MICRO-435

Exercises W12: Molecular Field Coupling Nanocomputing simulations

Introduction to ab initio simulation and molecular QCA modeling

In the previous lab, you have investigated the use of molecules as transistor. In this lab, you will investigate another computational paradigm based on molecules: Molecular Quantum-dot Cellular Automata (Molecular Field-Coupled Nanocomputing). The information is encoded in the charge distribution of the molecules and propagates thanks to local field interactions among neighbor molecules.

The laboratory is divided in two parts.

- **Analysis of Molecular FCN circuits.** In the first part, you will analyze simple Molecular QCA circuits using a tool developed at the Politecnico di Torino.
- **OPTIONAL: Bis-ferrocene molecule analysis** In the second part, you will analyze the behavior of a single bis-ferrocene molecule. This molecule is the building block of Molecular QCA circuits.

PART1: Analysis of Molecular FCN circuits

In the first part of this laboratory, you have to analyze some simple molecular QCA circuits. Two basic structures will be considered: the horizontal wire and the majority voter.

EEBESD_focus1: The horizontal wire

The first structure is the most simple QCA circuit, the horizontal wire. It is composed of 4 cells, each cell is represented by a couple of bis-ferrocene molecules. Its schematic representation is reported in Figure 1.

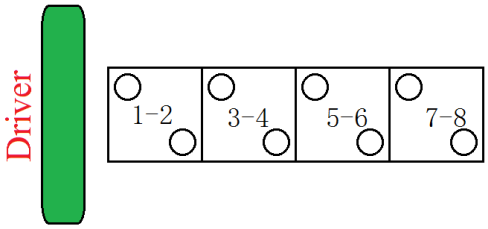


Figure 1: Molecular QCA wire composed by 4 cells, each cell is made by 2 Bis-ferrocene molecules.

Matlab input code for the horizontal wire is located inside the folder

Lab_molFCN/MolQCAcircuits

Execute the main script, *horizontalWire.m*, from Matlab.The outputs of the script are:

- a run time plot shows the input voltage and the charges computed along the wire in **each step of the self-consistent procedure**; In particular, the figure shows the current step (k) and the previous step (k-1) of the self-consistent procedure.
- some figures depicting the solutions of the circuit at **each time step** (saved in the folder *./SCERPA_OUTPUT_FILES/figures*).

Given the simplicity of this circuit, all molecules belong to the same clock phase.

SCERPA_focus1_Q1: Analyze with accuracy the variation of the charge distribution in each molecule between successive steps. Try to describe the propagation of the information in the wire. For each step, two figures are displayed. The top figure shows the input voltage on each molecule, the bottom figure shows the value of logical dots (DOT1 and DOT2) on the MQCA circuit. If you want to slow down the run time plot, then uncomment line 29.

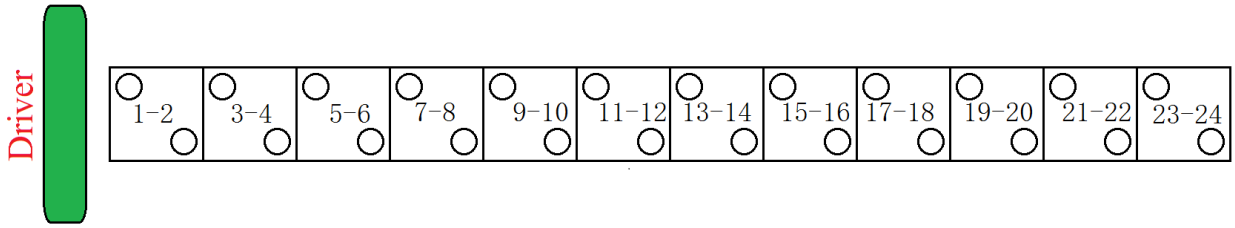


Figure 2: Molecular QCA wire composed by 12 cells, each cell is made by 2 Bis-ferrocene molecules.

Try now to simulate a longer wire, composed by 12 cells. To reach this goal open the *horizontalWire.m* file with a text editor, comment line 14 and uncomment line 15.

