of disorder (w = 2, 3, 6 and 8), which reflect the shape of bands in material.

Figure 6. shows the density of state for disordered system by using a numerical decimation method according to different disordered degrees in the following cases: crystalline numerically (pink color), w=3(blue), w=2(green), w=6(red), w=8(yellow), and analytically crystalline (black).
Using the FORTRAN and gnuplot programs, we calculated the band structure for (2-D) single orbital chain:

Figure 7. shows the band structure of (2-D) single atomic chain, where the contour surface involves the circles color. Green is $E = 2$, red is $E = -2$, and blue is $E = 0$ for the parameters: $\epsilon_0 = 0.0$. $\gamma = 1.0$, whilst $K_x = \frac{2n\pi}{N}$ and $K_y = \frac{2n\pi}{N}$ are between $-2\pi$ and $2\pi$.

From Figure 7 the contour surface involves the circles color, green is $E_{max} = \epsilon_0 + 4\gamma$, red is $E_{min} = \epsilon_0 - 4\gamma$, and blue is $E = 0$ where $\epsilon_0 = 0.0$. $\gamma = 1.0$, whereas $K_x$ and $K_y$ are between $-\pi$ and $\pi$. Therefore the bandwidth is $8\gamma$.

Figure 8. demonstrates the contour surface for (2-D) single atom where $K_x = \frac{2n\pi}{N}$ and $K_y = \frac{2n\pi}{N}$.
Figure 9. demonstrates the band structure for (2-D) single atom where $K_x = \frac{n\pi}{N}$ and $K_y = \frac{n\pi}{N}$.

Figure 10. demonstrates the contour surface for (2-D) single atom where $K_x = \frac{n\pi}{N}$ and $K_y = \frac{n\pi}{N}$.

Figure 11. shows the surface of constant energy according to equation 13, where $k_x$ and $k_y$ are small the circle all points which $k_x^2 + k_y^2$ is equal to constant have the same energy.

Figure 11 shows the Fermi Circle when the contour of the constant energy equal to Fermi energy $E = E_F$. In addition to that we expect the bandwidth will be $8\gamma$, for (2-D) chain, $k$ is going to be $k_x$ and $k_y$ so first and second Brillouin zone will appear as shown in Figure 10. Whereas Figure 11 illustrates the Fermi Circle when the contour of the constant energy equal to Fermi energy $E = E_F$. It is clear that
this \( k \) in two dimensions (2-D) lies along the direction of chain \( x \) and \( y \) to be \( k_x \) and \( k_y \) as shown in Figures (10 and 11), and then we can plot as contours, because these countors for two dimensions lattice are only line dimension \( k_x \) and \( k_y \) against the energy \( E_k \) as shown in Figure (10), that means we have three dimensions axes to make plot between them, and the contours might be the surface in the constant energy in (2-D), this surface might be corresponding to circle. If we choose the energy surface equal to the Fermi energy (for instance \( E_F = 3 \cdot 9 \text{ eV} \)), then that is called the Fermi Surface. It is the contour of constant energy that correspondence to the Fermi energy, and also the circle is called the Fermi Circle when the contour of the constant energy equal to Fermi energy \( E = E_F \), as shown in Figure 11. The energy circle does not involve radius, but it depends on the precise dispersion relation \( E_k \). From equation (13) where \( E_k \) is dispersion relation that is only dependent on the magnitude of \( k \), if \( k_x \) and \( k_y \) are small then that is approximately according to expansion Taylor would be:

\[
\cos k_x \approx 1 - \frac{k_x^2}{2} \quad \text{and} \quad \cos k_y \approx 1 - \frac{k_y^2}{2} \\
E_k = \varepsilon_o - 2\gamma \left( 1 - \frac{k_x^2}{2} + 1 - \frac{k_y^2}{2} \right)
\]

\[
E_k = \varepsilon_o - 4\gamma + \gamma(k_x^2 + k_y^2)
\] (15)

The equation (14) describes the circle of all points, where \( k_x^2 + k_y^2 \) is equal to constant possesses the same energy.

Using the MATLAB program, we plotted the band structure of one dimensional system that includes the Brillouin zone of diatomic chain, where two different atoms per unit cell leading to two independent chains. We have two energy bands in this system for each \( k \) value, and the system is modelled using different parameters as shown in the Figures 12 and 13. The calculations show that for the selected parameters as the following values: The left are \( \gamma_a = \gamma_b = 0. \varepsilon_a = 1. \varepsilon_b = 2. \alpha = 0 \cdot 08. \beta_1 = \beta_2 = 1. \) Whereas the right are \( \gamma_a = 0 \cdot 06. \gamma_b = 0 \cdot 1. \varepsilon_a = 1. \varepsilon_b = 2. \alpha = 0 \cdot 08. \beta_1 = 0 \cdot 04. \beta_2 = 0 \cdot 03. \) The left panel shows the band structure for crystalline lattice, where each unit cell contains two atoms arrange themselves in regular patterns on this lattice in one dimensional direction. The pink and blue lines are crossed, that means there is no energy gap and the electron can move freely through this lattices. On the other hand, the right panel shows that the two lines appear separated that means there is a gap.

