Molecular Quantum-Dot Cellular Automata

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***Abstract*—Quantum-dot cellular automata (QCA) is an approach to computing which eliminates the need for transistors by representing binary digits as charge configurations rather than current levels. Coulomb interactions provide device-device coupling without current flow. Clocked control of the device allows power gain, control of power dissipation, and pipelined computation. Molecular QCA uses redox sites of molecules as quantum dots. We present an *ab initio* analysis of a simple molecular system which acts as a clocked molecular QCA cell.**

Keywords-molecular electronics; quantum dots

I. INTRODUCTION

The exponential increase of computing power over the last decades has relied on shrinking transistors, but they cannot continue to shrink indefinitely. Quantum-dot cellular automata (QCA) is an approach to computing which eliminates the need for transistors by representing binary digits as charge configurations rather than current levels.

The basic unit of a QCA device is a cell composed of a small number of quantum dots. By "quantum dot", we mean a region in which charge is localized. Fig. 1 illustrates a schematic six-dot QCA cell. It has two mobile electrons which can tunnel from dot to dot within the cell. The Coulomb interaction between the electrons causes them to occupy opposite corners of the cell. This allows two degenerate ground states, to which we assign the bit values "1" and "0".

Placing a second cell nearby removes the degeneracy and determines the bit value of the first cell. This cell-cell interaction involves no current flow from one cell to another, only rearrangements of charges within the individual cells, but it enables computation. For a device to function reliably, the interaction must exhibit a nonlinear bistability. A small change in the state of one cell should induce a large change in the state of its neighbor. Nonlinearity restores signal levels and plays the role of gain in a conventional device.

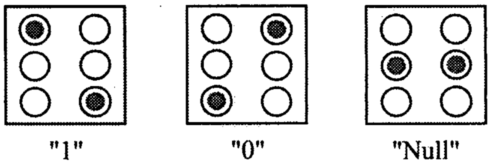

Figure 1. Ground states of the six-dot cell. Coulombic repulsion causes the two electrons (red circles) to occupy opposite corners of the cell, but by varying the potential of the middle dots, we either pull the electrons onto the middle dots, resulting in a null state of the cell, or push the electrons off the middle dots, resulting in a 1 or 0 state of the cell.

As shown in Fig. 1, six-dot cells have a "null" state in addition to the "1" and "0" states. We supply each cell with a clock, a device that controls the potential of the middle (extra) dots. When the clock raises the potential of these dots, the mobile electrons are attracted by them and the cell is forced into the null state. When the clock lowers the potential of these dots, the electrons are repelled by them and the cell assumes either a "1" or "0" state depending on the states of its neighboring cells. At sufficiently low potentials, the electrons will not tunnel through the middle dots, and the cell is locked: a change in the states of its neighbors will have no effect on it.

Power gain is possible because the clocks can supply power to the cells. The clocks control the switching speed of the cells, so adiabatic switching and low power dissipation can be ensured. Pipelining is also possible because we can place cells in a locked state, which acts as a latch, allowing a device to be broken into sub-devices, each working on different parts of a problem.

II. MOLECULAR QCA

QCA devices such as majority logic gates, wires, memories, and shift registers have been demonstrated experimentally, using small metallic dots at low temperatures [1,2] and such cells allow general-purpose computation [3]. However, to allow room-temperature operation, we would like to use QCA devices where each cell is composed of only one or two molecules. In such a molecule, redox sites, which can gain or lose an extra electron without breaking a bond, would act as quantum dots; while bridging ligands, which connect one

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This work was supported in part by Defense Advanced Research Projects Agency and the Office of Naval Research. This material is based in part upon work supported under a National Science Foundation Graduate Fellowship.

part of a molecule to another, would act as tunneling paths.

To make a clocked molecular six-dot cell two "V"-shaped three-dot molecules, such as the molecule shown in Fig. 2, are placed side by side with the middle dots lower in the z-direction than the outer dots. To construct a device, the cells are arranged in a plane with metal rods below them. (Of course, the rods are much larger than the molecules; this is not a problem.) The charges on the rods determine the potential in the device plane. Electrons over positively charged rods are pulled down towards the rods and onto the middle dots, inducing null states in the molecules, while electrons over negatively charged rods are pushed up away from the rods and onto the outer dots, inducing 1 or 0 states in the molecules.