SUGGESTION: If you don't want to see all the simulation steps, open the file *horizontalWire.m* and comment lines 27 and 29. This will speed up the simulation.

SCERPA_focus1_Q2: Does the circuit behaves correctly also in this case? Considering the results obtained in the previous point, did you expect this result? Try to explain.

As you can notice from Figures 1 and 2 the wire is driven by input molecules, called for this reason *Drivers*. Look at the code which set the driver polarization, file *horizontalWire.m*, line 19. The number represents the input voltage of the driver, that is the voltage between *Dot*1 and *Dot*2. Now try to change the driver polarization (line 16 of the script *horizontalWire.m*), changing the sign of the driver input voltage.

SCERPA_focus1_Q3: Try to explain what happens, does the circuit behaves correctly reaching the expected output?

EEBESD_focus2: Intermolecular distance

Molecular QCA circuits work thanks to electrostatic interaction among neighbour molecules. The distance among molecules plays therefore a fundamental role. The aim of this exercise is to understand how critical is the distance among molecules. Open again on the file *horizontalWire.m*

with a text editor and, after the modifications, execute this file in Matlab. The intermolecular distance along the z axis is set at line 11. The unity is Angstrom (10 angstrom = 1 nm). Try to increase/decrease the distance among molecules using a step of 1 angstrom. Simulate again the wire with 4 cells.

SCERPA_focus2_Q4: What do you expect it happen if you increase or decrease the intermolecular distance? Are your expectations confirmed by the simulations?

SCERPA_focus2_Q5: What is the maximum range where the circuit behaves correctly?

EEBESD_focus3: Adiabatic propagation in the horizontal wire

Wires in mQCA technology are normally divided into clock zones, where different clock signals are applied. This mechanics is generally required to assure correct information propagation. The circuit is depicted in Figure 3. It is a wire made by 12 cells, divided in 4 clock zones. The output of the script are several figures (saved in the folder *./SCERPA_OUTPUT_FILES/figures*) that represent the charge distribution and the 3D view of the circuit in different time steps of the simulation. If you want to see the run time plot, then uncomment line 29.

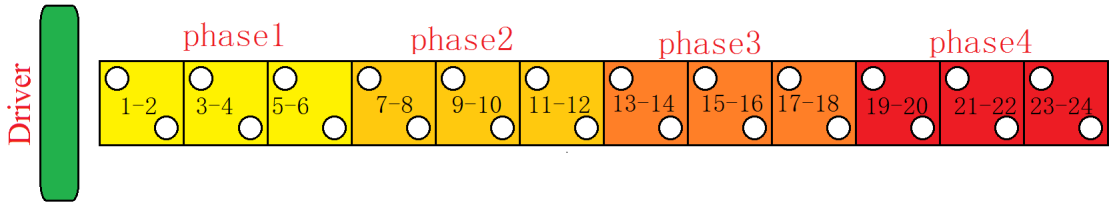


Figure 3: Molecular QCA wire with 4 clock phases.

Simulate the circuit. The input file is located in the folder

Lab_molFCN/MolQCAcircuits

Execute the *horizontalWire_4phases.m* file in Matlab.

SCERPA_focus3_Q6: How does the information propagate in the wire, is it consistent with your expectations?

Open the file *horizontalWire_4phases.m* with a text editor and, after the modifications, execute this file in Matlab. Distances among molecules is set in the file *horizontalWire_4phases.m*, line 11. The unity is Angstrom (10 angstrom = 1 nm). Try to increase/decrease the distance among molecules using a step of 1 angstrom.

SCERPA_focus3_Q7: What is the range of intermolecular distances in which the circuit works correctly?

SCERPA_focus3_Q8: Is the range different from the ranges that you have obtain in the exercise

, where no clock phases are used? Motivate your answer.

EEBESD_focus4: The Majority voter

The basic logic gate of molecular QCA technology is the majority voter, a logic gate where the output is equal to the majority of the inputs. The circuit is depicted in Figure 4. The circuit uses three clock phases, one for the input cells and one for the central and its neighbour cell. The output cell is on a separate clock phase. The outputs of the script are several figures (saved in the folder *./SCERPA_OUTPUT_FILES/figures*) that represent the charge distribution and the 3D view of the circuit in different time steps of the simulation.

