ABSTRACT

Ab-initio Models of Quantum Dot Cellular Automata Molecules Nishat Tasnim Liza, Ph.D. Advisor: Enrique P. Blair, Ph.D.

Molecular quantum-dot cellular automata (QCA) is a charge based, low-power, energy-efficient alternative to transistor-based, general-purpose computation. In molecular QCA, redox centers of a mixed-valence (MV) molecule function as coupled quantum dots, and localized charge states of the molecule encode binary information useful for classical computing. Molecular QCA promises ultra-high device densities, THzscale switching speeds and room temperature readout. While the fundamental principle of molecular QCA have been tested and established, major challenges must be overcome to successfully implement molecular QCA. This work applies *ab-initio* techniques in the design and modeling of candidate MV molecules for QCA. Here, we study and characterize \sim 1-nm-scale MV QCA molecules using first principle calculations. The structural and electronic properties of QCA molecules are calculated utilizing Hartree-Fock, Post-Hartree-Fock and Density functional theory (DFT) methods. Asymmetric, cationic, MV molecules are designed for spectroscopic state readout of QCA devices at room temperature. Tip-enhanced Raman spectroscopy is proposed to detect the state of QCA devices in a circuit if the QCA molecules have slightly dissimilar quantum dots. Clocked zwitterionic three-dot QCA molecules with built-in counterions at the center of the molecules are modeled. The choice and design of the central linkers of these molecules determines number of mobile charges in the

molecules for encoding the device states on the three quantum dots. These molecules show different device responses to applied clocking electric field based on different central linkers designed and used, similar to the complementary responses of PMOS and NMOS transistors to gated voltage control. Counterion effects on QCA candidate molecules are also explored in terms of electron transfer parameters. The complete active space self consistent field (CASSCF) method is used to calculate electron transfer (ET) matrix element and inner-sphere reorganization energy of the molecules in the presence of nearby counterions. Results demonstrate that randomly placed externel counterions may degrade device states by causing mobile charge to localize in undesirable ways on the QCA molecule. New zwitterionic molecules with a built-in counterion are proposed to eliminate unpredictable effects of external counterions in QCA circuits. Novel organometallic zwitterionic QCA molecules with ferrocene dots are designed and proposed for synthesis. The chemical stability of these ferrocene based molecules are evaluated by theoretical calculations. The synthesis of these stable zwitterionic molecules by collaborating experimental chemists is in progress and may open a new path to realize molecular QCA computing. A new machine-learningbased DFT functional, DM21 is investigated and benchmarked against traditional methods by comparing the calculated ET matrix elements of several QCA molecules. Preliminary results calculated from DM21 functional did not show significant improvements in accuracy and computational cost. Modification and improvement of the neural network used in the development of the functional, as well as the underlying code is proposed which might open new path to computationally inexpensive QCA calculations.

Ab-initio Models of Quantum Dot Cellular Automata Molecules

by

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A Dissertation

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Submitted to the Graduate Faculty of Baylor University in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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Accepted by the Graduate School December 2022

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ACKNOWLEDGMENTS

Firstly I would like to express my gratitude to Dr. Enrique Blair, my dissertation chairperson, for having faith in me. I appreciate and treasure everything you have taught me. I am grateful for your motivation when the results were not always positive and of course, for your patience in reading and correcting my manuscripts. Thank you for being an incredible advisor.

A very special gratitude goes to Dr. Yuhui Lu, my mentor, for training me in computational chemistry by providing scientific oversight and diligent advices. I would like to thank rest of my dissertation committee for their time and valuable feedback on this dissertation. In particular, I thank Dr. Julia Chan for her insightful ideas which helped me develop a broader perspective to my dissertation. I owe a debt of gratitude to Dr. Linda Olafsen for her careful attention to detail. I thank Dr. Scott Koziol for being always very positive with my work. Sincere thanks goes to my wonderful labmates: Jackson, Joe, Dylan, Collin, DJ and Luke, for all the interesting and stimulating discussions we had in the past years. Thanks for your contribution in this dissertation. I will always remember all of you.

I am grateful to my family for their unconditional love and sacrifices. Without them, I would not have made it this far. I am blessed to have my best friend, Tazin, whom I cannot thank enough for always being there, for listening to me when I was anxious and for being the constant emotional support system. Thanks to my dear friends at Arbors 1004, with whom I have shared moments of deep anxiety but also of big excitement. Life is beautiful with you around. And, I have saved this last word of acknowledgment for Shainan - my soulmate: for his love and patience, because he always understood.

DEDICATION

To Mom and Dad, for their courage and endless love.

CHAPTER ONE

Introduction

Mixed-valence molecules may be useful for an energy-efficient, post-Moore'slaw general-purpose computing paradigm known as quantum-dot cellular automata (QCA) [6]. QCA promises energy-efficient logical devices to replace complementary metal–oxide semiconductor (CMOS) transistor logic for nanoelectronics [7, 8, 9, 10]. A molecular implementation of QCA [11] could provide room-temperature, nanometerscale cells that approach THz-regime switching speeds [12] and surpass present-day transistor densities by 3-4 orders of magnitude.

While several promising QCA candidate molecules have been synthesized and tested, major challenges still remain in the realization of molecular QCA [13, 14, 15]. A charge-neutral, MV, zwitterionic class of QCA molecules is of interest, since the synthesis of such molecules does not produce counterions that localize randomly in the vicinity of each molecule. [16, 17]. While MV, zwitterionic molecules have been synthesized [18], stable device states have not yet been observed experimentally in these molecules. No samples of the synthesized zwitterionic molecules are known to exist for testing. Newer candidates are sought that may be readily synthesized and tested. Theoretical and experimental development is also necessary for molecular circuit layout, molecular circuit operation and the read out of classical bits from molecular circuits.

This dissertation focuses on *ab-initio* models of QCA molecules, where nanometerscale MV molecules function as QCA cells, with redox centers providing dots [11, 19]. QCA candidate molecules are designed, characterized and evaluated using various electronic structure methods. These candidates are screened based on key criteria required for basic QCA operation. Nuclear and electronic properties of these molecules are explored and investigated. Chapter 2 provides an overview of QCA, molecular QCA and *ab-initio* electronic structure methods used for the study of the molecules. This chapter also includes discussion on clocked QCA circuits. Chapter 3 presents design and modeling of simple, cationic double quantum dot (DQD) molecules to illustrate the proof of principle for spectroscopic readout of QCA device states. Quantum dots in these molecules are designed in a slightly dissimilar way and tip-enhanced raman spectroscopy (TERS) is proposed to use for detection of the device states of the molecules in a QCA circuit. This chapter concludes that the binary device states of an asymmetric DQD molecule have distinct Raman spectra which support room temperature readout of molecular QCA bits. In Chapter 4, neutral, MV, clocked QCA molecules are designed where various counterions are built into the center of the molecules. This chapter demonstrates the role of the central counterion in engineering the device behavior of QCA molecules. The choice of counterion determines the number of mobile charges in a QCA molecule and the response of the molecule to a clocking electric field. Chapter 5 investigates the effects of external counterions near a QCA molecule. The presence of nearby counterion affects the electronic properties of a QCA molecule in an unpredictable way which is detrimental for QCA device operation. These counterion effects are explored in terms of electron transfer matrix element and inner-sphere reorganization energy of the QCA molecules. This chapter proposes that the use of zwitterionic QCA molecules with built-in counterions can overcome the unpredictable effects from an external counterion. Computations on the zwitterionic molecules also show significant change in device characteristics. Chapter 6 focuses on design and modeling of novel zwitterionic, MV, ferrocene-based QCA molecules that may be synthesized by collaborating experimental chemists. Ab*initio* techniques are used to investigate the chemical stability of these potential QCA molecules. Several stable molecules are characterized and proposed for experimental testing and synthesis. In Chapter 7, electronic couplings for several molecules are calculated with a machine learning based DFT functional, DM21, which was developed by training a neural network on molecular data. Calculated electronic couplings are benchmarked against traditional HF method and DFT methods to evaluate the performance of the new functional in QCA computations.

