

Theoretical Treatment for Electron Transport throughout Molecular Wire Bridge

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Abstract

In this paper we present our theoretical treatment for electron transport through one scattering region attached to donor and left lead in the left side, while in the right side it is attached to acceptor and right lead. Our treatment is based on the time-dependent Anderson – Newns Hamiltonian. The equations of motion are derived for all subsystems then the stationary state is considered to obtain analytical expression for the transmission probability as a function of system energies. The scattering region is considered as molecular wire. The subsystems eigenvalues, the coupling interaction between them as well as the leads band width all are taken into consideration and highlighted. We concluded that the variation of the number of molecules gives the molecular wire one of the most interesting functional properties, that is the molecular on-off switching.

معالجة نظرية لنقل الألكترون خلال جسر سلك جزيئي

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الملخص

في هذا البحث تم تقديم معالجة نظرية لنقل الألكترون خلال منطقة أستطارة واحدة رُبطت بواهب وقطب أيسر في الجانب الأيسر بينما في الجانب الأيمن رُبطت بمستقبل وقطب أيمن. بنيت معالجتنا على هاملتونين أندرسون-نيونز المعتمد على الزمن. أشتقت معادلات الحركة لكل أجزاء النظام ثم تم اعتبار الحالة المستقرة لإيجاد صيغة تحليلية لأحتمالية النفاذية كدالة لطاقات النظام. تم اعتبار منطقة الأستطارة كسلك جزيئي. القيم الذاتية لأجزاء النظام وتفاعل الإقتران فيما بينهما بالإضافة إلى عرض حزمة الأقطاب تم أخذها جميعاً بنظر الاعتبار وتسليط الضوء عليها. نستنتج أن تغيير عدد الجزيئات يعطي السلك الجزيئي إحدى الخواص الوظيفية المثيرة للأهتمام، وهي أنه مفتاح جزيئي.

(1) Introduction

Transport through nano-scale devices based on single molecules has attracted a lot of interest over the last years [1-4]. The basic idea of such transport devices is that initially two metallic electrodes are separated by a gap, prohibiting any transport of electrons. However, already a single molecule trapped within this gap can serve as bridge and thereby allow for a small current of tunneling electrons. One of the most interesting aspects of such single-molecule devices is their size. The gap

can nowadays be fabricated and controlled on the nanometer-scale. The small size of the device make single-molecule transport devices particularly interesting for information technology, where the demand for device miniaturization is growing fast. Obviously, at such small scales, quantum mechanical effects become crucial [5]. In this paper, we study left lead-donor-scattering region-accepter-right lead system (see Fig. (1,a)). Where, the scattering region (i.e. the bridge) may consist of several nanostructures. The bridge system considered in our calculations is the

molecular wire. In our work, we will present our theoretical treatment to formulate general expression for the electron transport throughout one scattering region to study and calculate the electronic properties for the considered system. So, all the system eigenvalues and coupling interactions are taken into consideration to give obvious view for the system dynamics.

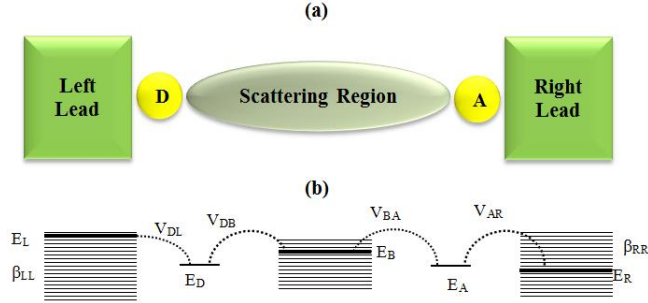


Figure (1):(a) An illustration for left lead-donor-scattering region-accepter-right lead system. (b)The corresponding energy diagram, the energy levels and coupling interactions between the nearest neighbors parts.

(2) Theory

In this work, general formula for the transmission probability for one scattering region will be derived for the system shown in Fig.(1). The different indices L, D, B, A and R denote left lead, donor, bridge, acceptor and right lead respectively (see Fig(1,b)). This energy diagram can be described by using time-dependent and spin less Anderson – Newns Hamiltonian [6], which neglects Coulomb interactions in all subsystem. This Hamiltonian is given by

$$\begin{aligned} \hat{H}(t) = & E_D n_D(t) + E_A n_A(t) + \sum_{k_B} E_{k_B} n_{k_B}(t) + \sum_{k_L} E_{k_L} n_{k_L}(t) + \sum_{k_R} E_{k_R} n_{k_R}(t) \\ & + \sum_{k_B} (V_{Dk_B} C_D^\dagger(t) C_{k_B}(t) + H.C.) + \sum_{k_B} (V_{Ak_B} C_A^\dagger(t) C_{k_B}(t) + H.C.) + \\ & \sum_{k_L} (V_{Dk_L} C_D^\dagger(t) C_{k_L}(t) + H.C.) + \sum_{k_R} (V_{Ak_R} C_A^\dagger(t) C_{k_R}(t) + H.C.) \end{aligned} \quad (1)$$