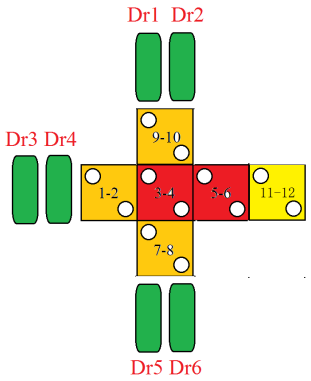


Figure 4: Molecular QCA majority voter.

Simulate the circuit. The required file is located in the folder

Lab_molFCN/MolQCAcircuits

Execute the *majorityVoter_3phases.m* file in Matlab.

SCERPA_focus4_Q9: How does the information propagate in the majority voter? Is it consistent with your expectations

To change the logic value of inputs you have to modify the variable *circuit.Values_Dr* at lines 23-28. Each column represents the values drivers assume in each time step. Try to understand how the drivers are set in the variable. Define a convention for the logic (i.e. which cell configuration encodes '0' and '1').

SCERPA_focus4_Q10: Try to apply all possible values to the input of the majority voter and write down the logic table of the device. Are the results consistent with your expectations? Explain.

SCERPA_focus4_Q11: Imagine fixing one of the three driver cells to '1', which logic function does the output represent w.r.t. the remaining two input cells? What if you fix one of the three driver cells to '0'

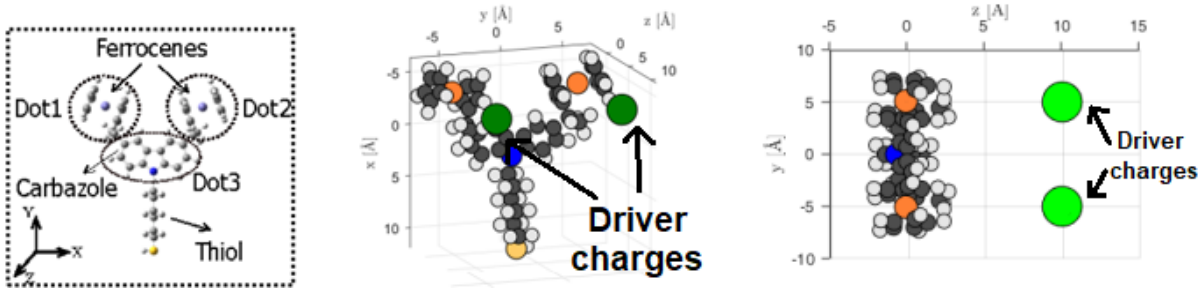
PART2: OPTIONAL, Bis-ferrocene molecule analysis

The Bis-Ferrocene molecule (Figure 5(a)) is a real molecule, synthesized ad-hoc for QCA purpose. The Bis-Ferrocene molecule is composed by two ferrocene units connected together by means of a carbazole. A thiol connects the carbazole to the substrate.

The thiol is an alkyl-chain ended with a sulfur element that is responsible for the interaction with the gold substrate for the self assembled monolayer (SAM) formation.

Particularly, the two ferrocenes represent the active/logical dots, responsible for boolean encoding, typically named (*Dot*1 and *Dot*2), while the carbazole acts as a central dot (*Dot*3). For a better description of the molecular electrostatics, a fourth dot (*Dot*4) is added. *Dot*3 and *Dot*4 together constitute the dot used to encode the "*NULL*" state.

Regarding the QCA cell and its functionality, since the Bis-Ferrocene molecule has only two logic dots (*Dot*3 and *Dot*4 are used only for the "*NULL*" state), the molecule could be considered as half QCA cell, a complete QCA cell could be implemented placing juxtaposing two molecules, so positioning one molecule near to a second one to obtain a square-shaped cell with four logic/active dots.



