



## Theoretical Study of Molecular Quantum-Dot Cellular Automata

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**Abstract.** We present an *ab initio* quantum chemistry study of  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$ , a molecular candidate for quantum-dot cellular automata (QCA) which has been synthesized and characterized recently. Our studies support the experimental interpretation that this molecule has a bistable electronic state, and that binary information can be encoded in the molecular charge configuration. We show that when molecules are properly arranged, one molecule can be switched by the Coulomb interaction produced by a neighboring molecule. Our studies also show this molecule is error-tolerant when the four-fold symmetry is broken by a C–C single-bond distortion.

**Keywords:** molecular quantum-dot cellular automata, *ab initio* quantum chemistry calculation

### Introduction

Quantum-dot cellular automata (QCA) is an alternative approach to binary computing which may be more suited for nano-scale electronics than conventional transistors and current switches [1]. A QCA cell represents a bit through the charge configuration in the cell. As shown in Fig. 1(a), each cell is composed of four quantum dots and two mobile electrons. The two charge configurations shown in the figure represents a binary “0” and “1”. A cell’s charge configuration will be influenced by the Coulomb effect of its neighboring cells as shown in Fig. 1(b). This cell-cell interaction is the basis of QCA device operation. A detailed discussion of QCA characteristics can be found in reference [1].

Successful operation of several QCA devices has been demonstrated at cryogenic temperatures [2,3]. In order to operate, the state energy difference must be greater than the thermal energy  $k_B T$  and with the metal dots used in the experiments, extremely low temperatures are required. However, the energy difference scales inversely with size and at the single molecule level, QCA devices will operate at room temperature. Hence, we seek to develop molecular QCA cells.

In this work, we report an *ab initio* quantum chemistry study of a molecular QCA candida-

te,  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$ , which has recently been synthesized and isolated [4]. The experimental evidence supports the interpretation that this molecule has a bistable charge configuration suitable for QCA. Our study is focused on addressing two important questions for QCA operation.

- (1) Does this molecule exhibit bistable charge configuration?
- (2) Can one molecule be switched by a neighboring molecule via the Coulomb interaction?

Question (2) is crucial because in QCA devices, information is transferred among molecules via Coulomb coupling rather than electronic currents. Current-switching is the fundamental source of high power dissipation in transistor-based devices [5]. Experimental work is not yet able to directly address question (2). We use the tools of computational quantum chemistry to explore it here.

### Bistable States

Molecule  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$  has been synthesized by Jiao et al. [4]. It contains four ferrocene groups occupying four corners

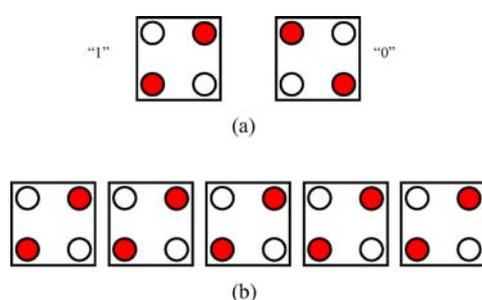


Figure 1. Schematics of QCA cells and QCA wire. (a) four-dot cell, two charge configurations represent binary information. (red dots represent mobile electrons) (b) QCA binary wire. Cells arranged in a line all take on the same value.

of a square. Each ferrocene group acts as a quantum dot, and a Co group in the center of the square provides a bridging ligand which acts as a tunneling path. This molecule has a 2-electron, 2-hole electronic structure, and due to the Coulomb interaction, these two mobile electrons (or holes) occupy the antipodal sites, thus providing two stable charge configurations to represent binary information. Further experimental investigations of attaching, orienting, and switching of this molecule are underway.

Our first step is to see whether quantum chemistry calculations support the experimental conclusion that this molecule has two stable charge configurations suitable for representing binary information. To simplify the calculation, we assume this molecule has a four-fold symmetry, with all four Fe coplanar, and each Fe occupying a corner of a square as shown in Fig. 2. The nuclear geometries of each functional groups are optimized separately at CCSD(T) level with a cc-pVTZ basis set for all atoms. The calculation of molecular

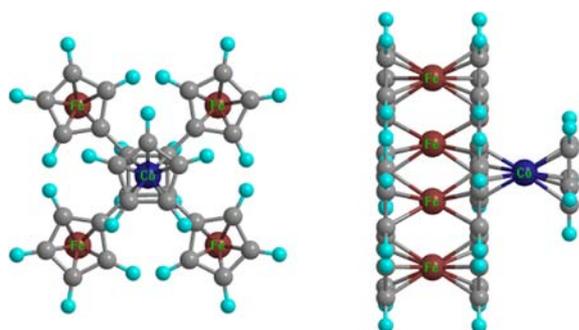


Figure 2. Self-assembly of 4 quantum dots of  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$ .

