OLIFE: Tight Binding Code for Transmission Coefficient Calculation

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Abstract A new and human-friendly transport calculation code has been developed. It requires a simple tight binding Hamiltonian as the only input file and uses a convenient graphical user interface to control calculations. The effect of magnetic field on the molecular junction has also been included. Furthermore the transmission coefficient can be calculated between any two points on the scatterer which ensures high flexibility to check the system. Therefore Olife can highly be recommended as an essential tool for pretesting, studying, and teaching electron transport in molecular devices that saves a lot of time and efforts.

1 Introduction
Molecular electronics field has enthused scientists worldwide for its spectacular features[1-3] such as high speed nanoscale junctions[4- 5] and the economical usage of power and resources[6]. Because of the nano-dimensions, quantum phenomena such as quantum tunneling [7-8] and quantum interference (QI)[9-11] are clearly revealed[12]. Therefore theoretical methods have continuously been developed to explain these phenomena [13 14] as well as the experimental techniques which eagerly seek to harness them [15]. However due to the complexity of the molecular structure[16, 17], junction design or both[18] the task has become far more intricate. Thus, theoreticians are working hard to analyse and investigate molecular behaviours[19, 20]. As a result, issues like the convenience[21] and efficiency of choosing a particular method for modelling and grasping signatures are the major difficulties theoreticians would definitely encounter[20-22]. Therefore these two problems will be closely examined in this paper.

The first problem we are aiming to discuss is the ability to easily simulate molecular structures and understanding electronic behaviours. Initially this issue stems basically from the intrinsic complexity of the molecule configuration [23-25]. For example porphyrin wheel is a single unit composed of an outer ring and inner spokes. The outer ring has six porphyrin molecules attached to each other by alkene chains on the circumference while the inner spokes consist of thirteen benzene molecules at the wheel.
Therefore overcoming this problem requires theoretical methods capable of envisaging the main features of the molecule without considering their very elementary details. The approach that successfully ignores details but yet preserves the principle peculiarities is the first order tight binding (TB) approximation. Tight binding approach neglects all interactions except for those between the nearest neighbours\cite{27,28}. Furthermore its validity has successfully approved through the impressive success\cite{29} to capture the main features reflected in the transmission curve of the system\cite{30} as it can be seen in the increased number of literature using this method\cite{31-33).

The second obstacle is how convenient is to apply theoretical approaches. Results such as the transport coefficient calculation cannot be deduced entirely from TB alone. Therefore theories specialized in describing the ballistic transport through molecules should be combined with TB. Landauer-Büttiker theory is cornerstone approach in the field of molecular electronic transport\cite{34}. They have managed to describe the probability of transferring an electron from one side of the junction to the other side and have also taken into account the effect of the leads on the molecule transmission probability. Based on this theory commercial and academic packages namely Gollum\cite{35} Sméagol\cite{36} and ONETEP\cite{37} have successfully described and calculated the conductance of a single molecule attached to external leads. However these softwares depend on other packages such as SIESTA\cite{38} or Gaussian\cite{39} to establish density functional Hamiltonian. As far as we know all transport codes including Olife need firstly the Hamiltonian of the system and secondly input instructions to derive the code. Although these packages may use simple tight binding Hamiltonian but they require sort of tedious inputs, a long preparation time, and finally their computing time itself can be very stressful especially for large systems in order just to be checked. On the other hand, efforts have been paid to make transmission calculations even simpler to be done and easy to be read. For instance Lambert and coworkers have suggested the Magic Ratio Rule (MRR) theory to compare between the conductance of different branches in hydrocarbon molecules such graphene and benzene\cite{40}. The bottom line is that easy to use numerical methods are crucial to first check the system and then study it with inexpensive time limits.

The main goal of this paper is to give a very easy and effective tool for transmission coefficient calculation. Olife code applies Landauer-Büttiker formalism based on a simple TB Hamiltonian of the system to depict the transmission features. It uses Matlab as programming language and offers a simple graphical user interface to facilitate the procedure of the calculations.

