2. Hardware nano-architecture



2a. Classical





Molecular switches: Isomerization of single azobenzene derivative

M. Alemani¹, K.-H. Rieder¹, F. Moresco¹, M. V. Peters², S. Hecht² and L. Grill¹

¹Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin, Germany ²Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

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The investigation of single molecules has become an important and well-established research field in the last years, driven by the prospect for fundamental electronic and mechanical device miniaturization [1]. Understanding and controlling conformational changes of single molecules is very important in this regard. For this purpose, the scanning tunneling microscope (STM) at low temperature constitutes a powerful tool, as it not only allows precise sub-molecular imaging of single molecules but also permits the manipulation of atoms and molecules [2, 3]. Looking for molecules suitable for application in molecular electronics, the current research interest is focusing on molecular switches [4, 5]. A molecular switch undergoes a reversible transformation between at least two distinct stable switching states, associated with different physicochemical properties [4]. The azobenzene molecule, based on a *trans-cis* isomerization mechanism, represents a very interesting example of such a molecular switch [6].



Figure 1: (a) TBA molecule. (b) STM image (40x40 nm²) of a molecular island on Au(111). (c) Corner of an island in an enlarged STM image, the molecular structure is indicated. (d) Shows the STM image of a single TBA molecule.

The aim of the presented work is to switch single molecules on a metal surface in a controlled way. Figure 1a shows the investigated molecule: 3,3',5,5'-tetra-tertbutyl-azobenzene, called TBA [7]. The performed experiments were under ultrahigh vacuum conditions at а temperature of 5 K using a home built STM. An overview STM image of TBA molecules on Au(111) after deposition is shown in Figure 1b. The molecules are mobile after adsorption, as they cover step edges and form islands. The position and orientation of individual molecules inside these islands is shown in Figure 1c: the molecules form parallel rows indenting with each other. Each molecule appears as four lobes with an apparent height of 2.7±0.1 Å arranged in a rhombic shape (Figure 1d). According to the dimensions of the molecule in the gas phase, the lobes can be assigned to the *tert*-butyl

groups while the central azobenzene part is not visible. All observed molecules are in the same planar configuration that we assign to the *trans* isomer (Figure 1a).

To induce the isomerization, voltage pulses of 2 V were applied with the STM tip positioned above an island. After these pulses, many molecules have changed appearance, showing a larger height of 4.1 ± 0.3 Å. These bright molecules are stable and to let them precisely restore their initial appearance we have to apply a further





pulse, as shown in Figure 2. As one can see in Figure 2a, the isomerization process has no consequence on the neighboring *trans* molecules, which remain unchanged. The *cis* form appears with a bright central intensity maximum, while three lateral lobes in an approximately triangular shape can be resolved, completely different from the planar *trans* conformation [8]. This shows that, in contrast to the *trans* isomer, the *cis* isomer is not planar, in agreement with the molecular conformation in the gas phase [6].

Such switching experiments can be reproduced several hundred times allowing us to conclude that the observed changes are due to the isomerization of single molecules



Figure 2: Isomerization process from cis to trans. (a) and (b) show STM images (both 3.5 nm x 3.5 nm) before and after the isomerization. The bright molecule in (a) is in the cis state and exactly returns to the trans state in (b), where all visible molecules are trans isomers, after applying a voltage pulse.

from the trans form to the cis form, and back to the *trans* form [7, 8]. The reversibility of the experiment and its high reproducibility exclude molecular dissociation or the presence of any contamination as cause for the observed change of the molecular appearance. The switching of an isolated molecule is very rare because, under the effect of a voltage pulse, the molecule can move or rotate. This effect is avoided in the islands when the molecules are stabilized by each other.

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Nano-architecture by covalent assembly of molecular building blocks

L. Lafferentz¹, M. V. Peters², S. Hecht² and L. Grill¹

¹Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin, Germany ²Institut für Chemie, Humboldt-Universität zu Berlin, 12489 Berlin, Germany

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The construction of electronic devices from single molecular building blocks, which inherit certain functions - such as switching or rectifying - and are connected by atomic scale wires on a supporting surface, is an essential goal of molecular electronics [1]. A key challenge in this regard is the controlled assembly of molecules into desired architectures by strong, i.e. covalent, intermolecular connections [2], enabling efficient electron transport [3] between the molecules and providing high stability [4]. Such large networks are difficult to be manufactured by traditional repetitive chemical synthesis and can hardly be deposited onto surfaces.



Figure 1: (a) Concept of the formation of covalently bound networks by connecting activated molecular building blocks. (b) Chemical structure of the Br4TPP (tetra(4-bromophenyl)porphyrin) molecule. From [5].

We have developed a method that overcomes this problem and creates covalently bound nano-architectures, i.e. macromolecular structures with controlled shape and size [5]. Our approach is based on small molecular building blocks with reactive side groups - "legs" - that form permanent chemical bonds at predefined connection points. This concept is illustrated in Figure 1a: A chemically stable, central molecular unit, is equipped with several legs. After dissociation of the substituent atoms in the first step by heating, the monomer building blocks are connected with each other through the activated legs directly on the surface upon thermal diffusion. The design of suitable molecules requires the incorporation of legs that can be activated selectively, without breaking the other bonds. For this purpose, carbon-halogen bonds were chosen. After selective thermal dissociation either on the surface or in the evaporator, the resulting activated fragments connect. Considering these requirements, we have chosen a porphyrin with four phenyl legs as a central building block (Figure 1b). At each leg, bromine was used as the labile substituent atom to be dissociated in a controlled manner.

The imaging and characterization of the molecular nanostructures were carried out with an STM at 7 K. The molecules were deposited onto clean Au(111), kept at room temperature during deposition. If the evaporator temperature was 550 K or below during the deposition of the Br4TPP molecules, large, highly ordered islands of intact molecules in a close-packed structure were found. The behaviour of the molecules changes fundamentally if the evaporator temperature is raised to at least 590 K: Most of the molecules become "activated" with the loss of several Br atoms in the evaporator. Upon thermal diffusion, these activated molecules react with each other to form intermolecular chemical bonds, thereby building macromolecular nanostructures of various shapes on the surface. The intermolecular bonds turn out to be relatively





strong, causing the entire molecular nanostructures to follow the pathway of the tip without fragmentation upon pulling on one end. Another signature of the covalent nature of the intermolecular bonds is revealed from spectroscopy measurements [5].



Figure 2: Results of different monomer building blocks with one (left panel), two (medium panel) and four (right panel) Br substituents, causing the formation of dimers, chains and networks, respectively. From [5].

In order to show the ability of controlling the nano-architecture of the macromolecular structures, we have synthesized different TPP-based molecules with one, two or four Br substituents (Figure 2). In the case of sufficient heating, characteristic molecular arrays are found on the surface. The topology of these nanostructures precisely corresponds to the molecular design (Figure 2): If only one Br substituent is used, exclusively dimers are observed, because each building block provides only one reactive site. Accordingly, porphyrin building blocks with two Br atoms in a linear geometry lead to the formation of linear chains. Finally, the use of four Br substituents enables the construction of two-dimensional networks. Hence, these results clearly show that the architecture of the nanostructures can be precisely controlled via the position of active end groups in the chemical structure of the molecular building blocks.