(a) (b) (c)

Figure 5: (a) Bis-ferrocene molecule structure (b) point charges emulating the driver (b) point charges emulating the driver (top view)

EEBESD_focus5: OPTIONAL: Charge analysis of the bis-ferrocene molecule

Matlab code for the analysis of the bis-ferrocene molecule is located in the folder

Lab_molFCN/bisferrocene/

Execute the script *Main.m*. In the first part of the script, it reads the output of ab initio simulations obtained with GAUSSIAN 09 and plots the distribution of charges. Four plots will appear, check Figure 6 for the details of the MATLAB figure. Notice that the three top plots are 3-D figures, you can rotate the plot as you prefer.

WARNING: the x-axis of the 1-D plot (Plot of Atomic charges) represents the labels of each atoms; the values corresponds to the labels you have seen with Avogadro in the previous exercise. The numbers in the plot of the aggregated charge are the values of aggregated charges. All charges are normalized w.r.t. the elementary charge. If you want, the .log file of the simulation can be also imported into the Avogadro tool to display the atom/label association.

The simulations have been carried out by inserting two point charges of variable values that emulate the presence of a driver molecule, see Figure 5(b) and a clock field. Consequently to the interaction between the molecule and the point charges, the distribution of charges of the bis-ferrocene molecule should change.
Select the simulation output associated to the bis-ferrocene, configuration 1, by uncommenting the proper lines in the setting section. Check the obtained figure.

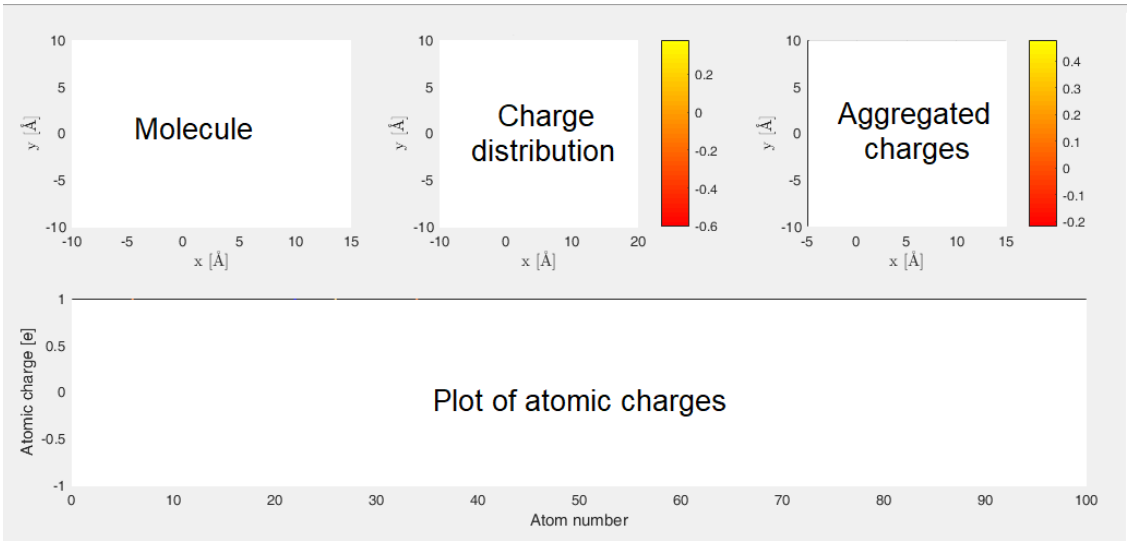


Figure 6: Output of the script

SCERPA_focus5_Q12: How is the charge distributed in the molecule? How are the aggregated charges distributed? Is there any correlation between the distribution of atomic charges and aggregated charges? Comment on it.

SCERPA_focus5_Q13: According to your knowledge, by looking at the distribution of charges, what is the value of the two point charges representing the driver? What about the clock field? Is it enhancing or prohibiting? Explain why.

Reminder: an enhancing clock favours the oxidation charge to occupy DOT1 and DOT2 so that the molecule CAN encode logic information.
Select the simulation output associated to the bis-ferrocene, configuration 2, by uncommenting the proper lines in the setting section. A green line will appear in the 1-D plot of the charges. This line represents the value of charges in configuration 1.

SCERPA_focus5_Q14: How is the atomic charge distributed in the molecule? What about the aggregated charges? Do you see any difference with the previous case? Is there any correlation between the distribution of atomic charges and aggregated charges? Comment on it.