## 2 Methodology

In Olife, the transmission coefficient of the molecules is restricted to be calculated through two leads only. The reason for this restriction is that the majority of experimental methods use two leads to measure the molecular conductance, for instance, the mechanical break junction (MBJ)\cite{41} technique and scanning electron microscope (STM)\cite{42}. However this temporary limitation is partially compensated by the merit that conductance can be calculated between any two points in the molecule which allows for high flexibility and practicality for testing the junction. A feature that, firstly, it is totally absent in experiments because they thoroughly depend on statistics for measurements\cite{43 44} and secondly it is time and resources consuming in ab-initio calculations since the best scenario is to do the calculation via a linear scaling codes like SIESTA\cite{45}. Therefore, Olife can be considered an indispensable tool for pre-testing the transmission behaviour of systems.

In this work and in order to calculate the transmission, the junction is divided into two parts as shown in 'Figure 1'. The first part is the external part which includes all leads and the second part namely the internal refers to the isolated molecule. These two parts can be combined together using Dyson’s equation\cite{46}:

$$\left( g(E)^{-1} - H \right) G(E) = I,$$

(1)
where $E$ is the energy, $g(E)$ is the Green's functions of the separated parts of the junction, $H$ is the connection Hamiltonian between the isolated molecule and leads, $G(E)$ is the total Green's function, and $I$ is the identity matrix. The definitions of each part of Eq (1) are shown below

\[
\frac{1}{g(E)} = \begin{pmatrix}
g_{a}^{-1} & 0 \\
0 & g_{b}^{-1}
\end{pmatrix} = \begin{pmatrix}
g_{a}^{-1} & 0 \\
0 & g_{b}^{-1}
\end{pmatrix}, \tag{2}
\]

\[
H = \begin{pmatrix}
0 & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
h_{a11} & h_{a22} \\
h_{a12} & h_{a21}
\end{pmatrix}. \tag{3}
\]

\[
G(E) = \begin{pmatrix}
G_{a1,a1} & G_{a1,a2} & G_{a1,b} \\
G_{a2,a1} & G_{a2,a2} & G_{a2,b} \\
G_{b,a1} & G_{b,a2} & G_{b,b}
\end{pmatrix} \tag{4}
\]

\[
g_{Am}(E) = -\frac{e^{i\gamma_{m}(E)}}{\gamma_{m}}, \quad m = 1, 2. \tag{5}
\]

The leads are represented by their surface Green's function $g_{AM}$. The parameters $\gamma_{m}$ and $k_{m}$ are the coupling and wave number in the lead $m$ respectively. The isolated molecule is represented by $g_{B}$ which is given by

\[
g_{B} = \left(E - H_{B}\right)^{-1}, \tag{6}
\]

where $H_{B}$ is the Hamiltonian of the isolated molecule and it is given by

\[
H_{B} = \sum_{n=1}^{N} \varepsilon_{n} |n\rangle \langle n| + \sum_{n=1}^{N-1} \left[h_{n} |n\rangle \langle n+1| + h_{n}^{*} |n+1\rangle \langle n| \right], \tag{7}
\]

\[
h_{n} = \gamma_{n} e^{-i\beta}, \tag{8}
\]

where $\varepsilon_{n}$ is the orbital onsite energy, $n$ is the orbital index, $N$ is the total number of sites, $\gamma_{n}$ is the coupling energy, and $\beta$ is the magnetic flux\cite{47}.

The retarded GF has two travelling waves; one moving to the left side of the scatterer and the other one moving to the right side. The left going waves are related to the reflection amplitudes while the right going waves are related to the transmission amplitude. These amplitudes can be deduced from the matrix elements of the total GF by using Fisher-Lee relation\cite{48,49} which shows that

\[
G_{a,a1} = \frac{1}{i\hbar v} e^{ik}, \tag{9}
\]

\[
G_{a,a} = \frac{1}{i\hbar v} \left( 1 + r \right) \tag{10}
\]

Therefore the transmission coefficient $T(E)$, the reflection coefficient $R(E)$, and finally the conductance $G(E)$ can be calculated from\cite{49}

\[
T(E) = |t'|^{2}, \quad R(E) = |r|^{2}, \tag{11}
\]
where \( r \) is the reflection amplitude and \( a \) and \( a+1 \) are the source point and post-scatterer point respectively. The group velocity is \( v \), the electron charge is \( q \), and \( \hbar (=2\pi/h) \) where \( h \) is Planck’s constant.

3 Olife Prerequisites
The only input file that Olife requires is the Hamiltonian of the system. This Hamiltonian can easily be built by hand for simple molecules or using some other softwares like Microsoft Excel or Matlab for big systems. In the supplementary information, a number of Hamiltonians has been included.