Where, $n_j(t) = C_j^\dagger(t) C_j(t)$ and the $C_j^\dagger(t) (C_j(t))$ denotes annihilation (creation) operators. The index k_j being a set of quantum numbers, with $j=L, B, R$. The equation of motion for $C_j(t)$ can be obtained by using [7],

$$\dot{C}_j(t) = -i \frac{d\hat{H}(t)}{dC_j^\dagger(t)} \quad (2)$$

to get,

$$\dot{C}_D(t) = -iE_D C_D(t) - i \sum_{k_B} V_{Dk_B} C_{k_B}(t) - i \sum_{k_L} V_{Dk_L} C_{k_L}(t) \quad (3)$$

$$\dot{C}_A(t) = -iE_A C_A(t) - i \sum_{k_B} V_{Ak_B} C_{k_B}(t) - i \sum_{k_R} V_{Ak_R} C_{k_R}(t) \quad (4)$$

$$\dot{C}_{k_B}(t) = -iE_{k_B} C_{k_B}(t) - iV_{k_B D} C_D(t) - iV_{k_B A} C_A(t) \quad (5)$$

$$\dot{C}_{k_L}(t) = -iE_{k_L} C_{k_L}(t) - iV_{k_L D} C_D(t) \quad (6)$$

$$\dot{C}_{k_R}(t) = -iE_{k_R} C_{k_R}(t) - iV_{k_R A} C_A(t) \quad (7)$$

For stationary state we define $C_j(t)$ by the following:

$$C_j(t) = \tilde{C}_j(E) e^{-iEt} \quad (8)$$

where E denotes the system eigenvalues, then accordingly, $\dot{\tilde{C}}_j(E) = 0$.

In order to get logic and simple formula for the transmission probability amplitude, we assume the following energy separation procedure [8]:

$$V_{k_B A} = v_{k_B} V_{k_B A}^{\beta\alpha}, V_{k_L D} = v_{k_L} V_{k_L D}^{\beta\alpha}, V_{k_R A} = v_{k_R} V_{k_R A}^{\beta\alpha}, \tilde{C}_{k_\beta}(E) = v_{k_\beta} \tilde{\bar{C}}_{k_\beta}(E) \quad (9)$$

where $\alpha=D, A$ and $\beta=D, A, B$, then we get,

$$\tilde{C}_A = \frac{1}{E - E_A} \{ V_{AB} \Gamma_B(E) [V_{BD} \tilde{C}_D + V_{BA} \tilde{C}_A] + |V_{AR}|^2 \Gamma_R(E) \tilde{C}_A \} \quad (10)$$

Then the transmission probability amplitude and transmission probability [9] can be calculated respectively as:

$$t(E) = \frac{\tilde{C}_A(E)}{\tilde{C}_D(E)} \quad (11)$$

$$T(E) = |t(E)|^2 \quad (12)$$

Where

$$\Gamma_\ell(E) = \sum_{k_\ell} \left\{ \frac{|v_{k_\ell}|^2}{E - E_{k_\ell}} \right\} \quad \ell = B, R \quad (13)$$

By using the following operator equation,

$$\lim_{\gamma \rightarrow 0} \frac{1}{E - E_n + i\gamma} = -i\pi \delta(E - E_n) + P \frac{1}{E - E_n} \quad (14)$$

Where P refers to the principal part, the functions $\Gamma_B(E)$ and $\Gamma_R(E)$ will take the following formulas,

$$\Gamma_\ell(E) = -i\pi \rho_\ell(E) + P \int \frac{\rho_\ell(E')}{E - E'} dE' \quad \ell = B, R \quad (15)$$

Where $\rho_\ell(E)$ represents the density of electronic states for the nanostructure which is given by [10]

$$\rho_\ell(E) = \sum_{k_\ell} |v_{k_\ell}|^2 \delta(E - E_{k_\ell}) \quad (16)$$

Then we can write the level self-energy [11],

$$\Sigma_{A\ell}(E) = |V^{A\ell}|^2 \Gamma_\ell(E) = -i\Delta_{A\ell}(E) + \Lambda_{A\ell}(E) \quad \ell = B, R \quad (17)$$