Attributions

Chapter 3 previously appeared as: N. Liza, D. Murphey, P. Cong, D. Beggs, Y. Lu, and E. Blair, "Asymmetric, mixed-valence molecules for spectroscopic readout of quantum-dot cellular automata," Nanotechnology 33, 115201 (2022). This work was funded by the Office of Naval Research under grant N00014-20-1-2420. N. Liza and D. Murphey performed *ab-initio* calculations. P. Cong modeled the output circuit response. D. Beggs developed MATLAB and Python scripts for processing and post-processing data. Y. Lu and E. Blair supervised over the project.

Chapter 4 previously appeared as: N. Liza, Y. Lu, and E. Blair, "Designing boron-cluster-centered zwitterionic Y-shaped clocked QCA molecules," Nanotechnology 33, 465201 (2022). This work was funded by the Office of Naval Research under grant N00014-20-1-2420. N. Liza performed the quantum chemistry computations. Scientific and engineering oversight was provided by Y. Lu and E. Blair.

CHAPTER TWO

Background

Quantum-Dot Cellular Automata

Quantum-dot Cellular Automata (QCA) is a charge-based classical generalpurpose computing paradigm with no interconnecting electric current flow between devices. In QCA, a mobile charge on a system of coupled quantum dots provides a device, called a *cell*. A cell's charge configuration encodes a classical bit. Cells arranged on a substrate couple locally via the electrostatic field to form circuits for classical information processing [20]. The simplest QCA cell consists of two quantum dots connected by a tunneling path. The quantum tunneling of mobile charge between these two dots in the cell enables device switching. Figure 2.1 shows a schematic representation of a double dot QCA cell. Two charge configurations based on the localization of the mobile charge represent state "0" and "1".



Figure 2.1: The charge configuration of a two-dot QCA cell provides two localized states. Each black circle represents a quantum dot. The dots are separated by a distance *a*. The black line represents an electronic tunneling path between the dots. The green circle represents a mobile charge. When the mobile charge occupies dot 0, the cell is in state "0". When the charge occupies dot 1, the cell is in state "1".

When one QCA cell is placed near another, two mobile charges repel and tend to minimize their mutual Coulomb interaction by occupying antipodal sites of the cells. Neighboring QCA cells couple locally by this Coulomb interaction. The polarization of one cell affects the neighboring cell as shown in Figure 2.2.



Figure 2.2: A QCA cell demonstrates a bistable, non-linear response when driven by a neighbor. Polarization of cell 1, P_1 induces an opposite polarization in cell 2, P_2 . Cell 2 is polarized for even a small polarization of cell 1.

This nonlinear Coulomb interaction between neighboring cells enables flow of binary information and is the basis of QCA operation. Adiabatic operation can minimize power dissipation, leading to energy-efficient computing [21, 22].

Implementations of QCA

QCA cells have been implemented using metallic dots [23, 24], semiconductor dots [25], and room-temperature atomic-scale dots [26]. Silicon based atomic scale dots have been demonstrated where implanted phosphorus could serve as dots [27]. In metal-dot QCA, binary wires [28], latches [29], and majority logic circuits [20] have been demonstrated experimentally. General-purpose computing may be achieved using these building blocks. More complex circuits have been designed, such as adders [30], memories [31], and even entire processors [32]. Memory and logic may be intermingled for computing architectures that go beyond the confines of von Neumann computing [33]. Circuits for writing classical bits onto nano-scale molecules have been designed [34, 35].

Clocking in QCA

In large QCA arrays, clocking is important to guide the flow of information [36]. A clocking field can control the charge states of QCA by switching the cells from an active to the null state, ie. turning the cell on or off. This results in electron transfer between the QCA dots within each QCA cell. QCA cells can be clocked if an additional dot, called null dot is added to the middle of a two-dot cell. An applied voltage (clock) can alter the energy of the middle dot and force charge into null or active dots as shown in Figure 2.3. The null dot adds an additional state, called the null state which bears no information.



Figure 2.3: A three-dot QCA cell provides three charge-localized states. The cell is clocked using an externally-applied electric field, E, generated by a buried conductor below the cell. The green circle represents a mobile charge. The resulting electric field from the conductor can draw the mobile charge upward or downward providing active and null states respectively.



Figure 2.4: Multiple charged clocking wires may clock an array of QCA cells by forming active and null domains. The anionic and cationic conductors (red and green respectively) buried below the substrate of the QCA array provide an electric field. When the conductor is negatively charged, the resulting electric field drives the mobile charges (electrons in this case) upward, and the cells are in the active state. When the conductor is positively charged, the electric field pushes the electrons down to the null dots, and the cells take the null state. The middle region in this array is known as switching region [1].

The electric field required for clocking at the QCA surface can be generated by applying a time-varying voltage on wires buried under the QCA cell layer as shown in Figure 2.4 [37]. These wires are called clocking wires. A grounded conductor is also used above the cell layer to draw the electric field lines upward or downward to control the field direction. The clocking field is a traveling sinusoidal wave which guides the data flow through the cell arrays by raising and lowering its potential. The QCA cells and devices can be much smaller in size than the buried conductors [38].

Clocking has numerous advantages in QCA. In clocked QCA architecture, clocking wires can supply power to each cell independant of the input. So, even if the input signal is removed, the cell can stay in its locked state and can act as input for the next cell. In large QCA arrays, the weak signals can be improved and restored in this way and true power gain is achieved [39]. Pipelining is another advantage of clocked control which makes QCA calculations easy. QCA arrays can be broken into sub arrays and devices into sub-devices by placing the QCA cells in a locked state (latch) [29]. Each sub-array or device may work on different parts of the computation. Clocked QCA supports adiabatic and reversible calculation and quasi adiabatic switching (switching the cells slowly compared to the tunneling time) which leads to low energy dissipation (Landauer's principle) [40]. Clocking in QCA promises minimal power dissipation with high efficiency. In our work, we predict clocked controllability of QCA candidate molecules.