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Picometer-scale control of charge injection inside a single molecule

A. Bellec, F. Chiaravalloti, D. Riedel and G. Dujardin

Bâtiment 210, Université Paris-Sud 91405, Orsay, France

Introduction

Several techniques, such as nano-gap junctions [1] and break junctions [2,3], have been used in an effort to study electronic conduction through single molecules. However, the contacts between the molecules and the electrodes are poorly defined and there is increasing evidence that the molecular contacts need to be controlled with an atomic-scale precision. When calculating the electron transfer through a single benzene 1,4-dithiol molecule connected to two gold electrodes, Di Ventra et al. [4] have shown that adding just one gold atom between the molecule and one of the electrodes could change the conductance by two orders of magnitudes. This demonstrates that the contact between the molecule and the electrode needs to be defined with an atomic scale precision. Another important problem is the localization of the contact inside the molecule. Recently, it has been demonstrated that the localization of charge injection can be controlled with a picometer-scale precision inside a single molecule [5]. Different molecular dynamics have been activated when injecting charges at different positions inside the molecule. This suggests that the precise location of the atomic-scale electronic contacts inside the molecule can influence the whole properties (electron transfer, dynamics) of the molecule.

Picometer-scale electronic control of molecular dynamics inside a single molecule



A single biphenyl molecule adsorbed at room temperature on a Si(100) surface behaves as a bistable molecule at low temperature (5K) [5]. In its bistable configuration, the biphenyl molecule has two equivalent stable positions, S_1 and S_2 , as shown in the STM topographies of Figure 1. The biphenyl molecule is seen as a pair of bright features representing the two phenyl rings of the molecule. This bistable adsorption configuration consists of one phenyl ring lying parallel to the surface and attached to a silicon dimer in the so called "butterfly" configuration through two C-Si chemical bonds [6]. This phenyl ring is centered over the silicon dimer row. The second phenyl ring, perpendicular to the surface, is attached to a silicon atom through a single C-Si chemical bond. This is the result of a dissociative adsorption of the second phenyl ring where one hydrogen atom of the phenyl ring is adsorbed into the Si atom of the dimer as shown in Figure 1.

Figure 1: (a) (23 Å by 23 Å) topography of a single biphenyl molecule in the stable configuration S_1 . The dots indicate the STM tip position (P_1 , P_2 and P_3) where the negative bias pulse is applied. (b) Same as (a) after the surface pulse. The molecule has switched to its second stable configuration S_2 . (c) to (e) Three typical tunnel current curves recorded during negative bias pulses (Vs = -3V) at P_1 , P_2 and P_3 give insight into the dynamics of the molecular switch.









The ability of the low-temperature STM to perform experiments with picometer-scale spatial resolution enables the investigation of both the electronic excitation processes and the ensuing molecular dynamics within a molecule. As previously reported [5], the reversible switching of the molecule from S₁ to S₂ can be activated through resonant electronic excitation by positioning the STM tip at different positions inside the molecule (for example positions P₁, P₂ and P₃ in Figure 1) and applying a pulse voltage (V_S = -2.5 V) on the surface. The S₁→S₂ switching requires one of the molecular phenyl rings (called the mobile phenyl ring) to break two

Si-C bonds in its butterfly position, to move over the Si-H bond and to make two new Si-C. Recording the tunnel current during the pulse voltage enables a detailed investigation of the dynamics of the molecule as a function of the time of excitation. Step features in the time dependence of the tunnel current measured at three different locations inside the biphenyl molecule (Figure 1) correspond to the reversible switching of the molecule between the two S_1 and S_2 stable configurations. The molecule has switched 1, 3, and 9 times when the STM tip is in position P_1 , P_2 and P_3 respectively. From the distribution of the time of excitation before switching, the switching yield has been derived at each position for V_s= -2.5 V; $Y_{S1 \rightarrow S2}(P_1) = 2.7 \pm 0.5 \ 10^{-12}$, $Y_{S1 \rightarrow S2}(P_2) = 2.5 \pm 0.3 \ 10^{-13}$ and $Y_{S1\rightarrow S2}(P_3) = 5.0\pm0.6 \ 10^{-11}$. This result shows that the switching yield varies by more than two orders of magnitude simply by moving the STM tip only 4 Å inside the molecule (from P₂ to P₃). Quite surprisingly, the switching yield is maximum when exciting the less mobile part of the molecule (location P₃). There are additional features in the tunnel current curves of Figure 1 consisting of narrow peaks that are far more scarce in curves P_2 and P_3 as compared to P_1 . We assign the narrow features to the movement of the molecule into a transient state (T) located between the two stable states (S₁ and S₂) of the bistable molecule. Transient states can be observed only if their lifetime is longer than ~ 1 ms because the frequency bandpass of our tunnel current detection is limited to about 1.3 KHz.

The markedly different molecular dynamics and switching yields at positions P_1 and P_3 inside the biphenyl molecule have been assigned [5] to injection of charges (injection





of holes, i.e. removal of electrons) into localized π_1 and π_2 molecular orbitals. Indeed, as seen in the dI/dV STM spectroscopy (Figure 2), the π_1 and π_2 molecular orbitals are localized at the positions of the mobile and fixed phenyl rings respectively. This localization of the molecular orbitals probably reflects the relatively weak coupling between the two phenyl groups of the molecule, which interact more strongly with the silicon surface. Thus, depending on the precise location of the STM tip inside the molecule, different electronically excited states (π_1 and π_2 resonances) of the molecular system can be produced, each associated with a specific molecular movement.



Figure 3: (a) Tunnel current during a negative bias pulse at P_2 (Vs = -4V, t = 8s). Desorption of the hydrogen atom occurs at time t_{d^*} (b) Tunnel current during a negative bias pulse (Vs = -4V, t = 8s) after hydrogen desorption. (c) and (d) 20 Å by 20 Å STM topographies of the biphenyl molecule before and after the hydrogen desorption. The arrow indicates the area where the hydrogen atom has been removed leading to a slightly higher local density of states.

Compared to other molecular quantum control methods based on the use of photon absorption selection or coherent control rules [7], the real space picometer-scale control method described here has the advantage of working with single molecules and of dealing with a completely different concept based on the selection of a specific electronically excited state through the spatial localisation of the excitation inside the molecule. We emphasize that in this particular case of the bistable biphenyl, the picometerscale electronic control is associated to the localization of initial molecular electronic states. However, similar effects can also occur in the case of initial fully delocalized molecular electronic states provided the charged excited electronic states are localized enough.