$\Delta_{AB}(E)$ is the acceptor level broadening due to acceptor level-bridge level coupling interaction, while $\Delta_{AR}(E)$ is the acceptor level broadening due to acceptor level-right lead's levels coupling interaction. $\Lambda_{AB}(E)$ and $\Lambda_{AR}(E)$ are the quantum shift that happen in the acceptor level due to the over mentioned coupling interactions. With [12],

$$\Delta_{A\ell}(E) = \pi |V^{A\ell}|^2 \rho_\ell(E) \quad \ell = B, R \quad (18)$$

And

$$\Lambda_{A\ell}(E) = P \frac{1}{\pi} \int \frac{\Delta_{A\ell}(E')}{E - E'} dE' \quad \ell = B, R \quad (19)$$

Also, we can define the self-energy $V^{AB}V^{BD}\Gamma_B(E)$, which refers to the indirect coupling interaction between the donor and the acceptor levels throughout the bridge, as

$$\Sigma_{ABD}(E) = V^{AB}V^{BD}\Gamma_B(E) = -i\Delta_{ABD}(E) + \Lambda_{ABD}(E) \quad (20)$$

With,

$$\Delta_{ABD}(E) = \pi V^{AB}V^{BD} \rho_B(E) \quad (21)$$

$$\Lambda_{ABD}(E) = P \frac{1}{\pi} \int \frac{\Delta_{ABD}(E')}{E - E'} dE' \quad (22)$$

Notably, $\Delta_{ABD}(E)$ determines the interference energy and $\Lambda_{AB}(E)$ is its corresponding quantum shift. Now we can write the transmission probability amplitude as

$$t(E) = \frac{\Sigma_{ABD}(E)}{E - E_A - \Sigma_{AB}(E) - \Sigma_{AR}(E)} \quad (23)$$

Note that, the acceptor and donor levels are broadened and thus they will have local density of states which take the following Gaussian forms respectively [13-15]

$$\rho_A(E) = \frac{1}{\pi} \frac{\Delta_{AR}(E)}{(E - E_A - \Lambda_{AR}(E))^2 + \Delta_{AR}^2(E)} \quad (24a)$$

$$\rho_D(E) = \frac{1}{\pi} \frac{\Delta_{DL}(E)}{(E - E_D - \Lambda_{DL}(E))^2 + \Delta_{DL}^2(E)} \quad (24b)$$

where $\Delta_{DL}(E)$ is the donor level broadening due to donor level-left lead's levels coupling interaction and $\Lambda_{DL}(E)$ is the corresponding quantum shift.

(3) Molecular Wire as a Bridge System

(3-1) The Molecular Wire Density of States

In the following, model parameterization will be presented for the molecular wire used as a bridge system. simply, the molecular wire can be defined as a chain of molecules connected serially. The Hamiltonian of this system is similar to that in eq.(1), thereby, the transmission probability amplitude take the same formula in eq.(23), where each molecule is a diatomic one (see Fig. (2)). The coupling interaction between the atoms in each molecule is denoted by t_{ab} , while the coupling interaction between the molecules in the wire is denoted by V .

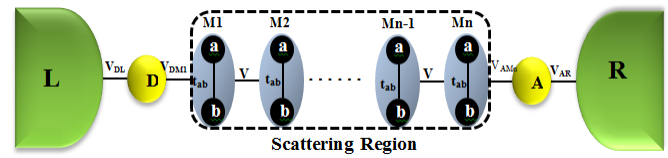


Fig. (2) shows the molecular wire considered in our treatment.

The bridge energy levels positions must be obtained following the tight binding model formula [18],

$$E_{B_j} = E_{basis} + 2V \cos\left(\frac{j\pi}{N+1}\right) \quad \dots (25)$$

Where $j=1, \dots, N$. N is the number of molecules, E_{basis} represents the energy of the molecular basis. In order to calculate the value of E_{basis} the following secular equation must be solved,

$$\begin{vmatrix} E_a - E & t_{ab} \\ t_{ab} & E_b - E \end{vmatrix} = 0 \quad \dots (26)$$

E_a and E_b are the energy levels of the two atoms in the molecules, which may be similar or different. Eq. (26) is solved to get the following the roots,

$$E_{basis} = E_{\pm} = \frac{E_a + E_b}{2} \pm \sqrt{\left(\frac{E_a - E_b}{2}\right)^2 + t_{ab}^2} \quad \dots (27)$$