SCERPA_focus5_Q15: According to your knowledge, by looking at the distribution of charges, what is the value of the two point charges representing the driver? What about the clock field? Is it enhancing or prohibiting? Explain why.

Select the simulation output associated to the bis-ferrocene, configuration 3, uncommenting the proper lines in the setting section. Check the obtained figure. The green line still represents the charges of configuration 1.

SCERPA_focus5_Q16: How is the charge distributed in the molecule? What about the aggregated charges? Do you see any difference with the previous case? Is there any correlation between the distribution of atomic charges and aggregated charges? Comment on it.

SCERPA_focus5_Q17: According to your knowledge, by looking at the distribution of charges, what is the value of the two point charges representing the driver? What about the clock field? Is it enhancing or prohibiting? Explain why.

EEBESD_focus6: OPTIONAL: The trans-characteristics

The first simple task involves the analysis of the V_{OUT} as function of the V_{IN} at different distances and with three cases of clock signals (no clock $0V/nm$, $+2V/nm$ and $-2V/nm$). The V_{OUT} is the voltage generated by a bis-ferrocene molecule. The V_{IN} is the input voltage, that means the output voltage generated by a neighbor bis-ferrocene molecule. The clock signal can be in three different states: no clock ($0V/nm$), clock reset ($-2V/nm$) and clock active ($+2V/nm$). Navigate to the folder

Lab_molFCN/VinVout

and execute from Matlab the file *VoltageCalculation.m*. The output is the Vout/Vin curve of the molecule when no electric field (clock) is applied. The Vout/Vin curve is evaluated considering three values of distance among two neighbor molecules, from 0.8 nm to 1 nm.

SCERPA_focus6_Q18: What is the gain (Vout/Vin) of the molecule for the three values of distance?

WARNING: you can evaluate the gain by evaluating the variation of the output voltage in the range $Vin = \pm 5$ V. We know that the gain will depend on the specific points you considered since the curves are far from being linear. You MUST specify how you get the gain values

Now, using the gain you have calculated, try to simulate what happens in a simple chain of five molecules. The first molecule has a fixed input voltage equal to 0.6 V. The Vin of the second molecule can be obtained from the Vin/Vout transcharactristics by fixing Vin=0.6 V. Then, calculate the Vout of the second molecule (i.e. the Vin of the third molecule) using the obtained second molecule Vin. Continue to find all the voltage of all molecules. Repeat the process for all three values of distance.

SCERPA_focus6_Q19: Does the information propagates correctly in these configurations?

Now, suppose you want to create a longer wire composed by N molecules.

SCERPA_focus6_Q20: What is the maximum length that a molecular wire can have to correctly propagate the information? (Consider the information to be valid if the absolute value of the input

voltage is $|V_{in}| > 0.2$ V)

Now change the file name in the file *VoltageCalculation.m*, line 5, to

bis-ferrocene_charge-distribution_ck-2.txt

corresponding to a clock signal equal to -2 V/nm (clock reset). Run again the main Matlab file e look at the resulting Vout/Vin characteristic.

SCERPA_focus6_Q21: Calculate the Gain Vout/Vin. Is it possible to propagate the information in this condition?

Finally change the file name in the file *VoltageCalculation.m*, line 5, to

bis-ferrocene_charge-distribution_ck+2.txt

corresponding to a clock signal equal to $+2$ V/nm (clock active).

SCERPA_focus6_Q22: What is the gain (Vout/Vin) of the molecule for the three values of distance in this case?

Now, using the gain you have calculated, try to simulate what happens in a simple chain of five molecules. The first molecule has a fixed input voltage equal to 0.6 V. The Vin of the second molecule can be obtained from the Vin/Vout transcharactristics by fixing Vin=0.6 V. Then, calculate the Vout of the second molecule (i.e. the Vin of the third molecule) using the obtained second molecule Vin. Continue to find all the voltage of all molecules. Repeat the process for all three values of distance.

SCERPA_focus6_Q23: Does the information propagates correctly in this configuration for all values of distance? What is the maximum length that a molecular wire can have to correctly propagate the information?