Mastering the molecular dynamics of a single molecule by single atom manipulation

We have seen in the previous part that the $S_1 \rightarrow S_2$ switching requires one of the molecular phenyl rings (called the mobile phenyl ring) to break two Si–C bonds in its butterfly position, to move over the Si-H bond and to make two new Si–C bonds to recover its butterfly position at the second silicon dimer

site. In the meantime, the other molecular phenyl ring (called the fixed phenyl ring) is expected to rotate around its single Si–C bond. It follows that the Si–H bond behaves as an obstacle to the operation of the bistable molecule since a part of the molecule has to pass over the hydrogen atom for switching to occur. Therefore, we decided to desorb this hydrogen atom with the STM tip in order to explore the resulting dynamics of the molecule. The desorption of hydrogen has been performed by using a negative surface voltage $V_S = -4$ V with the STM tip on top of the hydrogen atom (position P₂ in Figure 1). The desorption of the hydrogen atom after an excitation time t_d is clearly evidenced in the tunnel current curve of Figure 3. Indeed, before time t_d, the molecule switches only once from S₁ to S₂. After a time t_d, the molecule has a completely different behaviour. It switches much more often between the S₁, S₂ and T states. We





Pico-Inside

Figure 4: (23 Å by 23 Å) STM topographies of the four stable configurations of the biphenyl molecule after its H atom desorption. (a) and (c) depict the S_1 and S_2 configurations respectively. (b) and (d) show the two new stable S_3 and S_4 configurations. The series a) to d) (following the arrows) is a succession of molecular manipulations of the multistable molecule using negative surface pulses (Vs = -3.0 V) applied at the indicated black dots.

have found that the switching yields for excitation pulses of - 3.5 V are increased after hydrogen desorption by a factor 3 to 50 depending on the excitation position and the molecular movement ($S_1 \rightarrow S_2$ or $S_1 \rightarrow T$). Another interesting consequence of the hydrogen desorption is that the molecule can now be switched (by applying a pulse voltage ($V_S = -3.5 V$)) into any of the four molecular configurations imaged in Figure 4. The S_1 and S_2 states are the same as before hydrogen desorption, whereas two new states (S_3 and S_4) of the molecule can be imaged with the STM. The occurrence of the four stable states $(S_1 \text{ to } S_4)$ and the transient states (T) can be seen in the tunnel curve (Figure 4e). Compared to the operation of the bistable molecule, where the biphenyl molecule could be switched only between two stable states (S_1 and S_2), the operation of the multistable molecule after hydrogen desorption is much more complicated since it can now be switched between four stable positions $(S_1, S_2, S_3 \text{ and } S_4)$ [8]. So far, we have found the switching of the multistable molecule to be random. A sequence of switching shown events is in Figure 4. Nevertheless, further studies as a function of the pulse voltage and the position of the STM tip are required for a more complete understanding of the multistable molecule operation. These

results reveal that a precise control of each atom position around the molecule needs to be achieved if a quantitative operation of a molecular device is required. This single atom sensitivity can give rise to very interesting perspectives for engineering the performance of a molecular device. One can expect being able to control, by single atom manipulation, not only the operation of a molecular device but moreover its intrinsic performance (e.g the switching frequency or the number of stable states).

Conclusion

We have shown two examples demonstrating that the picometer-scale precision is required to properly control the operation of a single molecule. The localization of charge injection inside the molecule with a picometer-scale precision offers an interesting method to control the charge transfer through the molecule. This has been evidenced here by studying inelastic charge transfert. However, one can anticipate that this will be valid also to control elastic charge transfert. The second example demonstrates that the intrinsic performances of a single molecule device can be





controlled by manipulating a single atom nearby. These examples reveal the complexity of molecular electronics. However, they offer interesting grounds to develop new concepts for single molecule electronics.

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2b. Semi-classical





Semi-classical OR, AND, XOR molecule logic gate circuits

M. Hliwa ^{1, 2}, N. Jlidat² and C. Joachim¹

¹Centre d'Elaboration de Matériaux et d'Etudes Structurales (CEMES-CNRS) 29, rue Jeanne Marvig, BP 94347, 31055 Toulouse Cedex 4, France

² Faculté des Sciences Ben M'Sik, Université Hassan II- Mohammédia BP 7955, Sidi Othman, Casablanca, Morocoo

Introduction

То construct an electronic circuit, electronic devices normally are interconnected in series and parallel following the Kirchhoff electrical circuit laws. For mono-molecular electronics, one can follow the same: (1) to design specific chemical group able to perform like a wire, a rectifier, a switch and even like a transistor and (2) to create an intramolecular complex logic function by covalently bonding all those chemical aroups together. For such an intramolecular architecture, there are 2 main options: to copy the standard electronic circuit architecture inside a molecule or to use quantum intramolecular circuit properties to design the circuit. For standard circuit architecture, new and more efficient intramolecular diode have been designed and molecule integrated to form a molecule-OR and a molecule-NAND. For the molecule-XOR, intramolecular inelastic effects are necessary to provide the carry instead of using a zener diode as usually proposed in the literature. Finally, we have shown that already for a simple molecule OR gate, it is better to abandon the usual diode logic approach and to play with intramolecular electron transfer property to design better molecule logic while keeping a circuit design.

An efficient intramolecular diode logic

Standard molecule OR and AND diode logic have already been proposed in the literature. But the rectifier chemical groups used in those design were the original Aviram-Ratner rectifier. The electron transfer rate through such long molecule is too small to permit the design of an intramolecular circuit larger than an AND



Figure 1: A systematic study of the D-o-A molecular rectifiers using a simple CH_2 ligand between the D and A chemical group. (b) The I-V characteristics of our best molecular rectifier for a σ or a π adsorption. The tunnel current is now reaching 1 μ A in the rectification Voltage range.







Figure 2: Intramolecular tunnel circuit implantation of an AND, OR and XOR logic gate using a full diode logic implantation. A, B, C and D are the part of the molecule chemisorbed on the atomic scale electrode (See one example below using our N-ESQC routine)

molecule. We have selected very short Donor-Acceptor (D-A) rectifiers where the electronic decoupling between D and A is obtained via a very short saturated bridge. Our best one is with $A = NO_2$ and $D = NH_2$ as presented in Figure 1.

Having a very efficient molecular two of those were rectifier, integrated in a single molecule to the recover OR and AND functions within one molecule and to attempt the design of an XOR gate as proposed by the Mitre corporation. All the calculation were performed using our N-ESQC calculation technique at the Extended Huckel molecular orbital level of approximation taking into account the full valence molecular orbital of the molecule positioned between N electrodes. For the OR and AND gates, new molecules were designed as compared with

our previous design using the Aviram-Ratner. For the XOR, we have followed the Mitre corporation design as presented in Figure 2.

