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Molecular 'OR' and 'AND' logic gates integrated in a single molecule

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Abstract

Based on the *N* electrodes elastic scattering quantum chemistry (NESQC) technique, an intramolecular circuit simulator is presented for the design of electronic logic functions integrated inside a single molecule interconnected to the *N* electrodes. Using molecular rectifier groups, a molecule-OR and a molecule-AND are designed, their current-voltage characteristics calculated and their logic response presented. Both the OR and AND molecules have approximatively the targeted function. The running current of the OR gate, 10 fA, is quite low and the AND gate works only in an output voltage mode. This forbids the design of larger logic functions inside a single molecule with molecular rectifiers.

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1. Introduction

In hybrid molecular electronics [1], circuits are made of single molecular devices interconnected by metallic wires [2,3]. For these circuits, the Kirchhoff mesh and node laws apply when the wires are longer than a few 10 nm [4], the phase of the electrons being randomized in between the molecules in this case [5]. This condition forbids the miniaturization of the total circuit down to the nanoscale. To miniaturize further, Carter [6] suggested to integrate the wires and the devices inside a very single molecule. Many molecule-circuits have been drawn, culminating with the MITRE

Corresponding author. Fax: +33-5-62-25-79-99. *E-mail address:* hliwa@cemes.fr (M. Hliwa). molecular digital adder [7]. Here, the intramolecular design relies on the Kirchhoff laws when assembling the molecular groups to form the molecule-circuit. Unfortunately, the mesh Kirchhoff law do not apply inside a molecule [8].

To design an electronic circuit inside a molecule, we have developed an intramolecular circuit simulator respecting the quantum rules of association in series and parallel of molecular groups and their molecular orbital structure. In this Letter, the N electrodes intramolecular circuit simulator (NESQC) working at the extended Hückel molecular orbital (EHMO) level is first described. In Section 3, EHMO–NESQC is applied to the design of a molecule-OR interconnected to 3 electrodes and in Section 4 to a molecule-AND interconnected to 4 electrodes. In conclusion, the difficulties in designing larger intramolecular logic

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functions based on molecular rectifiers are discussed.

2. The intramolecular circuit simulator

The N electrode elastic scattering quantum chemistry (NESOC) technique calculates the electron scattering matrix of a single molecule interacting with N independent electrodes (Fig. 1). In its tight-binding version, NESQC was applied to simple intramolecular circuits like a 3-port splitter [8]. In this section, the extension of NESQC to EHMO Hamiltonian is briefly presented. The EHMO Hamiltonian of the Fig. 1 circuit has N identical block diagonal parts $H_{\text{Electrode }k}$ for the electronic band structure of each electrode, a block diagonal part H_m for the molecule-circuit and many off diagonal parts for the interactions between the molecule and the N electrodes. Each electrode k is a semi-infinite periodic chain made of the same unit cell. Each cell n (n > 1) of k is described by P Slater atomic orbitals $|s_{n,i}^k\rangle$. The molecule is described by L Slater atomic orbitals $|s_i^0\rangle$.

A transmission coefficient $T_{kk'}(E) = |S_{kk'}(E)|^2$ between electrodes k and k' through the molecule is



Fig. 1. Structure of the scattering circuit made of a central molecule interacting with N electrodes. The full circuit is calculated with EHMO–NESQC taking into account the EHMO valence molecular orbitals of the central molecule and the band structure of the electrodes in interaction with the molecule.

calculated from the full scattering matrix S of the Molecule-N electrodes system [8]. With no inelastic effects occurring inside the circuit, the wave function $|\psi\rangle$ of the entire Fig. 1 circuit is a solution of the eigenvalue problem $H|\psi\rangle = E|\psi\rangle$ with

$$|\psi\rangle = \sum_{k=1}^{N} \sum_{n=1}^{\infty} \sum_{j=1}^{P} x_{n,j}^{k} |s_{n,j}^{k}\rangle + \sum_{i=1}^{L} d_{i} |s_{i}^{0}\rangle.$$

A cell *n* is described by the vector $\psi_n^k = [x_{n,1}^k \cdots x_{n,P}^k]^t$ and the molecule by the vector $\psi^0 = [d_1 \cdots d_L]^t$.