Here, we focus on molecule **2**, shown in Fig. 2. It is a modification of molecule **1**, proposed by Aviram [5] and later studied by Hush [6], which we discussed in a previous work [7]. The three allyl groups function as dots. They form a "V", allowing clocking. The cation, studied here, has two allyl groups that are neutral but have unpaired electrons and one allyl group that has a positive charge. Molecule **2** lacks features such as surface attachment groups that would be necessary for a practical device, but it provides a useful model nonetheless. We will show that molecule **2** has the two basic properties necessary for clocked QCA: it exhibits a nonlinear response to a driver or another molecule; and it can be clocked by placing it in a varying electric field.

III. GROUND STATE CONFIGURATIONS

The extra positive charge may be localized on any of the three allyl groups, leading to the 1, 0, and null states shown in Fig. 3. Gaussian 98 [8] with unrestricted Hartree-Fock theory and the STO-3G basis set is used to find the iso-potentials shown in Fig. 3 and to perform all other calculations. See [9] for a discussion of the accuracy of this method.

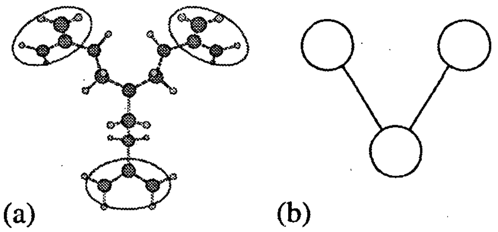

Figure 2. Molecule **2**. (a) Grey circles represent nuclei of carbon atoms; blue circles represent nuclei of hydrogen atoms. The molecule has three allyl groups (circled in red). These groups function as dots. (b) Schematic representation of molecule **2**. Each circle represents a dot. The "V"-shaped arrangement of the dots is necessary for us to achieve clocked control of the molecule.

These three electronic configurations give rise to slightly different nuclear configurations. In [7] we conclude that the differences in nuclear configuration are not of central concern for QCA, so we use a symmetrized structure which does not favor occupation of either of the upper allyls. However, the lower allyl has a different orientation which attracts the positive charge, so to make the 1, 0, and null states degenerate, an electric field is applied in the positive z-direction.

IV. SINGLE MOLECULE RESPONSE

Thus far, we have discussed four-dot and six-dot cells with two mobile electrons. Such cells are convenient because they tend to take on the same value as their neighbors. However, one may also consider two-dot or three-dot "half-cells". Two half-cells combine to form a whole cell. The half-cells function similarly to the whole cells, except that the coulomb repulsion between electrons causes them to take on the opposite value from their neighbors. They are still required to exhibit a nonlinear interaction with their neighbors, and, in the case of three-dot cells, they can still be clocked.

A three-dot cell composed of a single molecule offers the advantage of computational tractability. We will now examine the half-cell-half-cell interaction and clocking characteristics of molecule **2** using the arrangement shown in Fig. 4(a). The neighbor half-cell, or "driver", is modeled as a single hole which moves along a line parallel to the line connecting the upper allyls of molecule **2**, this simulates the movement of an extra positive charge between the two upper allyls of another instance of

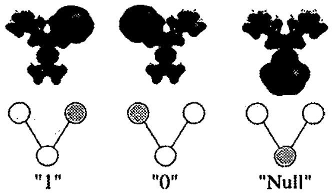

Figure 3. The three ground states of molecule **2**. At top we see the calculated iso-potentials of the three states, and below we see schematic representations of the states. The three states correspond to occupation of each of the three allyl groups by the excess positive charge, or hole. In the schematic drawings, the hole is represented by a green circle. The presence of the hole on an allyl group causes a bulge in the iso-potential surface around that group.

molecule **2**. (Note that holes are used here, instead of electrons, because we are working with the cationic form of the molecule.) To model the field of a metal rod placed below the molecule, we simply place it in a uniform electric field in the positive z-direction.