Molecular QCA



Figure 2.5: Charge configuration of a QCA molecule encodes binary information. (a) Cationic diferrocenylacetylene (DFA) molecule serves as a two-dot QCA cell. Localization of a mobile hole in the molecule provides two device states. (b) Zwitterionic MV diferrocenyl nido-carborane molecule provides three charge localized device states and serves as a three-dot QCA molecule. Green discs on the schematics and structural formulae represent holes and red discs represent electrons. For simplicity, the electron is not shown in the schematics.

Molecular QCA supports room temperature operation with ultra-high (10¹⁴ cm⁻²) device densities and ~THz scale switching speeds [11]. In molecular QCA, the redox centers in a molecule play the role of QCA dots whereas the molecule itself plays the role of a QCA cell. For molecular stability, non-bonding π or d orbitals host mobile charge at a redox center. MV molecules have been studied in literature as great candidates for molecular QCA [4, 19, 41]. In these molecules, an element or a functional group is present in more than one oxidation state. Typically, a functional

group provides a redox center. Mobile charges can tunnel between these redox centers within the molecule and localize in either dot, which results in multiple electronic states for the molecule. This localization of charge can be driven by nuclear relaxation of the molecule or by Coulomb repulsion from a neighbor molecule. Binary information is represented by these charge configurations of a QCA molecule. This is shown in Figure 2.5. In a molecular QCA circuit, the clocking field can be generated by applying a voltage on clocking wires buried under the molecular layer [37].

The main advantage of molecular QCA comes from the small size (\sim nm) of the cells and the switching speed. Because the switching of these QCA molecules depends on the time of electron transfer within the molecule, a significant reduction of heat dissipation is observed. Hence, molecular QCA shows very low power dissipation with high efficiency.

Several cationic QCA molecules have been synthesized, and characterized and have shown bistable device switching. STM imaging has been used to study the charge localization in these molecules [13, 15, 42]. Recently, an atomic force microscope (AFM) tip was used to switch localized charge states of a double-quantum-dot (DQD) cation, as well as to probe dissipation due to this single-electron transfer process [43]. Different schemes based on bit write-in and read-out of molecular QCA states have also been proposed [44, 45, 46]. In most of these molecules the working dots are designed by organometallics. Simpler models of QCA candidate molecules have allyl, ethene, and phenalenyl groups as the dots [44, 47, 48]. The key strategy is to use nonbonding p or d orbitals to act as QCA dots in these molecules.

To realize device states, most previously-studied MV molecules require chemical oxidation or reduction to a cationic or anionic state. External counterions are created during the synthesis of these molecules. One challenge of using these ionic molecules in QCA circuit is the effects of external counterions on the QCA devices which may disrupt the circuit. Charge states of QCA molecules are affected when the effect of external counterions are combined with the influence of the external applied field [13]. One strategy to eliminate these unwanted effects from randomly placed counterions in QCA circuits is to use neutral zwitterionic mixed-valence complexes as QCA cells. In these molecules, a central electron donor (or acceptor) is built in at an electrostatically symmetric position. The molecule then maintains charge neutrality by self-doping mechanism and mobile electrons (or holes) are generated in the working dots (charge centers) of the molecule [16, 18]. A neutral, mixed-valence zwitterionic species has been synthesized, even though no stable device state has been observed with STM imaging. No sample of this molecule is known to exist for further testing [18].

To form molecular QCA logic circuits, non-homogeneous arrays of molecules must be arranged on a substrate. A combination of top-down and bottom-up approaches could enable guided self-assembly of circuits. Techniques based on electron beam lithography (EBL) could be used to arrange DNA nanostructures [49], which serve as molecular circuit boards [50, 51]. DNA programmed with functionalization sites could allow the self-assembly of circuits using molecules designed with a ligand suitable for docking with the DNA structures at the programmed sites.

Choice of QCA Candidate Molecules

Design and synthesis of potential QCA candidate molecules are necessary for further experiment and testing. In this work we mostly focus on design and modeling of several QCA candidate molecules. Two most important criterion to be a good QCA candidate molecule are (1) bistable charge configuration and (2) electronic device switching by a neighbor molecule. That means, the molecule must have two stable charge configurations obtained by nuclear relaxation. And, when two molecules are placed side by side, one molecule must switch the other and they must show nonlinear cell-cell response as shown in Figure 2.2. We also characterize the candidate molecules based on electronic coupling, inner sphere reorganization energy and vibrational modes. We use *ab initio* calculations to obtain these device-level parameters. We use laws of quantum mechanics and quantum chemistry to study these molecules. Koopmans' Theorem and Marcus-Hush theory can be used to estimate the electron tunneling energy and reorganization energy respectively. In this work we use the adiabatic potential energy surfaces to calculate Electron Transfer (ET) matrix element and inner-sphere reorganization energy of the QCA molecules. To test the chemical stability of the molecules, we calculate charge localization, molecular orbitals and ionization potential of the molecules. These will be discussed elaborately later in the following chapters.

Electronic Structure Methods

Electronic structure methods are used to predict the energies and properties of atoms and molecules by applying the fundamental laws of quantum mechanics. These methods treat the nuclei as stationary object surrounded by moving electrons within a molecule. In our work, we utilize these methods to characterize and evaluate our QCA candidate molecules. We use several software packages including Gaussian16, Q-Chem 5.2 and PyScf to execute these electronic structure method calculations. Generally, the usual approximations used by electronic structure theory treat all electrons as nonrelativistic. The software packages that we use also treat the core electrons within an atom. However, this treatments provide correct results only for lighter atoms. For heavier atoms, electrons near the nucleus have large velocities. So, effective core potentials or pseudopotentials can be used to describe the heavier atoms. In our calculations of the simple QCA molecules, we do not include the relativistic effect of the core electrons. Some basic concepts of *ab initio* methods will be discussed here briefly.