To solve the Fig. 1 scattering problem, $H|\psi\rangle = E|\psi\rangle$ is first projected on the orthogonalized subspace of the *N* electrodes spanned by the states $|s_{n,j}^k\rangle$. This produces *N* second-order matrix difference equations [9]

$$\underline{b}^{t}\psi_{n-1}^{k} + \underline{a}\psi_{n}^{k} + \underline{b}\psi_{n+1}^{k} = 0, \qquad (1)$$

where <u>a</u> is a $(P \times P)$ matrix with $a_{x,y} = \langle s_{n,x}^k | H - E | s_{n,y}^k \rangle$ and <u>b</u> a $(P \times P)$ matrix with $b_{x,y} = \langle s_{n,x}^k | H - E | s_{n+1,y}^k \rangle$. Eq. (1) is usually rewritten in a transfer matrix form and solved using the multiple-propagative-channels spatial propagator technique [9] with $\chi_n^k = [\psi_n^k \psi_{n-1}^k]^t$ the corresponding propagated state vector. The $[\chi_2^k]$ vectors are connecting the N electrode parts of the circuit to the central molecule.

Then, $H|\psi\rangle = E|\psi\rangle$ is projected on the orthogonalized Hilbert subspace spanned by the states $|s_i^0\rangle$ and $s_{1,j}^k\rangle$. It results L + N.P second-order difference equations. They are separated into 2 subsets. One of *L* equations determines the probability amplitudes $[d_i]$ on the central molecule as a function of the probability amplitude vector $[\chi_2^k]f$.

$$\underline{C}[d_1d_2\cdots d_L]^{\mathrm{t}} + \underline{M}\underline{Q}[\chi_2^1\cdots \chi_2^N]^{\mathrm{t}} = 0, \qquad (2)$$

where \underline{C} is a $L \times L$ matrix describing the moleculecircuit atomic structure, including its topology, EHMO atomic orbital energy, overlap matrix and interactions elements with $C_{x,y} = \langle s_x^0 | H - E | s_y^0 \rangle$. The matrix \underline{M} is $L \times (N.P)$ and describes the EHMO electronic coupling between the terminal cell of each electrode and the molecule-circuit orbitals with $M_{x,(yP+z)} = \langle s_x^0 | H - E | s_{1,z}^{y+1} \rangle$ for $0 \leq y < N$ and $0 < z \leq P$. Finally, \underline{Q} is a rectangular $(N.P) \times$ (2N.P) matrix built to take into account only the ψ_1^k amplitudes [8]. The second subset of *N*.*P* equations determines the probability amplitude ψ_1^k on each propagative channel state of a terminal cell

$$\underline{F}\left[\chi_{2}^{1}\cdots\chi_{2}^{N}\right]^{t}+\underline{M}^{t}\left[d_{1}d_{2}\cdots d_{L}\right]^{t}=0,$$
(3)

where <u>*F*</u> is a $N.P \times 2N.P$ matrix built on the <u>*a*</u> and <u>*b*</u> matrix defined in (1).

Eqs. (2) and (3) form a homogeneous system of equations for the unknown vectors $[d_i]$ and $[\chi_2^k]$. But the d_i coefficients are not required to compute the *S* matrix. As in the effective Hamiltonian technique of the original version of ESQC, the $[d_i]$ vectors are eliminated from (2) and (3) to get

$$\left(\underline{F} - \underline{M^{\mathsf{t}}C}^{-1}\underline{MQ}\right) \left[\chi_{2}^{\mathsf{l}}\cdots\chi_{2}^{\mathsf{N}}\right]^{\mathsf{t}} = \tilde{F}\left[\chi_{2}^{\mathsf{l}}\cdots\chi_{2}^{\mathsf{N}}\right]^{\mathsf{t}} = 0.$$
(4)

Finally, to calculate the scattering matrix *S*, Eq. (4) is transformed using the decomposition of the $[\chi_2^k]$ vectors on the incoming and outgoing amplitudes of the electrode Bloch vectors on the *N* electrodes. This decomposition is performed per propagative channels and per electrodes like in the simple case of one propagative channel per electrode [8].