To assess each design, we have calculated the logic surface of each molecular logic gate. The logic surface is just the output current as a function of the 2 input voltages on the molecule. As presented in Figure 2, only the OR molecular gate is working almost fine. There are 2 logic level "1". But a good external threshold device will clear this problem. Furthermore and as expected, the running current of this OR gate is around 100 nA instead of 10 fA in the previous design. This is not the case for the AND and XOR molecule logic gates. For the AND gate, the problem comes from a bad optimisation of the 4th D branch supposed to mimic the output resistance in a diode logic approach. For the XOR gate, the proposed Mitre molecule was tested and compared to our own design (Figure 3). The Mitre idea of mimicking a zener diode by an intramolecular asymmetric tunnel barrier is not working. This demonstrates the limit of implementing intramolecular diode logic in a single molecule.



Figure 3: The surface logic of the AND, OR and XOR gate molecule given in Fig. 2. Only the OR surface (middle) is almost the answer of an OR gate.



A semi-classical XOR molecule

Since the standard diode logic approach is not working for logic gates more complex than an OR gate, we have explored inelastic effects to realise the threshold detection function required for an XOR gate. The intramolecular XOR design is based on diode logics, bonding together 2 molecular rectifiers to fulfil the a+b operation followed in series by an intramolecular gating effect based on the rotation of a short molecular wire activated by the a+b tunnelling current as formally illustrated in Figure 4. The main difference with an electrical circuit is that from the electrodes 2, 3 to the ground 1 on one side and to the XOR output 4 on the other side, there is no voltage drop inside the molecule at nodes 5 or 6. This peculiar property leads to molecule OR gates with 2 different current intensity outputs assigned to the same output logic status "1". In the following and as illustrated in Figure 4, this inconvenience was transformed in an advantage by using this large output current intensity to force the gate output current to zero when (a,b)=(1,1). The inelastic tunnel effect has been studied in detail for the XOR gate to work realistically.

The number of electrons transferred per second through the central pyrene controls now its conformation relative to the planar axis of the 3 electrode tunnel junction. A small variation of the pyrene rotation angle Φ has a large effect on the tunnelling current circulating in the output 1-4 meshes. The voltage source V of this 1-4 mesh brings the energy required to set-up the current intensity I_{14} of the XOR output. This mesh is independent of the 3-1 and 2-1 input meshes driven by the voltage input V_2 and V_3 . For the Φ = 120° pyrene equilibrium conformation, the N-ESQC $T_{12}(E)$ spectrum (respectively the $T_{13}(E)$ spectrum) from nano-electrode 1 to nanoelectrode 2 (respectively from 1 to 3) accumulates all the MO resonances of the pyrene and of both molecular rectifiers. The LUMO is almost degenerated and corresponds to the π^* nitrophenyl MO of the 2 molecular rectifiers. On the HOMO side, the incursion of the π pyrene





Figure 4: Design principle of the XOR molecular gate and its proposed implementation with a 4 terminal tunnel junction properly interconnecting a single molecule.



Figure 5: The T(E) spectrum of the full gate from the nano-electrode 2 to the ground 1. Notice how the HOMO is no more a rectifier state and how T(E) is almost symmetric around the Fermi level indicated by the dashed line.

and hybrid pyrene-phenyl MO is an indication of the difficulty to pill up many classical functions (here 2 rectifiers and one rotor) in a single molecule and expecting at the same time to preserve intact their individuality in the overall electronic structure of the final molecule. The HOMO of the molecule-XOR is now a π pyrene MO and not a rectifier MO. As a consequence, an almost symmetric T₁₂(E) spectrum arises around Ef from the HOMO to the LUMO resonances. At 120°, the mixing between all those states





is less pronounced than in a planar conformation which preserves a bit of the rectification effect.

Starting at the equilibrium $\Phi = 120^{\circ}$ conformation for V₂ = V₃ = 0.0 V where I₁₄(120°) encodes the "0" logic output depending on the V bias voltage, the dynamic equilibrium Φ is determined by Ic as a function of V₂ and V₃. A semi-classical inelastic tunnelling approach was used to model how I_c controls this pyrene conformation change. In this approach, the tunnelling current intensity calculated using the N-ESQC technique provides the necessary energy to force the rotation of the pyrene fragment. $I_c(\Phi)$ is maximum for $\Phi = 165^{\circ}$. But this is not the pyrene equilibrium angle at $\Phi = 120^{\circ}$. Therefore, $I_c(\Phi)$ drives the dynamic equilibrium angle up to an angle where the inelastic force equilibrates with the gradient of the rotation potential energy curve of the molecule. The position of 4 was optimised in such a way that for the pyrene inelastic tunnel constants and for V_2 or (exclusive) V_3 larger than 400 mV, the Φ value where both forces equilibrate is around 135°. For the nano-electrodes optimised position presented in Figure 4, this leads to the $I_{14}(\Phi)$ local maximum encoding for a "1". When now both V_2 and V_3 are reaching 400 mV, I_c doubles just by superposing the 2 meshes 1-2 and 1-3 current via the common pyrene branch. The dynamic equilibrium conformation is shifted toward Φ = 157° corresponding to the second $I_{14}(\Phi)$ minimum encoding for a "0".



Figure 6: The surface logic of the Molecule XOR proposed in Fig. 2. The ideal XOR response and its actual one are presented from the top for comparison.

The full surface logic of the P1.1 molecule-XOR is presented in Figure 6. The "0" output is corresponding to an I_{14} current around 100 pA for V = 100 mV. The "1" plateau is large enough to stabilise a I_{14} current around 220 pA for V= 100 mV. The difference



Figure 7: Atomic scale implantation of a 3 electrode detector based on the rotation of the pyrene angle as a function of incident tunnelling current intensity. Electrode 3 is here to detect the pyrene rotation.

between "0" and "1" is large enough to be detectable even if as presented in the Figure 6 insert. Our design deforms the ideal XOR response logic and therefore reduces the immunity of the molecule-XOR gate to input voltage noise especially for the "0" inputs.

To support the design this XOR intramolecular logic gates where a non-linear effect is clearly required we have considered vibrational and rotational excitation effected by the tunnelling electrons. The calculation technique developed links the elementarv electron transfer through the phenomenon molecule to its vibrational degrees of freedom. A time dependant generalisation of the Davidov vibronic Hamiltonian is first used.



The time dependence is compulsory to respect the detail quantum time dependent process of the superexchange mechanism through the molecule. Then, two averaging procedures are done. One for the electron transfer process to get the tunnel current intensity using the Erhenfest theorem and one for the mechanical degree of freedom of the This is self-consistent molecule. process between the electronic and the mechanical degree of freedom. The outcome is the average geometrical change of the molecule as a function of the tunnelling current intensity. This is a generalisation of the procedure introduced for a single Xe atom tunnelling heating process. complication with a large The molecule is to determine what are the active and not active mechanical degrees of freedom during an electron transfer process since the selection rules are not the same as if the electrons were transported ballistically through the molecule.