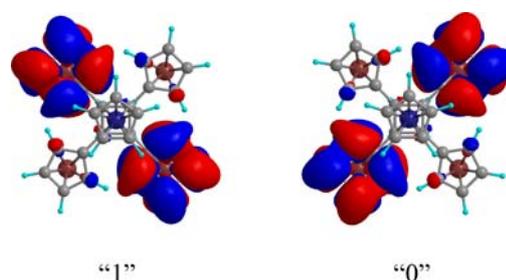


Figure 3. The HOMOs of the two stable states of the  $\{\eta^5\text{-C}_5\text{H}_5\}\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$ .

charge configuration has been done at the unrestricted Hartree-Fock level, using STO-3G basis set for C and H, and ECP basis set LANL2DZ for transitional metals Co and Fe. All calculations in this work were performed using the Gaussian 98 software package [6].

Our calculation shows that this molecule has two degenerate ground-state conformations shown in Fig. 3, with two mobile electrons localized on either upper-left-lower-right or upper-right-lower-left dots. The two states can be distinguished by the opposite sign of their quadrupole moments. We refer to the state with a positive quadrupole moment as the “1” state. For this state, two mobile electrons occupy upper-left and lower-right dots. The state with a negative quadrupole moment, two mobile electrons occupying upper-right and lower-left groups, as the “0” state. We have also tried to localize two charges on two neighboring dots, however, all these calculations fail to converge to a stable wavefunction. Our calculation as well as chemical intuition suggests for this 4-dot molecule, the two mobile charges occupy two antipodal positions, and thus have two stable charge configurations which can be used to represent binary information.

### Molecule-Molecule Response

Another key requirement of a QCA molecule is that one molecule should be switched by the Coulomb coupling of its neighboring molecule. Our next step is to study the molecular interaction between two neighboring molecules. To this end, we construct a supramolecular system by putting two molecules next to each other as shown in Fig. 4, with the distance between two cell centers (Co atoms) fixed as two times of the square lateral length, and calculate one molecule’s response to its neighboring molecule. We use the Mulliken charge distribution of one molecule to model its electrostatic

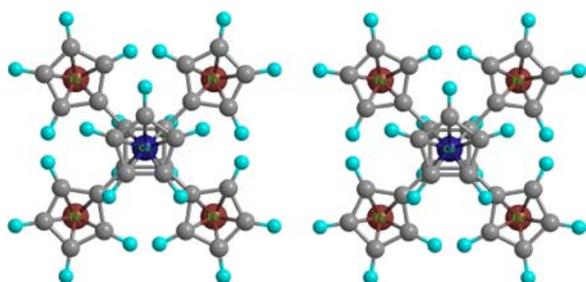


Figure 4. The geometry of two molecules coupled to each other by Coulomb interaction. In our calculation, the left molecule is modeled by the Mulliken charge distribution in the space. The response of the right one is calculated by solving its Schrödinger equation at Hartree-Fock level.

effect on the other. The electronic charge configuration of one molecule responding to its neighboring molecule represents a quadrupole-quadrupole interaction. To find this response function, we linearly interpolate the quadrupole moment between “0” and “1” states of a single molecule as the input value (a driver molecule), and for each value, we solve the Schrödinger equation for the output molecule.

Figure 5 shows the calculated electric quadrupole moment of the output molecule as a function of the quadrupole moment of the input molecule. Data represented by the blue curve are the induced quadrupole moment at 0 K, and the red curve represents the response at 300 K. The nonlinearity in the response curve shows that one molecule can be switched by its neighboring molecule even at room temperature. In the vicinity of the neutral polarization, a small input quadrupole moment induces a large quadrupole moment in output, suggesting a small change of input charge configuration switches its neighboring molecule from one state

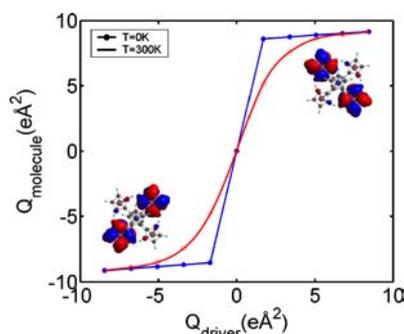


Figure 5. The molecular response function when driven by a neighboring molecule.

to the other. These results then do support the idea that Coulomb coupling between such molecules could be used to couple binary information from molecule to molecule. It is important to note that all the internal “screening” of the intermolecular potential is included automatically in these calculations.