3. Architecture and results for an intramolecular OR gate

For a tunnel regime of transport through a molecule-circuit, the Kirchhoff node law is valid when the molecular branches of the circuit are each connected externally to independent metallic electrodes [8]. Here, this law is applied to design the molecule-OR Fig. 2a where a central phenyl node is chemically bonded in series with two Aviram-Ratner rectifiers [10]. The output current I_A is collected directly on this phenyl node by a short polyne chain terminated by a thiol group. The acceptor part of each rectifier is π bonded in a planar conformation to the electrodes B and C. The Smatrix of this 3-port molecule is calculated using the EHMO-NESQC technique described above with L = 497. There are P = 30 gold atoms (one 6s atomic orbital per Au) per unit cell in the electrodes leading to an average of 16 propagative channels.

The 3 transmission coefficients $T_{AB}(E)$, $T_{AC}(E)$ and $T_{BC}(E)$ of the molecule-OR are presented in Fig. 2b. Molecular orbitals can be well identified on those spectra like the π (HOMO) and π^* (LUMO) doublets of the 2 weakly electronically coupled rectifiers groups. Through these 2 rectifiers, $T_{BC}(E)$ is 10 orders of magnitude lower than $T_{AB}(E)$ or $T_{AC}(E)$ showing the good electronic insulation of our design. The central phenyl is a bad tunnel splitter due to the methyl groups introduced between this phenyl and each rectifier group. This design maintains a weak electronic π coupling between the 2 rectifiers inside the molecule to preserve the molecular orbital of their donor part. Better intramolecular tunnel three-way splitters can be optimized [8]. But performing it on the molecule-OR will reduce again its electronic transparency which is already very low (Fig. 2b).

 I_A was calculated using the multi-channel Landauer-Büttiker formula generalized to N electrodes [8]. To compare the logic surface of this molecule-OR (Fig. 3d) with a standard OR gate response (Fig. 3b), I_A have been calculated over a large range of C and B bias voltage. In those calculations, E_F was positioned at -10.875 eV, at the threshold of the LUMO resonance to compensate for the absence of inelastic effect in our scattering formalism. Furthermore, finding the relative position of the Fermi level to the HOMO-LUMO molecular orbital gap is one of the critical tasks for the theory of molecular electronics [12] and it is one of the crucial tasks for molecular electronics. Choosing the Fermi level in the middle of the OR and AND molecule HOMO-LUMO gap will reduce by a few order of magnitude the output current of the molecular circuit and the rectifier character of each rectifier group will be less pronounced. Therefore, to test the capability of our circuit simulator, we have preferred to re-enforce the rectifier character of the molecular group, leaving the detail study of the Fermi level positioning for a next step. This step can be included in a next version of our simulator, taking into account the electric field effect across the junction. However, our Fermi level positioning near the LUMO has not a large consequence on the charge transfer at the metal-molecule interface. This resonance is very damped because the acceptor groups electronic coupling with the electrodes B and C is different from the one of the thiol group with the electrode A. Therefore,



Fig. 2. The calculated EHMO–NESQC transmission coefficients through the molecule-OR. (a) The atomic structure of the molecule-OR with its acceptor (acc) and donor (don) intramolecular groups. The chemical structure of the molecule OR is explained in Fig. 3c. (b) The 3 transmissions coefficients $T_{AB}(E)$ (solid line), $T_{AC}(E)$ (dash–dot line) and $T_{BC}(E)$ (dash line). A molecular orbital identification had been performed around the HOMO–LUMO gap of the molecule and are indicated on the resonance. Inset: detail of the tunnel spectrum around the HOMO resonance showing the π orbital doublet, one resonance per donor group.

the charge transfer at the metal-molecule interface will remain much lower than one even if E_F is positioned near the LUMO. Calculated with the N = 2 EHMO-ESQC technique [13], this produces a very good rectifier characteristic for this simple metal-single rectifier-metal junction.

The law of superposition of the tunneling current inside the molecule-OR works perfectly (see Fig. 3d) as compared to the ideal OR surface Fig. 3b. But from inside the molecule, there is no means to equalize the '1' resulting from one input sets at 0.3 V and the '1' resulting from two input set at 0.3 V. This will have to be performed outside the molecule-OR. The second problem with a logic circuit base on intramolecular rectifiers is the very low fA value of I_A . Shorter molecular rectifier groups have to be designed as proposed by MI-TRE [7] to compensate for the exponential decrease of I_A with the length of the rectifier. But to preserve the molecular orbital optimization per rectifier, a weak electronic interaction have also to be maintained between the rectifier groups. This is against a large I_A since saturated chemical groups will have to be used along the molecular circuit in this case. In the present design, an attempt had been made to increase I_A by re-enforcing the acceptor-electrode electronic coupling with a direct chemisorption of the end of each acceptor to the electrode. This is not enough to reach a reasonable I_A for logic circuit applications.