Before applying our technique to the XOR molecule gate presented in Figure 4 and as a first application of our I-ESQC approach, a simple 3 terminal single electron detector molecule interacting with 3 electrodes was studied as presented in Figure 7. The multi-channel multi-electrode problem being calculated using our N-ESQC routine with a full valence molecular orbital description of the junction.

We have calculated 2 essential characteristics of the 3 terminal device presented in Figure 7: 1) The detail mechanics of the pyrene rotation with and without the third electrode using a fairly good precision MP2 (6-31G) quantum chemistry technique and 2) the electronic transparency of the molecule as a function of the pyrene torsion angle using the N-ESQC technique (See Figure 8). Those 2 characteristics are used to self consistently calculate the inelastic induced conformation



Pico-Inside

Figure 8: (a) Variation of the molecule potential energy as a function of the pyrene rotation angle with and without the detection tip on. (b) Electronic transparency variation through the full molecule as a function of the pyrene rotation angle.



Figure 9: Variation of the pyrene rotation angle as a function of tunneling current intensity passing trhough the molecul. The 2 electrodes atomic scale implantation is also presented.





change of the molecule in a semi-classical approximation.

One curve of interest is the permanent rotation angle of the pyrene as a function of the current intensity (Figure 9). At very low tunnel current intensity and starting at the equilibrium 48° equilibrium conformation, this curve is almost linear until saturation occurs due to large spring constant of the pyrene rotation. This model was used to calculate the logic surface of the molecule logic gate presented in Figure 4.

Using intramolecular circuit rules to design a simple OR gate



Figure 10: The T(E) spectrum of a simple molecule-OR designed without any molecular rectifier chemical groups. There is a conjugation break along the branch 2 and 3 which is creating a faster tunnelling decay with length between 2 and 3 than between 2 and 1 (3 and 1).

A first consequence of the work on the XOR molecule above is that it is very difficult to pill up in a single molecule many classical logic function and to recover the detail spectrum of each classical part in the T(E) spectrum of the final molecule. Pilling up MO resonances of different elementary logic functions like wire, rectifiers and switches produces a T(E) spectrum formally equivalent to the one of the XOR where the rectifiers resonances are no more the one which play a role in the molecule XOR. For a complex logic function, it seems more "natural" to pill up those resonances playing with interference effects than to simply superpose those levels.

A second consequence comes also from the absence of the HOMO rectifier state in determining the overall logic performance of the semi-classical molecule XOR (Figure 5). Since a rectification effect is not required to get the XOR, we have decided to explore the design of an OR function without any rectifier. This is not possible with standard electrical classical circuit, but very easy to get inside a molecule and in the tunnel regime.

The explanation for an OR design without any molecular rectifiers is the following. In a standard electrical circuit, the two rectifiers of an OR gate are required to avoid any direct current from one input to the other in a 01 or

10 input configuration. But with molecular wires, the tunnelling current decay exponentially with an increase of the length of the wire. Therefore and relative to the output electrode, a simple way to isolate the 2 inputs whatever the input logic configuration is to play with this exponential decay which must be much faster between the 2 inputs than between one input and the output. The T(E) spectrum of a simple molecule designed following this principle is presented in Figure 10. In Figure 11, a simple molecule without any break of its conjugation is presented. Here, all the 3 T_{ii}(E) are equivalent. A series of those molecules are now under synthesis.

Conclusion

A molecule OR logic gate built by assembling two Ratner-Aviram diodes delivers a too small output current intensity (in order of fA, when the input branches are biased up to 100 mV) to be used as building block for a mono-molecular logic device like for





example to construct a half-adder or a full one-bit adder. This is the main limitation of a semi-classical approach of monomolecular electronics. By reducing the molecular diode length, we have designed a molecular logic gate where the output current intensity is of order of few ten nA (for input applied bias voltage of 100mV). However, this improvement is not sufficient for integrating these gate inside a large logic circuits and to obtain a measurable output current intensity.

Notice that the output current intensity does not depend only on the molecular length of the circuit but also on the intrinsic electronic structure of each of these components, on the degree of molecular orbital mixing and on the amplitude of the electronic clouds associated with these components. An electronic component chemical group (diode, or elementary logic gate) embedded inside a molecule can plays the role assigned to it. But in this case, its structural and electronic identity must be protected inside the molecule chemical structure. It can be done only by inserting insulating aliphatic chains

in between these chemical groups. But this separation goes against the necessity of a delocalization of the electronic cloud over the full molecule to achieve a measurable output current intensity.

The electronic interactions between the molecular orbitals of different chemical groups (diodes, branches...) of a molecule circuit induces (by superposition of the symmetry adapted levels) interference phenomena, resonances and T(E) transmission peak overlapping in the valence region of the electronic spectrum. This modifies in a drastic way the electronic behaviour of the individual chemical group initially optimized to perform a given logic function inside a large molecule. These modifications have an incidence on the nature of the frontier orbitals, on the width of the homo-lumo energy gap and then on the shape of the logic responses.

These remarks bring us to the final conclusion that the assembling of a circuit chemical group by chemical group expecting the larger molecule to behave like a complex logic function is not working for molecular electronics. New strategies must be followed instead of forcing a molecule to mimic the shape of an electronic circuit.



Figure 11: The T(E) spectrum of a simple molecule designed without any molecular rectifier chemical groups nor any conjugation breaking. As a consequence there is no independence of the 2 inputs in comparison with the Figure 10 molecule.

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2c. Quantum (qubits and QHC)





Geometrical Approach of Quantum Hamiltonian Computer

N. Renaud ¹, P. Solinas ², R. Mosseri ²and C. Joachim ¹

¹ CEMES, 29 rue Jeanne Marvig, 31055 Toulouse, France ² LPTMC, CNRS et UPMC, 4 Place Jussieu, 75252 Paris, France

1 Introduction

Recent progresses in atomic-scale technologies are opening the possibility to control the intrinsic time evolution of a unique quantum system like a single molecule. This evolution, described by the time dependant Schrödinger equation, can be used to realize a quantum logic gate. In one design studied by Pico-Inside, the energy necessary for the quantum system to compute is brought by the preparation of a non-stationary state, the data are encoded directly in the Hamiltonian and the results of the calculation are measured on the occupation probability of the system on the target states beforehand defined [1] [2].

In this Quantum Hamiltonian Computer (QHC) approach, it can be easily shown that, in order to compute, the system requires at least three quantum states. A complete representation of the evolution of this system on its quantum state space is required to appreciate how the quantum trajectory is controlled by the input. Without loosing information, the Bloch representation can only map the evolution of two states systems. In Pico-Inside we explored an other approach, adapted from a representation originally proposed by E. Majorana in 1932 [4] in the context of high spin systems, and which allows to completely describe the evolution of a N states system.