Schrödinger Equation for Molecular Systems

The time-independent Schrödinger's equation for molecular system is a function of only the coordinates of the nuclei and the electrons. This equation describes the associated energy of the molecular system. Equation 2.1 shows the molecular Hamiltonian operator in the time-independent, non-relativistic limit of the Schrödinger equation.

$$\hat{H} = -\sum_{i}^{\text{electrons}} \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A}^{\text{nuclei}} \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i}^{\text{electrons nuclei}} \sum_{A}^{e^2 Z_A} \frac{e^2 Z_A}{r_{iA}} + \sum_{i>j}^{\text{electrons}} \frac{e^2}{r_{ij}} + \sum_{A>B}^{\text{nuclei}} \frac{e^2 Z_A Z_B}{r_{AB}}$$
(2.1)

The first and second terms of Equation 2.1 are the electronic and nuclear kinetic energy operators, respectively. The third, fourth and fifth terms represent electronnuclear attraction, electron-electron repulsion and nuclear-nuclear repulsion (E_{NRE}) respectively. We can ignore the second term, since nuclei are much heavier and move much more slowly than the electrons, ie. { m_A } \gg { m_e } [52]. The final term is trivial to evaluate since we only need to know the charges on the nuclei and their distances between them. We can make certain approximations and write the Born-Oppenheimer Schrödinger Equation as follows.

$$\hat{H}_{\rm BO}\Psi\left(\mathbf{r}_{e}\right) = \left(\sum_{i}^{\rm electrons} \frac{-\nabla_{i}^{2}}{2} + \sum_{i}^{\rm electrons} \sum_{A}^{\rm nuclei} \frac{-Z_{A}}{r_{iA}} + \sum_{i>j}^{\rm electrons} \frac{1}{r_{ij}}\right)\Psi\left(\mathbf{r}_{e}\right) = E_{\rm BO}\Psi\left(\mathbf{r}_{e}\right)$$

$$(2.2)$$

From this equation, the total energy of the system is then found as

$$E_{\text{total}} = E_{\text{BO}} + E_{\text{NRE}} \tag{2.3}$$

The Schrödinger equation may be solved exactly for only one-electron systems, e.g. the hydrogen atom.

The Hartree–Fock Method

The Hartree Fock method is an approximate, iterative computational method for solving the time-independent Schrödinger equation of many-body electronic systems. This is a fundamental concept for all *ab initio* quantum chemistry methods [53, 54, 55].

The time-independent Schrödinger equation is only solvable for the hydrogen atom and a few single-electron systems, like He⁺. To approximate the the electronic structure for more complex multi-electron systems, molecular orbital (MO) theory was developed [56]. Hartree-Fock theory is equivalent to MO theory. The HF approximation constructs a multi-electron wavefunction from a set of one-electron wavefunctions, called molecular orbitals (MOs). These electronic wavefunctions are built from basis sets, which are functions centered on each nucleus. Basis functions can be considered as representing the atomic orbitals of the atoms. Basis functions are combined linearly to model MOs. The many electron wavefunction is then built as an antisymmetric combination of MOs so that the Pauli principle of antisymmetry is obeyed. Ideally, the many electron wavefunction should be written as a linear combination ie. sum of Slater determinants. Because, a single Slater determinant is a single electron configuration and the occupation of orbitals is not known, we need to include all possible configurations in the solution to the Schrödinger equation. However, it is not feasible to solve the Schrödinger equation for infinitely many electron configurations. Certain approximations are developed in the Hartree-Fock method, and the multi-electron wavefunction, $\Psi(\vec{r})$ is approximated as a determinant of singleelectron wavefunctions, i.e., single Slater determinant as given below, where, n is the total number of electrons in the system, ϕ is the MO, \vec{r} is the position vector, $\alpha(m)$ and $\beta(m)$ are the alpha and beta spin functions for electron m.

$$\Psi(\vec{r}) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(\vec{r}1)\alpha(1) & \phi_1(\vec{r}1)\beta(1) & \phi_2(\vec{r}1)\alpha(1) & \phi_2(\vec{r}1)\beta(1) & \cdots \\ \phi_1(\vec{r}2)\alpha(2) & \phi_1(\vec{r}2)\beta(2) & \phi_2(\vec{r}2)\alpha(2) & \phi_2(\vec{r}2)\beta(2) & \cdots \\ \phi_1(\vec{r}3)\alpha(3) & \phi_1(\vec{r}3)\beta(3) & \phi_2(\vec{r}3)\alpha(3) & \phi_2(\vec{r}3)\beta(3) & \cdots \\ \phi_1(\vec{r}4)\alpha(4) & \phi_1(\vec{r}4)\beta(4) & \phi_2(\vec{r}4)\alpha(4) & \phi_2(\vec{r}4)\beta(4) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \end{vmatrix}$$
(2.4)

Here, the single-particle wavefunctions are chosen to minimize the ground state energy, $E_0 = \langle \psi_0 | \hat{H} | \psi_0 \rangle$. The variational theorem is used iteratively to find the set of single-particle wavefunctions that will minimize E_0 . Because the many electron HF wavefunction is a single Slater determinant, only the electron exchange effects are taken into consideration. Exchange interactions are due to the Pauli exclusion principle, as it states that if two electrons have parallel spins then they will not be allowed to be at the same place at the same time. This approximation gives rise to an effective repulsion between electrons with parallel spins. The correlated motion between electrons of anti-parallel spins are not taken into account fully. Under the HF approximation, each electron's motion can be described by a one-particle function (spin orbital) and the motion does not depend on the true motion of the other electrons, but rather mean value of their motions. Each electron exists in the field of nuclei and experiences the influence of the other electrons only in an averaged way [57]. The correlation of the motions of the electrons is not considered in HF approximation. The Hartree Fock method is also known as the self-consistent field method because of its non-linear iterative way of solving the Schrödinger's equation [58, 59].

Even though the Hartree-Fock approximation is greatly useful in solving manybody wave functions, it is insufficient to predict the energies and structures of molecules accurately. This inaccuracy mostly arises from lack of electron correlation and the way of solving the equation. Many accurate computational methods are based on HF equation, but this electron correlation problem by adding more equations to the model. They are known as post-Hartree Fock methods. The semi-empirical methods and the Kohn–Sham implementation of the density-functional theory are also based on the Hartree-Fock method. However, HF method can approximate charge localization in a molecule properly. In our calculations, we use this method to optimize the geometries and obtain charge configurations for several QCA molecules.

Restricted Open Shell Hartree–Fock (ROHF) Method

Restricted Open Shell Hartree–Fock (ROHF) method is used for open shell atoms and molecules with an even or odd number of electrons. In ROHF method, electrons are paired initially with in doubly occupied molecular orbitals, and the last unpaired electrons are treated in singly occupied orbitals. For example, all but one electron is spin-paired in a doublet, and all but two electrons are spin-paired in a triplet system. The advantage of using ROHF method is that there is no spin contamination in the calculations. The total calculated spin of a system is accurate, because ROHF wave function is an eigenfunction of the total spin operator, \hat{S}^2 [60].

Post-Hartree-Fock Methods

Post-Hartree-Fock methods were developed to improve the accuracy of HF method by adding the electron correlation which arises from repulsions between instantaneous motion of electrons in a many body system [61]. These methods are expensive as shown in Figure 2.6. Some popular Post-Hartree–Fock methods are: configuration interaction (CI), møller–Plesset (MP_n) perturbation theory, coupled cluster (CC) theory, multi-configurational self-consistent field (MCSCF), and the complete active space self-consistent field (CASSCF) [62]. In our calculations, we use MP_n and CASSCF theory among these methods.


Figure 2.6: Computational cost of the *ab-initio* methods increase with the increase in their accuracy.

Configuration interaction (CI). In Configuration interaction (CI) method, the multielectron wave function is written as a linear combination of different electron configurations and HF wave functions are used for each configuration. This method includes all possible dynamical and nondynamical correlations, thus provides exact solution to time-independent Schrödinger's equation. However this method is too computationally demanding.