For an electric field of 1.3 V/nm, the response shown in Fig. 4(b) is obtained. The dipole moments are used as measures of the position of the positive charges. The molecule assumes the opposite bit value from the driver (a bit value of 1 corresponds to a positive dipole moment), as expected from electrostatics, and the highly nonlinear and bistable response obtained is ideal for QCA operation.

To investigate clocking, we calculate the response of the molecule to the driver in the presence of electric fields of different strengths. The results are shown in Fig. 5. For fields greater than about 1.1 V/nm, we obtain a response very similar to the one shown in Fig. 4. However, for fields lower than about 0.6 V/nm, the molecule exhibits almost no response to the changing driver dipole moment. For fields this low, the extra positive charge on the molecule is always on the lower allyl. A field greater than 0.6 V/nm is required to move the charge off the lower allyl because of the asymmetry in the molecule, which we discussed above. Although a field of 1.1 V/nm may seem large, electrochemical experiments routinely involve larger fields.

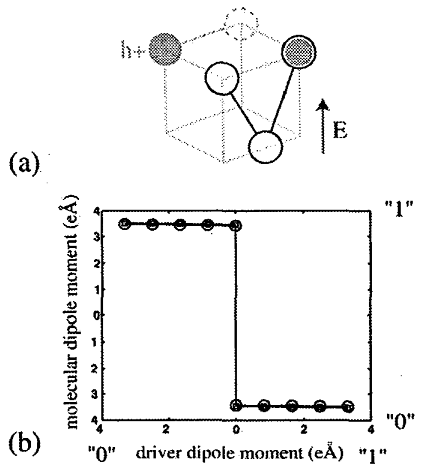

Figure 4. Response of molecule **2** to driver. (a) Arrangement of molecule, hole (driver), and electric field. The driver (labeled "h+") moves along the dashed line. (b) Calculated response of molecule to driver. As the driver moves, its dipole moment along the axis of motion varies, inducing a dipole moment in the molecule. The change in the molecular dipole moment corresponds to a movement of the excess positive charge, or hole, on the molecule. We define a bit value of 1 as a positive dipole moment and a bit value of zero as a negative dipole moment. We see that the bit values of the driver and the molecule are always opposite. We also note that the response curve exhibits the nonlinear bistability required for QCA operation.

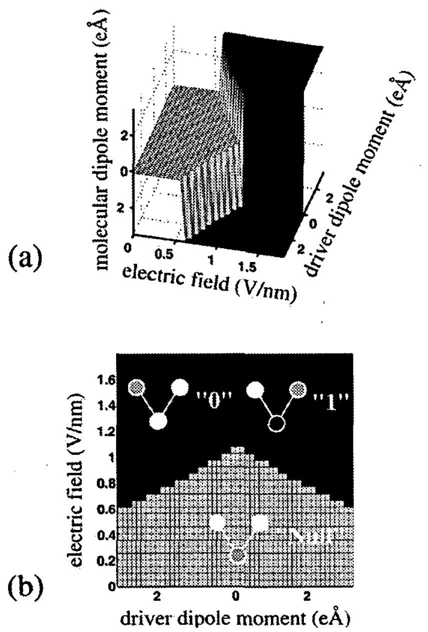

Figure 5. Calculated response of molecule 2 to driver and varying electric field. (a) The molecular dipole moment as a function of the electric field and the driver dipole moment. For fields greater than about 1.1 V/nm, we obtain a response very similar to the one shown in Fig. 4(b) — when the driver dipole moment is negative, the molecular dipole moment is positive, and vice versa. For fields less than about 0.6 V/nm, we obtain a drastically different response — the molecular dipole moment remains essentially 0 for all values of the driver dipole moment. (b) Top view. In the red area the molecular dipole moment corresponds to a but value of 0; in the blue area the molecular dipole moment corresponds to a bit value of 1; and in the greeen area the molecular dipole moment corresponds to a bit value of null.