2 Design of a Quantum Hamiltonian Logic Gate

Like any quantum machine, a QHC needs energy to work [3]. An elegant solution to supply this energy is to initially prepare the system, described by a Hamiltonian H in a non stationary state $|\Psi_0\rangle$ increasing its energy with respect to its ground state energy. This state can be written on the eigenbasis of the system, $\{|\phi_1\rangle ... |\phi_n\rangle ...\}$, as:

$$|\psi_0
angle = \sum_n a_n(0) |\phi_n
angle$$

The system will then evolve spontaneously, following the time dependant Schrödinger equation:

$$i\hbar\frac{d|\psi(t)\rangle}{dt}=\mathcal{H}|\psi(t)\rangle$$

leading to the standard expression for $|\Psi(t)\rangle$:

$$|\psi(t)\rangle = e^{-i\mathcal{H}t/\hbar}|\psi_0\rangle = \mathcal{U}(t)|\psi_0\rangle$$

where U(t) is the evolution operator which drives the evolution through the Hilbert space. For this evolution to allow for a computation process, the input data have to be encoded somewhere in the system. This can be done either in the Hamiltonian H or in the initial state $|\Psi_0\rangle$. In the QHC approach, the first strategy is followed: the initial state is fixed (among the local basis states) whereas the Hamiltonian H(θ_1 , θ_2 , ..., θ_n) depends of the input data θ_i . Starting from this constant initial state, the system therefore experiences different time evolutions (distinct paths through the Hilbert space) depending on the Hamiltonian. This is in sharp contrast with the well known





quantum computer qubit approach where unitary transforms associated with the different logical gates are driven by constant Hamiltonians, while the input data are coded in the initial state $|\Psi_0(\theta_1, \theta_2, ..., \theta_n)\rangle$ (in addition, handling linear combination of basis states is central in that approach).

The simplest way in which the result of the computation could be read from the system time evolution is to measure the population, P(t), of a beforehand defined target state, at a specific measurement time (called here t_m). Besides, periodic evolutions should allow to perform the measurement not only at t_m but at each odd multiple of t_m .

$$\mathcal{P}(t_m) = |\langle \psi_{target} | \mathcal{U}(\Theta_1, \Theta_2 \dots \Theta_n)((2k+1)t_m) | \psi_0 \rangle|^2$$

One expects for instance that the population of the target state reaches exactly one, whenever the (logical) result of the computation is expected to be one, and be zero otherwise. Note once again that the above expression supposes that one has been able to define a system which behaves periodically with a quantum state oscillation between the initial and the target state.

The general scheme of a quantum Hamiltonian computer is illustrated in Figure 1.



Figure 1: General scheme for a quantum Hamiltonian computer

3 Realisation of a quantum Hamiltonian XOR gate

input 1	input 2	output
0	0	0
0	1	1
1	0	1
1	1	0

Figure 2: Truth table of a XOR gate

To give a clear example of a QHC, we present here a simple analytical model of an *XOR* gate embodied in a four level system. The truth table of a such gate is recalled on Figure 2. We have studied the four level quantum system shown in Figure 3 represented by the Hamiltonian 5, where μ and e are fixed parameters, and α and β are the two parameters which will be used to encode the input data of the computation.







The initial state is the first state of the basis and the target state is the last one. The input data can be either encoded in the phase of the two parameters α and β or in the strength of those couplings. In the following we present Hamiltonian H generating periodic evolution leading to P(t_m) = 1. It can be proved that a periodic evolution is obtained for commensurate eigenvalues of the Hamiltonian.

Figure 3: Four level system chosen to perform a XOR gate

 $\mathcal{H} = \hbar\omega \begin{pmatrix} 0 & \mu & -\mu & 0\\ \mu & e & 0 & \alpha\\ -\mu & 0 & e & \beta\\ 0 & \alpha & \beta & 0 \end{pmatrix}$

3.1 Encoding in the phase of the couplings

If one only allows for phase control in the Hamiltonian entries, the inputs parameters can be written a: $\alpha = e^{i\phi_1}$ and $\beta = e^{i\phi_2}$. In this case the Hamiltonian is:

$$\mathcal{H} = \hbar \omega \begin{pmatrix} 0 & \mu & -\mu & 0\\ \mu & e & 0 & e^{i\phi_1} \\ -\mu & 0 & e & e^{i\phi_2} \\ 0 & e^{-i\phi_1} & e^{-i\phi_2} & 0 \end{pmatrix}$$

The eigenvalues of this system are given by:

$$\lambda = \hbar \omega \frac{e}{2} \pm \frac{1}{2} \hbar \omega \sqrt{e^2 + 4\{(1+\mu^2) \pm \sqrt{1+\mu^4 - 2\mu^2 \cos(\phi_1 - \phi_2)}\}}$$

To simplify the study of the eigenvalues commensurability, we can impose e=0. Note, nevertheless, that this is not a necessary condition and equivalent results could be reached with $e \neq 0$. In the 00 and 11 configurations, so when $\phi_1 = \phi_2 = \phi$, the result of the computation must be equal to zero. In this case the eigenvalues are given by the simple formula: $\lambda = \hbar \omega 2^{\frac{1}{2}}$ [- μ , -1, 1, μ]. Computing the evolution of the system of the target state we find it is never populated along the evolution. To understand this interference phenomenon we can apply a $\pi/4$ rotation defined by:

$$\mathcal{R}(\theta) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(\theta) & \sin(\theta) & 0 \\ 0 & -\sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

on the two central state of the Hamiltonian. This rotation does not change the initial and the final state, applying the rotation we find:

$$\tilde{\mathcal{H}} = \mathcal{R}^{\dagger}(\frac{\pi}{4})\mathcal{H}\mathcal{R}(\frac{\pi}{4}) = \sqrt{2}\hbar\omega \begin{pmatrix} 0 & \mu & 0 & 0 \\ \mu & 0 & 0 & 0 \\ 0 & 0 & 0 & e^{i\phi} \\ 0 & 0 & e^{-i\phi} & 0 \end{pmatrix}$$





So as the initial and the target state are still the first and the last on the basis we clearly see here that they are not connected by the Hamiltonian. This explains why the population of the target state remains zero during the evolution. In the two others configurations, i.e when $\phi_1 \neq \phi_2$, the eigenvalues are $\lambda = \hbar\omega 2^{\frac{1}{2}}[-(1+\mu^2)^{\frac{1}{2}},0,0,(1+\mu^2)^{\frac{1}{2}}]$, and the population of the target state must reach one. Applying the same rotation on the Hamiltonian we find:

$$\tilde{\mathcal{H}} = \frac{\hbar\omega}{\sqrt{2}} \begin{pmatrix} 0 & 2\mu & 0 & 0\\ 2\mu & 0 & 0 & e^{i\phi_1} - e^{i\phi_2}\\ 0 & 0 & 0 & e^{i\phi_1} + e^{i\phi_2}\\ 0 & e^{-i\phi_1} - e^{-i\phi_2} & e^{-i\phi_1} + e^{-i\phi_2} & 0 \end{pmatrix}$$

So if $\phi_1 = \phi_2 + \pi$ one coupling in the Hamiltonian is null since $e^{i\phi_1} + e^{i\phi_2} = 0$ and the system is like a three states system, where the initial and the target state are coupled through a third state, this situation is represented by the Hamiltonian:

$$\tilde{\mathcal{H}} = \sqrt{2}\hbar\omega \begin{pmatrix} 0 & \mu & 0 & 0\\ \mu & 0 & 0 & e^{i\phi}\\ 0 & 0 & 0 & 0\\ 0 & e^{-i\phi} & 0 & 0 \end{pmatrix}$$

In this configuration a necessary condition to have a resonant evolution is to have the two modules of the coupling equals, so we must have $|\mu| = 1$. In a three state system, we already know which values of the energy of the central state gives a resonant evolution [5]. Then, we can modify the energy of the central state in the Hamiltonian and compute the inverse rotation. Doing this we find more complex Hamiltonians with resonant evolution. To give a clear example, we show on Figure 4 the evolution of the population of the target state in the four different input configurations in the simplest case, i.e where e=0, $\mu=1$ and the two phases can take two values 0 or π .