 $M
otin ler-Plesset (MP_n)$ perturbation theory. Møller-Plesset (MP_n) perturbation theory is derived from many body perturbation theory of mathematical physics. In the MP_n method, accuracy is improved by including dynamical electron correlation and the energy is representated in a perturbative form [63, 64, 65]. Generally, perturbation theory approximates an exact solution of a problem by starting from a related problem. The exact solution for this related problem is already known which is known as the zeroth-order or unperturbed problem. Whatever remains from the real problem is the perturbation to this solution. This method adds higher excitations to Hartree-Fock theory as a non-iterative correction. Even though third (MP3) or fourth (MP4) order corrections can be used for greater increase in accuracy, MP2 method increases the accuracy of QCA calculations significantly.

Complete active space self-consistent field (CASSCF) method. The complete active space self-consistent field (CASSCF) method is used in computing excited states for small-medium molecular systems [66, 67]. The CASSCF calculation is combination of SCF computation on the full molecule and CI calculation on a subset of molecular orbitals. A full CI calculation is carried out within a given set of active orbitals that are previously selected. The participating orbitals are carefully chosen in a way so that they play a major role in the chemistry of the studied system. The CASSCF method can be used to study reactions involving both ground state and excited state potential energy surfaces. This method includes nondynamical or static correlations.

Density Functional Theory (DFT)

Density-functional theory (DFT) solves the time-independent Schrödinger equation of many-body electronic systems with a different approach. In DFT theory, the three-dimensional one-body density, i.e. the probability distribution, is used as the basic variable to describe interacting electrons instead of the many-body wave function [68, 69]. The Hohenberg–Kohn and Kohn–Sham theorems are foundations of DFT [70, 71]. According to these theorems, the total electron density of any system determines all ground-state properties of the system. So, the total energy of a many-electron system can be written as functionals of the density and an effective one-electron-type Schrödinger equation can be derived. The following expression can be given for the pure form of DFT:

$$E_{DFT}[\rho(\vec{r})] = T[\rho(\vec{r})] + V_{NE} + J[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$$
(2.5)

Here, $\rho(\vec{r})$ is the total electron density, T accounts for the kinetic energy of an electron, and V_{NE} accounts for the attraction it has for each of the nuclei. J is the Coulomb operator which represents the Coulomb repulsion between an electron in one orbital, and the charge distribution created by another electron in another orbital. The final term E_{XC} is the new quantity, the exchange-correlation term introduced by DFT. This term accounts for all electron correlations and models the electron-electron interactions neglected by Hartree-Fock theory. However, unfortunately, the exact term is not known and different approximations are made to evaluate this term. Based on different approximations, different DFT functionals have been proposed and used widely in computational chemistry.

In hybrid functionals, the DFT exchange-correlation term is defined as a sum of Hartree-Fock exchange and pure DFT exchange-correlation, mixed in some fixed percentages:

$$E_{XC}^{hybrid}[\rho(\vec{r})] = c_{HF}E_X^{HF} + c_{DFT}E_{XC}^{pure}[\rho(\vec{r})]$$
(2.6)

The constants c specify the percentages of each term, E_X^{HF} is the HF exchange term. In Double hybrid functionals, MP2 energy is incorporated for correlation:

$$E_{XC}[\rho(\vec{r})] = d_1 E_X^{HF} + d_2 E_X^{DFT} + d_3 E_X^{DFT} + d_4 E_C^{MP2}$$
(2.7)

The constants d_i specify the percentages of each term.

Determination of the total energy from the electron density is independent of the number of electrons in the system as density is a function of only three spatial coordinates (x, y, z) unlike the many-body electronic wave function which is a function of 3N coordinates of all N atoms in the system. For these reasons DFT is very popular, inexpensive and computationally feasible even for large systems. However, DFT has many limitations such as delocalization error and static correlation error [72]. In our research, we seek to avoid delocalization error and fractional charges, where an electron is delocalized over the two charge centers in a molecule. For this reason we avoid DFT methods in our calculations.

CHAPTER THREE

Asymmetric, Mixed-valence Molecules for Spectroscopic Readout of QCA

N. Liza, D. Murphey, P. Cong, D. Beggs, Y. Lu, and E. Blair, "Asymmetric, mixed-valence molecules for spectroscopic readout of quantum-dot cellular automata," Nanotechnology 33, 115201 (2022).

Abstract

One challenge for molecular implementation of QCA is read-out of classical bits from QCA molecules. While single-electron transistors (SETs) and single-electron boxes (SEBs) could provide low-temperature solutions for reading the state of a \sim 1nm-scale molecule, we propose a room-temperature read-out scheme for molecular QCA. Here, mixed valence (MV), double-quantum-dot (DQD) molecules are designed with slightly dissimilar quantum dots. The configuration of mobile charge on a cationic DQD molecule encodes a bit of classical information robust at room temperature. *Ab initio* calculations show that the binary device states of an asymmetric molecule have distinct Raman spectra. Additionally, the dots are similar enough that mobile charge is not trapped on either dot, allowing device switching driven by the charge configuration of a neighbor molecule. Here, we propose a technique such as tip-enhanced Raman spectroscopy (TERS) to detect the state of a circuit comprised of several QCA molecules.

Introduction

Various cationic QCA candidates have been synthesized, and scanning-tunneling microscopy (STM) imaging has been used to detect charge localization and device switching in molecules [73, 42]. Recently, an atomic force microscope (AFM) tip was used to switch localized charge states of a double-quantum-dot (DQD) cation, as well as to probe dissipation due to this single-electron transfer process [43].

Here we focus on a molecular implementation of QCA, where cationic doublequantum-dot (DQD) mixed-valence molecules function as nanometer-scale cells. Within each molecule, redox centers provide dots. At these scales, bit energies (~ 400 meV) are much larger than even the room-temperature thermal noise floor of $k_BT \sim 26$ meV [11]. the molecules. Their 1-nm length scale precludes the devices from emitting or absorbing optical photons. While single-electron boxes (SEBs) [74] or single-electron transistors (SETs) [75, 45] could be used to detect sub-nm charge tunneling events, these also require cryogenic temperatures. Room-temperature read-out may be preferred for room-temperature molecular QCA.

We propose asymmetric QCA molecules for spectroscopic state readout at room temperature. Redox centers may be designed to have different masses so that various charge configurations are spectroscopically distinct. Tip-enhanced Raman spectroscopy (TERS), for example, could be used to detect the state of individual molecules or the states of several molecules at room temperature [76]. Care must be taken so that mobile charge does not strongly favor one molecular dot over another. An extremely strong preference could mean that the mobile charge is trapped on one dot, leaving the molecular cell unswitchable and rendering it useless as a device. A stuck cell could, however, be useful in an application where fixed device states are desirable [77].