![Figure 12](image_url)  
*Figure 12.* The calculation of band structure \( E(k) \) for diatomic chain. The parameters introduce as the following values: The left are \( \gamma_a = \gamma_b = 0. \varepsilon_a = 1. \varepsilon_b = 2. \alpha = 0 \cdot 08. \beta_1 = \beta_2 = 1. \) Whereas the right are \( \gamma_a = 0 \cdot 06. \gamma_b = 0 \cdot 1. \varepsilon_a = 1. \varepsilon_b = 2. \alpha = 0 \cdot 08. \beta_1 = 0 \cdot 04. \beta_2 = 0 \cdot 03. \)
The parameters of the equation 14, which are $\gamma_a, \gamma_b, \varepsilon_a, \varepsilon_b, \alpha, \beta_1, \beta_2$ and the wave vector $k$, giving different forms of the band cross and energy gap. This attributed to change in the bond and on-site energies along the diatomic chain. We expect that the electron can move only on the site of atoms for perfect system and it may hop to the nearest neighbor site due to quantum tunneling.

![Graph](image)

**Figure 13.** The calculation of band structure $E(k)$ for diatomic chain. The parameters introduce as the following values: The left are $\gamma_a = \gamma_b = 0, \varepsilon_a = \varepsilon_b = 1$. $\alpha = 0, \beta_1 = \beta_2 = 1$. Whereas The right are $\gamma_a = \gamma_b = 0, \varepsilon_a = 1, \varepsilon_b = 2$. $\alpha = 0.08, \beta_1 = \beta_2 = 1$.

4. Conclusion

To conclude, we investigated the electronic properties for some quantum models which are the basic one and two dimensional chains. The calculations of most relevant properties of electron transport in molecular systems such as the energy bands and density of states were implemented by using quantum theory (QT) combined with Tight-binding approach. The simple tight binding Hamiltonians and decimation method were introduced using the FORTAN and MATLAB programs. Both appeared powerful techniques to get simply qualitative understanding of electronic structure calculation in the crystalline systems.

Acknowledgement

The authors would like to thank Professor Colin J. Lambert from Lancaster University, UK for his supporting. Also we want to thank the Ministry of Higher Education and Scientific Research- University of Al-Qadisiyah, Iraq.

References

[1] Sutton, Adrian P. Clarendon Press, 1993.
[2] Leary, Edmund, et al. *Journal of the American Chemical Society* 140.2 (2018): 710-718.
[3] Famili, Marjan, et al. *Advanced Functional Materials* 28.15 (2018): 1703135.
[4] Noori, Mohammed, et al. *Scientific reports* 6 (2016): 37352.
[5] Liu, Longlong, et al. *Nanoscale* 8.30 (2016): 14507-14513.
[6] Algharagholy, Laith, et al. *Journal of Materials Chemistry C* 3.39 (2015): 10273-10276.
[7] Al-Galiby, Qusiy H., et al. *Nanoscale* 9.14 (2017): 4819-4825.
[8] Al-Galiby, Qusiy, et al. Journal of Materials Chemistry C 3.9 (2015): 2101-2106.
[9] Al-Galiby, Qusiy H., et al. Nanoscale 8.4 (2016): 2428-2433.
[10] Lambert, C. J. Chemical Society Reviews 44.4 (2015): 875-888.
[11] Al-Galiby, Qusiy, and Colin Lambert. Diss. Lancaster University, 2016.
[12] Song, Hyunwook, Mark A. Reed, and Takhee Lee. Advanced Materials 23.14 (2011): 1583-1608.
[13] Sadeghi, Hatef. arXiv preprint arXiv:1607.02484 (2016).
[14] Kato, Takashi, Norihiro Mizoshita, and Kenji Kishimoto. Angewandte Chemie International Edition 45.1 (2006): 38-68.
[15] Batail, Patrick. (2004): 4887-4890.
[16] Sutton, Adrian P., et al. Journal of Physics C: Solid State Physics 21.1 (1988): 35.
[17] Leadbeater, M. and C. Lambert,. Annalen der Physik, 1998. 7(5-6): p. 498-502.
[18] C. Kittel, John Wdey & Sons, Inc. (New York), 1986.
[19] L. Van Hove, Phys. Rev. 89, 1189–1193 (1953).