Figure 4: Evolution of the population of the target state for $\mu = 1$, e = 0, $a = e^{i\phi_1}$, $\beta = e^{i\phi_2}$ and $\phi_i = 0$ or π

The truth table of a *XOR* gate is satisfied since measuring at $t_m = (2k+1)\pi/(2\omega)$ the population of the target state will be one in the case of 01 and 10 input configurations and will be zero in the two other cases.





3.2 Encoding in the amplitude of the couplings

In the second solution, α and β take only two values 0 or 1, like their classical logic gate input counterparts. The optimisation in that case is trickier. In the 00 configuration, since the target state is not coupled with the rest of the system, its population will remain equal to zero. In the 11 configuration the system, like in the previous section, is again in a perfect interference case, so the population of the target state will remain equal to zero too. We now have to tune the 01 and the 10 configurations in such a way that the population of the target state reaches one at equal times. We first need to determine the value of μ . It can be shown that the only value of μ which allows the population of the target state to reach one is: $\mu = (1/2)^{1/2}$. We have then to find the values of e (a real quantity) which approach a periodic evolution.

$$\mathcal{H} = \hbar\omega \begin{pmatrix} 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0\\ \frac{1}{\sqrt{2}} & e & 0 & \alpha\\ -\frac{1}{\sqrt{2}} & 0 & e & \beta\\ 0 & \alpha & \beta & 0 \end{pmatrix}$$

The eigenvalues of the Hamiltonian (12) are:

$$\lambda = \hbar\omega \frac{e}{2} \pm \hbar\omega \frac{\sqrt{e^2 + 2\left[(\alpha^2 + \beta^2 + 1) \pm \sqrt{(\alpha^2 + \beta^2)^2 - 4\alpha\beta + 1}\right]}}{2}$$

In the 01 case, the eigenvalues become:

$$\lambda_{01} = \hbar \omega \frac{e}{2} \pm \hbar \omega \frac{\sqrt{e^2 + 2(2 \pm \sqrt{2})}}{2} = \begin{cases} \lambda_1 = \hbar \omega \frac{e}{2} - \hbar \omega \frac{\sqrt{e^2 + 2(2 + \sqrt{2})}}{2} \\ \lambda_2 = \hbar \omega \frac{e}{2} - \hbar \omega \frac{\sqrt{e^2 + 2(2 - \sqrt{2})}}{2} \\ \lambda_3 = \hbar \omega \frac{e}{2} + \hbar \omega \frac{\sqrt{e^2 + 2(2 - \sqrt{2})}}{2} \\ \lambda_4 = \hbar \omega \frac{e}{2} + \hbar \omega \frac{\sqrt{e^2 + 2(2 - \sqrt{2})}}{2} \end{cases}$$

For a periodic evolution, the Hamiltonian must have four commensurate eigenvalues. We can tune easily the system to present at least two commensurate eigenvalues by finding the e values which lead to:

$$p(e) = \frac{\lambda_3(e)}{\lambda_2(e)} \in \mathbb{Q}$$

Solving (15) we find:

$$e = \pm (p-1)\sqrt{\frac{2-\sqrt{2}}{2p}}$$

where $p \in Q$. We can then optimize p such that the four eigenvalues are almost commensurate. One simple example is p = 42/10 leading to:

$$e = \pm 3.2 \sqrt{\frac{2 - \sqrt{2}}{8.4}}$$

which gives the eigenvalues: $\lambda \cong 1/\lambda_2$ [-3.6, -1, 4.2, 6.8]ħ ω , and the evolution presented in Figure 5. This evolution is quasi-periodic since λ_1 and λ_4 are not commensurate with λ_2 and λ_3 .





Figure 5: Evolution of the population of the target state for $\mu = 2^{-\frac{1}{2}}$, $e \sim 0.85$, a = 0 or 1 and $\beta = 0$ or 1

Like in the previous case, the truth table of a *XOR* gate is satisfied, since the population of the target state reaches almost one. For instance $P(t_m) > 90$ % in the 01 and 10 configurations for k values as big as 10^3 , with:

$$t_m = \frac{2k+1}{\omega} \frac{2\pi}{\sqrt{e^2 + 2(2+\sqrt{2})} - \sqrt{e^2 + 2(2-\sqrt{2})}} \approx \frac{2k+1}{\omega} 4.57$$

4 Study of the trajectory of a N state system by the Majorana representation

There are several ways to represent the evolution of a quantum system. For two-state systems, which are ubiquitous in physical systems, the most useful representation is the so-called *Bloch representation* where the quantum state is represented as a point on a sphere. In this case, the Hamiltonian is even displayed as a vector, threading the sphere around which the representative point precess, in full analogy with a spin $\frac{1}{2}$ precessing around a magnetic field.

For *N*-level quantum systems, the situation is more complex. An unambiguous quantum state representation is still possible with *N*-1 points on a sphere, by considering the old, but poorly known, Majorana high spin representation. But in this case, as discussed below, the nature of the quantum state evolution can be rather complex on the sphere.

For a *N*-level quantum system, we associate to the state $|\Psi\rangle = \{a_1, a_2, ..., a_N\}$ a polynomial of degree *N*-1 defined as:

$$\mathcal{P}_{\psi} = \sum_{j=0}^{N-1} (-1)^j \begin{pmatrix} d \\ j \end{pmatrix}^{\frac{1}{2}} a_{j+1} z^j = a_{N-1} \prod_{j=1}^{N-1} (z - z_j)$$

In this way the state $|\Psi\rangle$ can be associated to the the N - 1 roots of the equation $P_{\Psi}=0$. These roots z_i (i=1,..,N - 1) are complex numbers, which can be represented on a sphere by means of an inverse *stereographic projection:*

$$(x(z_i), y(z_i), z(z_i)) = \frac{1}{1 + |z_i|^2} \{ \Re(z_i), \Im(z_i), 1 - |z_i|^2 \}$$







Figure 6: Evolution on the Majorana sphere for the XOR phase gate given by Hamiltonian (6). The evolution start with all the points at the south pole (cyan point) and the target state is reached when all the points are at the north pole (orange point). The curves represent the evolution of the points on the Majorana sphere.