If the interaction V is switched on, the system energy spectrum can be calculated by using eq. (25). Both basis energies are considered in our calculation. And the density of states for this bridge system, which we derive, is:

$$\rho_B(E_{B_j}) = \left| \frac{N}{4\pi V \sin(\frac{j\pi}{N+1})} \right| \quad \dots (28)$$

(3-2) Calculations and Discussion

As a model parameterization, the transmission probability is calculated for each basis for the same set of parameters i.e. $V_{DB}=V_{AB}=-0.1\text{eV}$, $V_{AR}=-3.0\text{eV}$, and $\beta_R=-3.0\text{eV}$, for the case of different atoms $E_a=-1.1\text{eV}$ and $E_b=-1.15\text{eV}$ for odd and even numbers of molecules. Our results are presented in Figs. ((3)-(8)) for three different cases $V=t_{ab}$, $|V| > |t_{ab}|$ and $|V| < |t_{ab}|$. According to these figures, one can report the following,

- 1- The number of resonates is determined by the number of molecules.
- 2- All the figures show certain critical energy at both basis, at which $T(E)=1$ for odd number of molecules and it is nearly zero for even number of molecules, for all coupling cases. At the critical energies, the number of molecules has no rule.
- 3- The variation of the number of molecules gives the molecular wire one of the most interesting functional properties, that is the molecular on-off switching.
- 4- Increasing t_{ab} leads also to change the transmission probability peaks, which in turn modifies the physical features and the functional properties of the scattering region.

The calculation for the case of identical atoms is also accomplished for the same structure parameters and compared with the case of different atoms. The results are coinciding in their behavior but there is small shift in energy due to the difference in the basis energies.

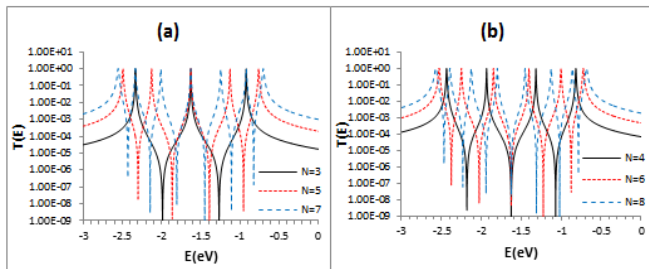


Fig. (3): the transmission probability as function of the system energy with $E_a=-1.1\text{eV}$, $E_b=-1.15\text{eV}$, $E_{\text{basis}}=-1.625$, $t_{ab}=-0.7\text{eV}$, $V=-0.5\text{eV}$, $V_{DB}=V_{AB}=-0.1\text{eV}$, $V_{AR}=-3\text{eV}$, $\beta_R=-3\text{eV}$.

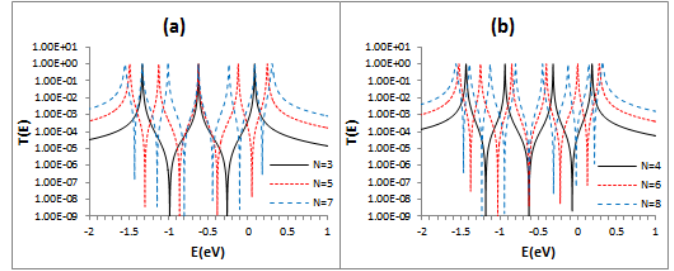


Fig. (3): the transmission probability as function of the system energy with $E_a=-1.1\text{eV}$, $E_b=-1.15\text{eV}$, $E_{\text{basis}}=-1.625$, $t_{ab}=-0.7\text{eV}$, $V=-0.5\text{eV}$, $V_{DB}=V_{AB}=-0.1\text{eV}$, $V_{AR}=-3\text{eV}$, $\beta_R=-3\text{eV}$.

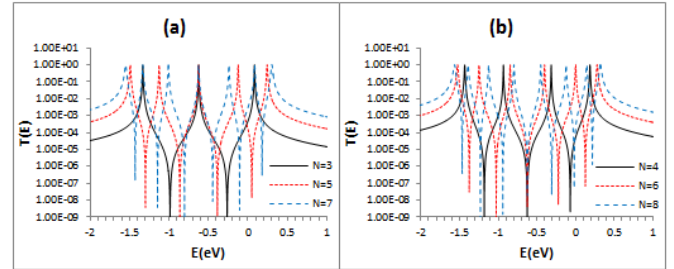


Fig. (4): the transmission probability as function of the system energy with $E_a=-1.1\text{eV}$, $E_b=-1.15\text{eV}$, $E_{\text{basis}}=-0.624$, $t_{ab}=V=-0.5\text{eV}$, $V_{DB}=V_{AB}=-0.1\text{eV}$, $V_{AR}=-3\text{eV}$, $\beta_R=-3\text{eV}$.