Fig. 3. Logic response of the molecule-OR circuit. (a) The classical design of an OR gate using 2 perfect switches. (b) The corresponding ideal logic surface giving the logic output status of the OR as a function of the input voltage for a threshold switching voltage of 0.1 V. Logic level '0' is for $I_A = 0$ and logic level '1' for $I_A = 0.3/R$. (c) The detail chemical structure of the molecule-OR connected as indicated in Fig. 2a. (d) The corresponding logic surface of the gate calculated for each combination of the bias voltage on *B* and *C* using the 3 EHMO–NESQC transmission coefficients of Fig. 2b in the generalized Landauer–Büttiker formula [11].

4. Architecture and results for the intramolecular AND gate

In the design of an AND gate using semiconductor rectifier, a voltage drop is normally used to limit the current and stabilize the output voltage. But there is no voltage drop defined inside a molecule-circuit [8]. Therefore, the molecule-AND Fig. 4c was designed by keeping the central rectifier-phenyl-rectifier molecular bridge of the Fig. 3c molecule-OR. For ideal switches, this corresponds to keep the central switch of the OR gate (Fig. 3a) but with a different output connection for the AND gate (Fig. 4a). It was not possible to bond both the power supply V_D and output V_A molecular wires on the central phenyl of the bridge. The



Fig. 4. Logic response of the molecule-AND. (a) The design of an AND gate as a dual of the OR gate. (b) The corresponding ideal logic surface for the same conditions than in Fig. 3b. (c) The chemical detail structure of the molecule-AND connected to 4 electrodes in the same way than the molecule-OR in Fig. 2a. (d) The corresponding logic surface of the gate calculated using the 6 EHMO–NESQC transmission coefficients as in Fig. 3d.

polyne oligomer of the molecule-OR was kept and another phenyl node introduced. In charge of the bias current, a long alkane chain of very low electronic transparency is bonded to it. A 2nd molecular wire is bonded to this new phenyl node for the output potential to be measured on electrode A [11]. The scattering matrix for this 4-port molecule has been calculated using the EHMO– NEQSC technique with L = 746 and the same gold unit cell.

The logic surface combining now 6 transmission coefficients is presented in Fig. 4d and compared with the ideal AND response Fig. 4b. The molecule-AND logic surface is very close to the ideal one. This results from a very precise tunning of the alkane chain length. The reverse current flowing in the rectifiers is compensated by the current passing in D. When B and C are grounded, the potential of the reservoir A is slightly positive to compensate for the current coming from D. This remains true when B or C are negatively biased. The reverse bias voltage rectifier characteristics is also visible Fig. 4d. When B or C are too negative, the current from D is not efficient anymore and the potential of Astarts to decrease (Fig. 4d). Now, when one of the input electrode is set up to a logic level '1', the potential on A must remain small. When C is forced to +0.3V, the potential on A changes and the current from C to A equals the current from Ato B. Then, the current from D is negligible as compared to the direct current.

5. Future architecture of larger intramolecular logic circuit

An extension of the NESQC technique for the calculation of the electronic characteristics of realistic intramolecular circuits have been presented. AND and OR single molecule have been designed and their logic responses calculated. Already with these simple molecules, we are facing with 2 problems. First, the running current intensity is very low for circuits to be assembled with these elementary functions. Second, it had been proposed that more complex intramolecular logic functions like an XOR [7] can be obtained by bonding together molecule-OR and molecule-AND in a single molecule. This is impracticable due to the difficulty to design a molecule-AND working in a current output mode. Like with the semiconductor diodes in the 1950s, molecular rectifiers groups are not adapted for integrating a large logic circuit inside a single molecule. Finally, a molecule made of molecular electronic functional groups is a new molecule whose circuit laws escape from the standard Kirchhoff ones. This requires a specific designer program. The EHMO–NESQC technique is the first generation of such molecular circuit simulator routine.

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