Figure 7: Evolution on the Majorana sphere for the XOR aplitude gate given by Hamiltonian (12). The evolution start with all the points at the south pole (cyan point) and the target state is reached when all the points are at the north pole (orange point). The curves represent the evolution of the points on the Majorana sphere.

Therefore, the Majorana representation allows to describe a quantum state (and its evolution) with N-1 points on the sphere. To show how the Majorana representation can be useful in describing the quantum evolution, we analyse in details the two logical gates constructed in section 3 in both phase and amplitude cases. Since we are dealling with a 4-level system, the quantum state is described by three points on the Majorana sphere. The initial state, with respect to the local basis used in (5), is $|\Psi_0\rangle = \{1,0,0,0\}$ while the target state is $|\Psi_{\text{targget}}\rangle = \{0,0,0,1\}.$ Then, starting from $|\Psi_0\rangle$, if after a defined time interval the system ends up in the target state $|\Psi_{\text{targget}}\rangle$, the logical 1 value is assigned to the computation; if it does not end up in $|\Psi_{target}\rangle$ the logical 0 is assigned.

In the Majorana representation these states correspond to the (three) points gathered at the *south pole* ($|\Psi_0\rangle \rightarrow (0,0,-1)$) or at the *north pole* ($|\Psi_{targget}\rangle \rightarrow (0,0,1)$). Then, for the studied gate, we expect the system to reach the final state $|\Psi_{targget}\rangle$ if the logical input in the Hamiltonian (6) are (1,0) or (0,1). In terms of evolution on the Majorana sphere, we expect the three points to evolve from the *south pole* to the *north pole*, as can be seen in Figure 6.

For the logical 0 output (logical (0,0) and (1,1) inputs), the points never reach (simultaneously) the north pole, Figure 6. Note that, in these cases, only two curves are shown meaning that the third point remains at the *south pole* during all the evolution. We have further degree of freedom with the Majorana representation in order to simplify or to clarify some aspects the evolution. of Particularly useful is the possibility to describe the evolution is the basis which diagonalise the





Hamiltonian (5). In this case the initial and the final states no more sit at the poles, but the evolution on the Majorana sphere is simplified.

These simple examples show that the Majorana representation can be useful to describe the evolution of a quantum system. The possibility to visualise the quantum state on a sphere allows to clarify some features that in other cases should be more difficult to grasp. For example, in case of non-periodic evolution, the corresponding curves of the points on the Majorana sphere are not closed, as can be readily seen in this representation.

5 Performance of the XOR gate in phase and amplitude implantation

What is the most efficient implementation of an *XOR* gate in a QHC architecture? To answer this question we need to find a criterion which allows us to quantify the efficiency of those two approaches. One good solution is to compare the energy required for the computation. The initial non-stationary state presents an higher energy, $\langle \Psi_0 | H | \Psi_0 \rangle$ than the ground state energy E_0 of the system. Therefore the energy required for the computation is given by:

$$\Delta E = \langle \psi_0 | \mathcal{H} | \psi_0 \rangle - E_0$$

For the same computation time we can then estimate how much energy is required in the two versions in the different input configurations. The time-energy inequality ΔE $\Delta t \geq \hbar$ can also be used as a criterion to compare the efficiency of the logic gates. We have seen that the computation time for the *XOR* phase gate is $t_m = 1/_{2}\pi\hbar$. We have now to force the amplitude-*XOR* gate to have the same computation time. We just have to multiply its Hamiltonian by the ratio of the two computation times. Since the initial state is not the same on the eigenbasis for all the different configurations, the energy required is not the same. Following this approach we find the results shown in Figure 8.

Logical Input	E_{phase}	E_{Amp}
00	$\sqrt{2}\hbar\omega$	$1.92\hbar\omega$
01	$2\hbar\omega$	$2.75\hbar\omega$
10	$2\hbar\omega$	$2.75\hbar\omega$
11	$\sqrt{2}\hbar\omega$	$3.05\hbar\omega$

Figure 8: Energy required to perform the computation in the same time for both phase and amplitude implantation

The performance of the two implementations is quite the same even if the phase implementation is a little better in terms of energy, especially in the 00 and 01 configurations. Another interesting point is the encoding of the information in the system. In the classical case, the words used here are quite easy since they contain only two binary letters. As soon as we change the two parameters in the Hamiltonian we change its four eigenvalues, the four eigenvectors, and the development of the initial state in the eigenbasis. So eight real numbers are changed to encode the *XOR* four possible input configurations. Therefore this quantum input word contains in fact the four eigenvalues and the four coefficients of the initial state on the eigenvectors (eight in the generic case where eigenvectors may have complex coordinates). Following this procedure for the *XOR* amplitude gate we find the result shown in fig 9.

cWord				qW	Vord			
00	-0.663	0.000	0.845	1.508	0.833	0.000	0.000	-0.552
01	-0.950	-0.264	1.109	1.795	0.571	-0.635	0.310	-0.416
10	-0.950	-0.264	1.109	1.795	-0.571	-0.635	0.310	-0.416
11	-1.053	-0.663	1.508	1.898	0.000	-0.833	0.552	0.000

Figure 9: Encoding of the input data to go from a classical word (cWord) to a quantum word (qWord)





In the tabular 9 the four first numbers of the quantum word are the eigenvalues of the system and the last four are the coefficients of the initial state on the eigenbasis. Even if we still need new tools to understand better this translation process from the classic to the quantum word, we clearly see here that the classical logic input word is turned into a complex quantum word.

6 Conclusions

We have shown here how to design an *XOR* gate taking in account only the intrinsic quantum evolution of a three state system. The criteria of fidelity impose the system to present a periodical evolution and then commensurable eigenvalues in each input configurations. Even if finding a *N*_k*N* Hamiltonian with commensurable eigenvalues is an easy task, finding an Hamiltonian $H(\theta_1, \theta_2, ..., \theta_p)$, depending of *p* binary parameters with commensurable eigenvalues in each 2^{ρ} input configurations is much more complex problem. We can get around this difficulty finding quasi-periodc evolution of the population of the target state. Those kinds of evolutions are able to reach almost one and the measurement can be performed during many quasi-period of the evolution. However this periodicity problem plus the difficulty to access the exact wave function of the system at a very specific time leads, in the context of Pico-Inside, to design logic gates with others measurement process. One of those processes could be to encode the result of the computation in the frequency of the evolution of the population of the target state since we know that this frequency is related to the intensity of tunnelling current through the system.

The use of the Majorana representation provides a geometrical representation of the evolution of a general *N*-states system without any loss of information. Consequently it is a good tool to follow the evolution and understand the control of its trajectory by its own Hamiltonian.

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