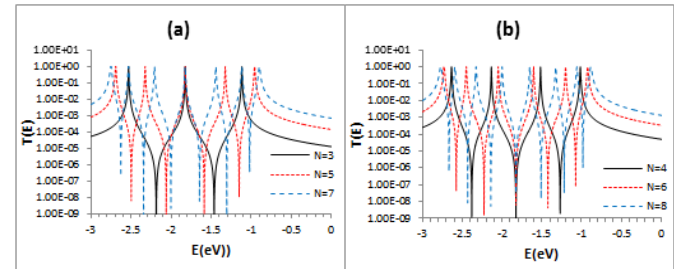


Fig. (5): the transmission probability as function of the system energy with $E_a=-1.1\text{eV}$, $E_b=-1.15\text{eV}$, $E_{\text{basis}}=-1.825\text{eV}$, $t_{ab}=-0.3\text{eV}$, $V=-0.5\text{eV}$, $V_{DB}=V_{AB}=-0.1\text{eV}$, $V_{AR}=-3\text{eV}$, $\beta_R=-3\text{eV}$.

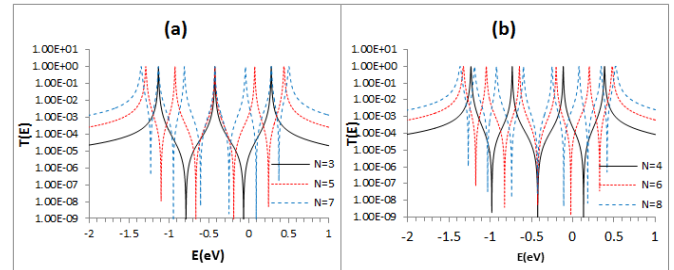


Fig. (6): the transmission probability as function of the system energy with $E_a=-1.1\text{eV}$, $E_b=-1.15\text{eV}$, $E_{\text{basis}}=-0.424$, $t_{ab}=-0.7\text{eV}$, $V=-0.5\text{eV}$, $V_{DB}=V_{AB}=-0.1\text{eV}$, $V_{AR}=-3\text{eV}$, $\beta_R=-3\text{eV}$.

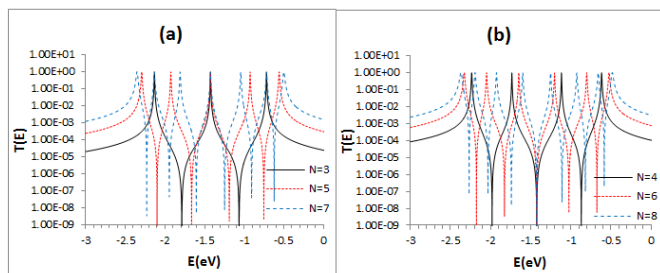


Fig. (7): the transmission probability as function of the system energy with $E_a = -1.1\text{eV}$, $E_b = -1.15\text{eV}$, $E_{\text{basis}} = -1.426\text{eV}$, $t_{\text{ab}} = V = -0.5\text{eV}$, $V_{\text{DB}} = V_{\text{AB}} = -0.1\text{eV}$, $V_{\text{AR}} = -3\text{eV}$, $\beta R = -3\text{eV}$.

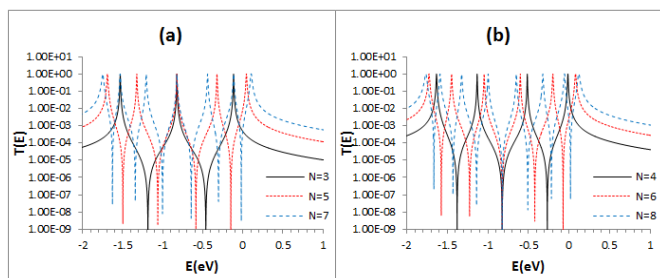


Fig. (8): the transmission probability as function of the system energy with $E_a = -1.1\text{eV}$, $E_b = -1.15\text{eV}$, $E_{\text{basis}} = -0.823\text{eV}$, $t_{\text{ab}} = -0.3\text{eV}$, $V = -0.5\text{eV}$, $V_{\text{DB}} = V_{\text{AB}} = -0.1\text{eV}$, $V_{\text{AR}} = -3\text{eV}$, $\beta R = -3\text{eV}$.

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