### Error Tolerance

QCA devices should be error tolerant. Ideally, this 4-dot molecule has a planar, 4-fold symmetrical geometry such that the bistable configurations are exactly energetically degenerate. This would be accomplished in real implementations by functional groups binding the molecules to the surface and immobilizing various degrees of freedom. Nevertheless, at room temperature some vibrational distortions of the nuclear geometry are inevitable. If the QCA-enabling molecule-molecule interaction requires exquisite perfection in the molecular geometry, molecular QCA would not be a practical approach. In particular, the C—C single bond has a fairly low energy barrier to distort away from the symmetrical geometry. If the exact 4-fold symmetry is broken up by the C—C single bond distortion, does the Coulomb interaction still couple the bit transfer from one molecule to the neighboring molecule?

To address this we allow one ferrocene dot to distort by a rotation about the C—C single bond, while the rest of the molecule remains fixed in the planar geometry. We calculate cell-cell coupling interaction, as represented by the electric quadrupole moments, between this unsymmetrical molecule and its neighboring molecule as shown in Fig. 6. For the case where this rotated dot is 5 degrees away from the planar geometry, the molecule is still bistable and can be switched by a neighboring molecule, the only influence of the symmetry-broken-up is a horizontal shift of response function, which is shown in Fig. 6(a). This shift is caused by the lifting of the exact degeneracy between “0” and “1” states, thus a nonzero quadrupole of the neighboring molecules is needed to equalize these two binary states. Increasing the rotation to 10 degrees and 15 degrees (shown in Fig. 6(b)), this molecule continues to work properly, with the further shift of the response function. For shifts much in excess of 15 degrees, the cell is effectively locked into the “0” state regardless of the state of the driver cell.

The above discussion suggests that even if  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$  has an unsymmetrical geometry, it is still possible to be

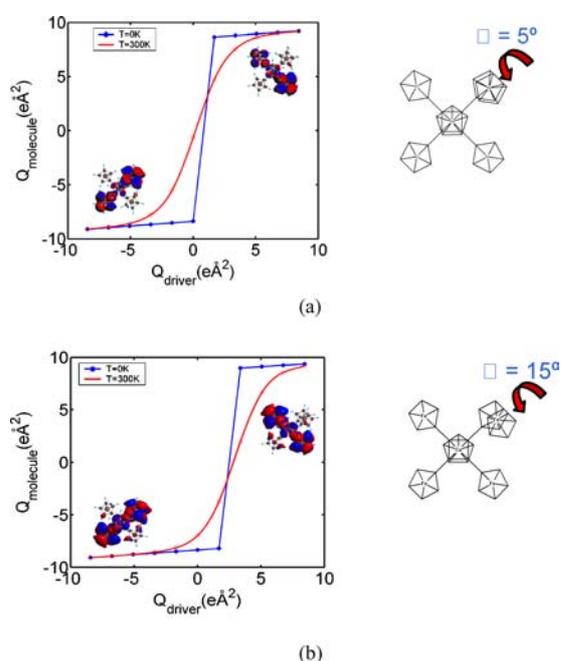


Figure 6. The response function of molecule in an unsymmetric geometry driven by its neighboring molecule. For one ferrocene group is distorted away from the planar geometry of  $5^\circ$  (a),  $15^\circ$  (b).

switched by a neighboring molecule due to the strength of the intermolecular Coulomb coupling.

## Conclusion

In this paper, we present an *ab initio* quantum chemistry analysis of a molecular QCA candidate,  $\{(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\}_4(\eta^4\text{-C}_4)\text{Co}(\eta^5\text{-C}_5\text{H}_5)^{2+}$  which has been recently synthesized. This molecule has a bistable charge configuration in which the

binary information can be encoded. We have shown that one molecule can be switched by a neighboring molecule, satisfying the key requirement for QCA operation. Our studies also show this molecule is error tolerant when the 4-fold symmetry is broken by a C—C single-bond distortion. This illustrates the robustness of information encoding in the QCA scheme. Because a fairly gross feature of the molecule—the sign of the quadrupole moment—is being used to represent binary information, small distortions and deviations from an ideal geometry are not catastrophic.

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