In this work, simple, cationic QCA DQD systems are modeled using *ab initio* techniques to demonstrate the proof of principle for devices which support spectroscopic readout. Molecules may be designed to maintain both electronic switchability and spectroscopically distinct device states. Ethene groups are used as dots, and $H \rightarrow X$ substitutions for various substituents X are used on one dot to break the symmetry between the pair of dots. This enables the spectroscopic detection of device states.

Methods

All *ab initio* calculations were performed using GAUSSIAN 16 software package [78]. Several cationic DQD devices are considered, including a molecule with identical dots (symmetric) and other molecules with dissimilar dots (asymmetric). For each cation, geometry optimizations are performed to obtain binary device states, "0" and "1", with geometries R_0 and R_1 , respectively. Optimizations are performed and Raman spectra are calculated at the Hartree-Fock level of theory [56]. The Raman calculations immediately predict whether the binary device states are spectroscopically distinct.

Next, the ability of a cationic DQD to function as a QCA device is evaluated. Adiabatic potential energy surfaces are calculated for the electronic ground state and first excited state over several linear combinations of R_0 and R_1 . For each geometry, the electronic ground state E_0 and the first excited state E_1 are calculated using a state-averaged complete active space self-consistent field (CASSCF) method [79, 80]. An active space of three electrons and four orbitals is used. Weighting coefficients of 0.5 are used for both the ground state and the first excited state in the CASSCF state average to mix the two states equally. The ground state energy surface E_0 is used to predict the chemical bias between the two device states, Δ_0 , identified here as the device's natural detuning. It is necessary in QCA that the state of a device may be driven by a neighboring molecule. If a neighboring molecule can provide an electronic bias E_k , termed the "kink energy," then for electronic switchability, we require $|\Delta_0| < E_k$. Ideally, $\Delta_0 = 0$; however, in an asymmetric molecule, it is likely that $\Delta_0 \neq 0$. After evaluating switchability, the molecule's response to the dipole field of a neighboring molecule is calculated, again using a state-averaged CASSCF method.

The 6-31g^{*} basis set was used for all atoms (H, C, F) of molecules **1-3c** and molecule **5**. The 6-311g^{*} basis set was used for all atoms (H, C, Cl) in all calculations for molecule **4**.



Figure 3.1: Molecule 1 provides a two-state QCA cell. (a) Two ethene groups each provide a quantum dot. (b) A localized mobile hole provides two logical device states, 0 and 1. The device states are shown using spin density plots (upper) and schematic diagrams (lower). (c) A driver molecule near 1 is simulated using two point charges, Q and 1 - Q. The value of Q is varied from 0 to 1. The distance between two charges is a, the distance between the centers of the two dots (ethene groups) of molecule 1. The driver molecule is placed at a distance d = a from the target molecule.

Results

Symmetric Diethene Cation

A 1,8-nonadiene cation (1) functions as a QCA cell. Here, two ethene groups each provide a quantum dot, as shown in Figure 3.1a. Circles represent dots in a device schematic drawing, and the dots are labeled "0" and "1." Localized states of the mobile hole on the quantum dots provide the binary device states of the DQD QCA cell. These states are shown in Figure 3.1b using spin density plots (upper row) and schematically as devices (bottom row). In the schematic, the mobile hole is represented using a green disc. We assign each localized state on dot $m \in \{0, 1\}$ the symbol $|m\rangle$.

The molecule has a C_2 symmetry which maps one dot to the other dot under a 180° rotation. Under this rotational symmetry, the charge states 0 and 1 are indistinguishable. We use the nuclear coordinates R_0 and R_1 , corresponding to device states $|0\rangle$ and $|1\rangle$, respectively, to form intermediate geometries, R(q):

$$R(q) = \left(\frac{1+q}{2}\right)R_0 + \left(\frac{1-q}{2}\right)R_1.$$
(3.1)

Here, q is a unitless reaction coordinate that parametrizes the linear combination, with $R_0 = R(1)$ and $R_1 = R(-1)$.



Figure 3.2: The dipole moment of a nearby charge configuration drives bistable device switching in molecule **1**. Here the molecular dipole moment of **1** is calculated as a function of the driver dipole moment. This response is calculated at the transition state geometry (q = 0).

A useful QCA molecule must have a state that can be driven by neighboring molecule(s). This may be tested by calculating the molecule's response to a nearby distribution of charge, which simulates a driver molecule, as shown in Figure 3.1c. Let a = 8.43 Å be the dot-to-dot distance of molecule **1**. Then, a pair of point charges Q and 1 - Q separated by a simulates the dots of a driver molecule. This distribution is placed at a distance d = a away from the test molecule so that the driver dots and the molecule dots form a square. The value of Q, with units of fundamental charge, is varied over [0, 1], and the electronic structure of **1** is calculated at the transition-state geometry, R(0).

Molecule 1 demonstrates bistable charge switching under the influence of a driver, as shown in Figure 3.2. Here, the induced molecule dipole moment, μ , is plotted as a function of the driver dipole moment, μ_{drv} . The driver induces an opposite μ in the target molecule, resulting in a symmetric, non-linear cell-cell response plot. This is consistent with Coulomb repulsion between the mobile hole of the target molecule and that of the driver. At $\mu_{drv} = 0$, the target molecule's mobile hole is evenly delocalized between two dots and the molecule favors neither device state.

For a QCA molecule to be readily switchable under the influence of nearby molecules, it is important that neither device state be preferred strongly for an isolated molecule. The natural detuning, Δ_0 , is a measure of the bias toward one device state:

$$\Delta_0 = \langle 1|\hat{H}|1\rangle - \langle 0|\hat{H}|0\rangle, \qquad (3.2)$$

where \hat{H} is the Hamiltonian for the isolated two-state DQD molecule. A preference for state 1 has $\Delta_0 < 0$, and a preference for state 0 has $\Delta_0 > 0$. The condition for switchability, then, is that the absolute value of the natural detuning, $|\Delta_0|$, should be smaller than the maximum bias, E_k , that a neighboring cell can provide:

$$|\Delta_0| < E_k,\tag{3.3}$$

In the context of QCA, E_k is known as the *kink energy* and is interpreted as the energy cost of the wrong state [9]. Given a cell of length a, the maximum driver bias at distance d may be calculated using electrostatics:

$$E_k = \frac{q_e^2}{4\pi\varepsilon_0} \left(\frac{1}{d} - \frac{1}{\sqrt{a^2 + d^2}}\right),\tag{3.4}$$

where ε_0 is the permittivity of free space and q_e is the fundamental charge. The calculated kink energy for molecule **1** for a driver distance d = a = 8.43 Å is $E_k = 500.5$ meV.

Ideally, $|\Delta_0| \ll E_k$ for a QCA candidate, since this provides no impediment to device switching. If $|\Delta_0|$ is too large, the driving bias from a neighboring molecule

cannot overcome Δ_0 , and the device is stuck in its preferred state. This makes for an unswitchable molecule, ineffective for use in the QCA application.