V. DOUBLE MOLECULE RESPONSE

We examine the response of a six-dot whole-cell composed of two instances of molecule **2** to a driver composed of two holes which model a second six-dot cell. The 1, 0, and null states of the double molecule are shown in Fig. 6. The arrangement of the molecules and driver is shown in Fig. 7(a). In the presence of an electric field of 2.6 V/nm in the positive z-direction, the response shown in Fig. 7(b) is obtained. The quadrupole moments of the driver and of the double molecule are now used to measure the positions of the positive charges. The double molecule assumes the same bit value as the driver (a bit value of 1 now corresponds to a positive quadrupole moment), as we expect from electrostatics. As discussed above, this is the architectural advantage of six-dot cells — with half-cells we must keep track of the number of cells in an inverter chain. Again, we see the desired nonlinear bistable transfer characteristic.

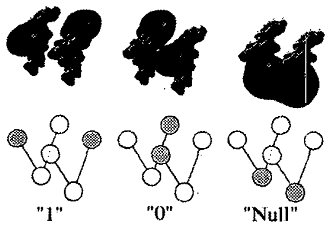

Figure 6. Ground states of the double molecule. At top, we see the calculated iso-potentials for the three states and, below, the schematic representations of the states. As for the single molecule, the holes (represented by green circles in the schematic drawings) give rise to bulges in the iso-potential surfaces.

VI. DISCUSSION

We have seen that clocked QCA has several advantages in terms of power gain, power dissipation, and pipeling. We have used a simple model system to explore the possibilities of clocked molecular QCA. In the presence of positive electric fields, the single molecule and double molecule exhibited the nonlinear bistable response to a driver that is required for QCA operation. We also saw that we could control the response of the single molecule to the driver by varying the electric field. In particular, we could force it to remain in the null state despite a large driver dipole moment, by using an electric field. This response to the electric field allows the molecule to be clocked.

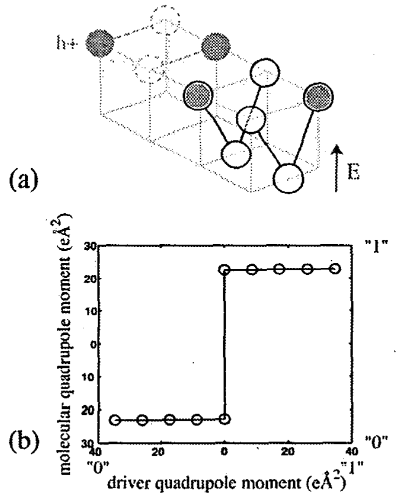

Figure 7. Response of double molecule to driver. (a) Arrangement of double molecule, quadrupole driver (composed of two holes), and electric field. As the holes move, their quadrupole moment changes, inducing a varying quadrupole moment in the double molecule. We define a bit value of 1 as a positive quadrupole moment and a bit value of 0 as a negative quadrupole moment. We see that the bit values of the double molecule and the driver are always equal. Just as for the single molecule, the response curve exhibits the desired nonlinear bistability.

REFERENCES

[1] A. O. Orlov, I. Amlani, G. H. Bernstein, C. S. Lent, and G. L. Snider, "Realization of a functional cell for quantum-dot cellular automata," Science, vol. 277, pp. 928-930, August 1997.

[2] I. Amlani, A. O. Orlov, G. Toth, G. H. Bernstein, C. S. Lent, and G. L. Snider, "Digital Logic Gate Using Quantum-Dot Cellular Automata," Science, vol. 284, pp. 289-291, April 1999.

[3] C. S. Lent and P. D. Tougaw, "A device architecture for computing with quantum dots," Proc. of the IEEE, vol. 85, pp. 541-557, April 1997.

[4] A. Aviram, "Molecules for memory, logic, and amplification," J. Am. Chem. Soc., vol. 110, pp. 5687-5692, August 1988.

[5] N. S. Hush, A. T. Wong, G. B. Bacskay, and J. R. Reimers, "Electron and energy transfer through bridged systems. 6. Molecular switches: the critical field in electric field activated bistable molecules," J. Am. Chem. Soc., vol. 112, pp. 4192-4197, May 1990.

[6] C. S. Lent, B. Isaksen, and M. Lieberman, "Molecular Quantum-Dot Cellular Automata," J. Am. Chem. Soc., vol. 125, pp. 1056-1063, January 2003.

[7] Gaussian 98 (Revision A.11), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2001.

[8] B. Isaksen and C. S. Lent, unpublished.