4. Tests and Results

4.1. Basic checks
The first example to test the results of the code is by assuming a perfectly crystalline one dimensional chain. The chain and the leads are all have the same onsite energies (= 0) and coupling elements (= 15) as the first case. The second example represents the same system but with weak coupling between the chain and the leads (equals to one third of the first case). The last scenario is when the coupling between the leads and the chain (molecule) is nullified. The results of the three cases are shown in Figure. These rudimentary examples are crucial to test the code because they clearly show the basic expected results of changing the transmission probability with the coupling between the molecule and the leads. In the first curve the transmission coefficient is equal to one because the system is purely periodic so that the de Broglie wave of the electron would have the same probability everywhere along the system. The third one shows zero \( T(E) \) since the connection between the molecule and the leads is cut, i.e. the electron wave cannot move from one side to the other.

4.2. Quantum interference
The moving de Broglie waves of the electrons in the molecule branches can interact with each other resulting in the so-called quantum interference[50]. To show that our code is able to illustrate quantum interferences, three types of connections of the leads to a single benzene ring have been separately considered. The first connection is the para connection where the two leads make 180 degrees with each other; the second one is the meta when the angle between the leads is 120 degrees; and finally an ortho configuration when the leads confine an angle of 60 degrees[51] as shown in Figure. All onsite energies are nullified. The coupling energies in the leads and benzene ring are equal to -1.5 whereas the coupling between the leads and the molecule was set to -0.5. The transmission curves at the centre of the band show that the para and ortho connections exhibit higher transmission values than meta configuration as shown in the inset of 'Figure'.
4.3. Fano resonance

Fano resonance emerges in the transmission curve when a side group is attached to the main molecule, i.e., a localized state attached to the main continuum states. Fano resonance is very sensitive to any variations in the states of the extra connected molecule which results from changing the structure of the molecule or the surrounding environment[30-52]. Therefore to show that our code is capable of showing such a type of resonance, an extra site has been attached to six-site chain as shown in 'Figure a'. In this example all onsite energies are kept equal to zero and the coupling between the chain and leads is -0.5 which is the same for the coupling between the molecule and the attached unit. In addition, the coupling used for the chain was -1.5 and the values of the onsite of the pendant group are arbitrarily chosen to be -1 and 1.7 to produce distinctive states of Fano resonances. 'Figure b' illustrates the variation of the Fano resonance with change of the onsite energy of the pendant group.
4.4. Magnetic field

Magnetic field is one of the main means to tune electron conductance in molecules [47-53] and understand phenomena like quantum Hall effect and de Haas – van Alphen effect [54]. For these reasons and to ensure a high applicability of Olife, we have included the effect of the magnetic field. The model system used to show the effect of the magnetic field is a benzene ring and the corresponding transmission curves are shown in Figure 4. The parameters used to produce the results in Figure 4 are zero for all onsite energies and -1.5 for all coupling energies except for those between the leads and the benzene which set to -0.5.

4.5. Magic Ratio Rule

A beautiful and simple theory suggested by Lambert and his team is the Magic Ratio Rule (MRR) theory [40 55]. In this theory they have illustrated that constructive and destructive interferences can easily be deduced for graphene-like molecules without resorting to the expensive DFT calculations. The significance behind polycyclic aromatic hydrocarbons (PAHs) is that they represent perfect systems to understand the transport in molecular devices which use graphene as a building unit [40]. The calculations for some results of MRR are illustrated in Figure 4 which shows the transmission coefficient of anthanthrene [40] and pyrene [55] molecules with different connection points. Figure a shows the effect of different connection points on the transmission coefficient of anthanthrene molecule which is schematically shown in Figure b and Figure c. The same procedure is repeated to obtain the results in Figure d which shows the transmission coefficient of pyrene molecule corresponding to the configurations shown in Figure e and Figure f. Our results are in good agreement with the related papers of the molecules. The parameters used in Figure a and Figure d are: all onsite energies are equal to zero, the coupling energies in the leads and molecules are -1.5, and the lead-molecule coupling was -0.5.
5 Conclusions
Olife is a very easy simple and efficient tool for transmission calculation because it uses very simple inputs. It is also very fast code owing to the fact that it uses simple tight binding Hamiltonians. Therefore this code is essential for studying pre-checking and teaching the transmission coefficient of molecules.

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