For a molecular cell, Δ_0 may be calculated from the ground state Marcus potential energy surface, as shown in Figure 3.3. The difference between the two local minima of the adiabatic ground state energy curve, E_0 , is the value of Δ_0 .



Figure 3.3: The natural detuning, Δ_0 , may be found from the ground state potential energy surface, E_0 , as a function of the unitless reaction coordinate, q. Δ_0 is the energy of state 1 (q = -1) relative to that of state 0 (q = 1). In the adiabatic Marcus curves shown here, this is found by subtracting the electronic ground state energy of state 0 at its corresponding geometry, $E_0(1)$, from the energy of state 1 at its corresponding geometry, $E_0(-1)$.

To generate the adiabatic energy surfaces for cation 1, CASSCF calculations were performed. The potential energy surfaces were calculated directly by finding the eigenvalues $E_0(q)$ and $E_1(q)$ of \hat{H} for several values of the reaction coordinate, q. $E_0(q)$ and $E_1(q)$ are the energies of the ground state and the first excited state, respectively. Figure 3.4 shows the adiabatic curves for molecule 1. The energy $E_0(q)$ exhibits bistability, with degenerate minima at R_0 and R_1 . The natural detuning, Δ_0 , is found by subtracting $E_0(1)$ from $E_0(-1)$:

$$\Delta_0 = E_0(-1) - E_0(1) . \tag{3.5}$$

For 1, the natural detuning is $\Delta_0 = 0$, consistent with the C_2 symmetry noted above. Molecule 1 is an ideal QCA candidate in terms of switchability, since $|\Delta_0| = 0 \ll E_k = 500$ meV.



Figure 3.4: The potential energy surfaces of ground state E_0 and the first excited state E_1 of molecule **1** are plotted against reaction coordinate, q. The ground state has two local minima which is consistent with the bistable nature of the molecule.

While **1** is easily switchable, its C_2 symmetry results spectroscopically indistinguishable device states. This is seen in the Raman spectra of states 0 and 1, calculated and plotted in Figure 3.5.

Asymmetric Cation 2: 1,1,2-trifluoronona-1,8-diene

To achieve spectroscopically-resolvable QCA states, a molecule like 1-but lacking C_2 symmetry-is desirable. We break the C_2 symmetry in 1 using three $H \rightarrow F$ substituions on dot 1. This changes 1 into the 1,1,2-trifluoronona-1,8-diene cation (2) of Figure 3.6a. The total mass of dot 1 is now higher than that of dot 0. The device states of 2 are depicted in Figure 3.6b. Molecule 2 is a suitable QCA candidate in terms of both switchability and spectroscopically-differentiable device states.



Figure 3.5: The device states of molecule **1** are spectroscopically indistinguishable. The calculated Raman spectra of states 0 (solid blue line) and 1 (dashed orange line) are identical because the molecule's C_2 symmetry maps state 0 onto state 1 under a 180° rotation. Arbitrary units are used for intensity.

The adiabatic potential energy surface $E_0(q)$ of Figure 3.7 shows that molecule 2 maintains switchability. Here, the natural detuning is $\Delta_0 \sim 60$ meV. For 2, the dotto-dot distance, a = 8.44 Å. The bias provided by a neighboring molecule at d = a is $E_k = 499.8$ meV, easily overcoming the much smaller $|\Delta_0|$.

It may seem counterintuitive that a significant change in electronegativity from the three $H \rightarrow F$ substitutions results in only a small Δ_0 ; however, F substituents have both activating and deactivating electronic effects on a molecule. They may show either electron-withdrawing (-I) or donating (+M) character depending on substituent position. Thus, different F substituents make different contributions to the detuning Δ_0 , as shown in Figure 3.8. Here, the $E_0(q)$ potential energy surface is calculated for different single fluorinations on one ethene group of molecule 1. These singlyfluorinated molecules are designated **3a**, **3b**, and **3c**. While $\Delta_0 < 0$ for **3a** and **3c**, $\Delta_0 > 0$ for **3b**. When all three fluorinations are present, as in **2**, there is enough



Figure 3.6: Molecule **2** provides an asymmetric two-state QCA cell. (a) The ethene group and the trifluoroethylene group function as two quantum dots. (b) Two logical device states are shown using spin density plots (upper) and schematic diagrams (lower).

competition between the various -I and +M effects to prevent $|\Delta_0|$ from growing too large and strongly biasing the molecular device to either state.



Figure 3.7: The potential energy surfaces of molecule 2 demonstrates the bistable charge localization driven by nuclear reorganization.

Figure 3.9 shows the bistable electronic switching of molecule 2 when placed near a driver molecule. The trend in the dipole response, μ , of 2 to the driver dipole, μ_{drv} , is very similar to that of the symmetric 1, with subtle differences. When the



Figure 3.8: The position of a single $H \to F$ substitution on dot 1 of molecule 1 affects the sign of Δ_0 . For each molecule, **3a**, **3b**, and **3c**, Δ_0 is calculated from its ground state potential energy surface, $E_0(q)$. In molecule 2, all three single fluorinations are present, and competing activating and deactivating effects from the three substitutions combine to yield a small Δ_0 .

geometry of 2 at q = 0 is used to calculate the molecular dipole moment in presence of the nearby molecule, the response function (blue data) is slightly asymmetric with respect to $\mu_{\rm drv}$, unlike the response of 1. This reflects the broken symmetry between the two device states of 2 and its natural bias toward state 1: $\Delta_0 < 0$, and $\mu(\mu_{\rm drv} =$ 0) > 0. A second dipole response (orange data) is also provided at the reaction coordinate q = 0.075. This coordinate was chosen because the peak in the $E_0(q)$ surface of Figure 3.7 indicates this to be the transition geometry. At q = 0.075, the molecule's response $\mu(\mu_{\rm drv})$ is symmetric. This indicates that neither device state is preferred at R(0.075), consistent with this being the transition state geometry.

Calculations of the Raman response of 2, plotted in Figure 3.10, show that its device states are spectroscopically distinct. State 0 and state 1 each have a unique Raman spectrum, most distinguishable in the neighborhood of $\nu \sim 2000$ wavenumbers. The distinguishing peaks arise from the presence or absence of the mobile hole on dot 0 or 1. When the mobile hole is localized on dot 0 (state 0), the C=C symmet-



Figure 3.9: The dipole moment of a nearby charge configuration drives bistable device switching in molecule **2**. At the reaction coordinate q = 0 (blue data), the cell-cell response is asymmetric and favors state 1 slightly. At the transition state geometry (q = 0.075, orange data), the response is much more symmetric.



Figure 3.10: The calculated Raman spectra for the binary device states of molecule **2** are distinguishable by strong Raman peaks near $\sim 2000 \text{ cm}^{-1}$. The distinguishing peaks occur at 2060 cm⁻¹ (state 0) and 1848 cm⁻¹ (state 1) with a separation of $\sim 200 \text{ cm}^{-1}$.

ric stretch on dot 1 is 2060 wavenumbers. This changes to 1840 wavenumbers when dot 1 is occupied (state 1). We denote this distinguishing change in frequencies as $\Delta_{\nu} = 212.16 \text{ cm}^{-1}.$

Molecule **2** has both switchability $(|\Delta_0| \sim 60 \text{ meV} \ll E_k \sim 500 \text{ meV})$, as well as spectroscopically distinct device states.

Asymmetric Cation 4: 1,1,2-trichloronona-1,8-diene



Figure 3.11: (a) Molecule **4** is similar to molecule **2**, but with Cl substituents. (b) Molecule **5** provides a two-dot QCA cell. One dot is deuterated to make the molecule asymmetric and spectroscopically readable.

Here, we explore the use of more massive substituents on **1** for driving spectroscopic distinguishability. Three Cl substituents on dot 1 result in the 1,1,2-trichloronona-1,8-diene cation (**4**), shown in Figure 3.11a. The total mass of dot 1 on molecule **4** is greater than that of dot 1 on molecule **2**. Nonetheless, **4** retains switchability as well as spectroscopically distinct device states. Two charge localized states, states 0 and 1, are obtained from geometry optimization.

As before, the potential energy surface $E_0(q)$ for 4 shown in Figure 3.12 suggests switchability: $|\Delta_0| \sim 75 \text{ meV} \ll E_k \sim 500 \text{ meV}$. The two minima of the ground state potential energy surface demonstrate that the mobile charge can be localized by nuclear relaxation alone.



Figure 3.12: The potential energy surfaces of the ground (E_0) and excited (E_1) states of molecule 4 demonstrates the bistable charge localization by nuclear relaxation in the molecule.

Under electronic driving, **4** also exhibits electronic bistability in Figure 3.13. Here, the dipole response of **4** is plotted as a function of the driver dipole moment, $\mu_{\rm drv}$. At the reaction coordinate q = 0 (blue curve), $\mu(\mu_{\rm drv} = 0) > 0$ indicates that state 1 is preferred. The dipole at this point is larger than the dipole of molecule **2** at q = 0 and $\mu_{\rm drv} = 0$. This suggests that the mobile hole prefers state 1 in molecule **4** more than in molecule **2**. This also agrees with the fact that **4** has a larger natural detuning, Δ_0 , than does **2**. The larger Δ_0 in **4** may be attributed to the fact that the hyperconjugative effects present in **2** also are present in **4**, but they are weaker. The C-Cl bond length is longer than the C-F bond length, preventing the C and Cl atomic orbitals from overlapping to the same degree that the C and F orbitals overlap. The orange μ plot at q = 0.17 is much closer to having odd symmetry than the blue q = 0 plot. This indicates that q = 0.17 is closer to the transition state geometry.

The calculated Raman spectra for states 0 and 1 of molecule 4 shown in Figure 3.14 demonstrate distinct features for each state. When the mobile hole occupies dot



Figure 3.13: Molecule **4** has a bistable electronic response to the charge configuration of a neighbor. At reaction coordinate q = 0 (blue data) and zero driver dipole, a natural bias toward state 1 is evident. The electronic response μ at q = 0.17 (orange data) is more symmetric, with $\mu(\mu_{\rm drv} = 0) = 0$. This indicates that R(0.17) is close to the transition state geometry.

0, the C=C symmetric stretch in dot 1 is 1753.7 cm⁻¹. The same stretch shifts to 1566.5 cm⁻¹ when the mobile hole occupies dot 1. The spectral shift in this Raman peaks is $\Delta_{\nu} = 187 \text{ cm}^{-1}$. Two other distinguishable Raman peaks occur at 1686.0 cm⁻¹ and 1858.7 cm⁻¹ for the dot 0 C=C symmetric stretch for states 0 and 1, respectively.

Asymmetric Cation 5: 1,1,2-trideuteronona-1,8-diene

Isotopic substitutions on one dot of molecule 1 provides a less drastic approach to breaking its C_2 symmetry. Deuteration introduces H substituents that are electronically identical, but heavier than the original H atoms. In molecule 5 of Figure 3.11b, each of the H atoms in one ethene group of 1 is replaced by a deuterium. Both nuclear relaxation and electric-field coupling drive bistable charge switching. The natural detuning between the two device states is 0 since the two states are degenerate.



Figure 3.14: Molecule 4 shows distinguishing spectral features for states 0 and 1. The Raman spectrum for state 0 has a sharp peak at 1753.7 cm⁻¹ for the C=C symmetric stretch in dot 1. State 1 has a strong peak for the same stretch at 1566.53 cm⁻¹. The separation between these two peaks is ~ 187 cm⁻¹.

The advantage of using isotopes is that the electronic properties remain unchanged, but vibrational properties are changed.

Figure 3.15 shows the calculated Raman spectra for states 0 and 1 of molecule 5. The C=C symmetric stretch for the deuterated dot occurs at 1795 wavenumbers for state 0. For state 1, the C=C symmetric stretch on the non-deuterated dot occurs at 1879 wavenumbers. The separation between these two distinct peaks is $\Delta_{\nu} = 84.2$ cm⁻¹.

Comparison of Molecules

Table 3.1 lists the most distinct Raman peaks for states 0 and 1 of molecules 1, 2, 4 and 5. The separation, Δ_{ν} , between two peaks is calculated for each molecule. The value of Δ_{ν} is a spectroscopic measure of how distinct the two states are from each other. The distinguishing peaks for molecule 2 have the largest separation. A large value of Δ_{ν} may be helpful for identifying the states of the molecule spectroscopically.



Figure 3.15: Molecule **5** has distinct Raman spectra for states 0 and 1. The two most distinguishable peaks occur at 1795 cm⁻¹ (state 0) and 1879.18 cm⁻¹ (state 1).

	State 0		State 1		Δ_{ν}
Molecule	ν	C = C	ν	C = C	$({\rm cm}^{-1})$
	(cm^{-1})	Stretch	(cm^{-1})	Stretch	
1	1879.18	Dot 1	1879.18	Dot 0	0.0
2	2060.58	Dot 1	1848.42	Dot 1	212.16
4	1753.70	Dot 1	1566.53	Dot 1	187.17
5	1795.03	Dot 1	1879.18	Dot 0	84.15

Table 3.1. Separation of distinguishing Raman peaks in different QCA molecules.

Molecule 2 appears to be the best molecule among those studied in terms of switchability and spectroscopically-distinguishable states. Its device states are readily distinguishable, and it has a relatively small $|\Delta_0|$. Molecule 5 also provides spectroscopically distinct device states, but with $\Delta_0 = 0$.

Discussion

We have proposed the use of asymmetric molecules to enable the spectroscopic read-out of molecular QCA bits. The results presented here were for ethene dots with a butyl linker. $H \to X$ substitutions were used on one dot to achieve distinct spectra for the two device states of a DQD molecule.

To lower the signal-to-noise ratio, it may be possible to copy a bit onto a circuit of many asymmetric molecules. TERS may be applied to all the molecules of the circuit, rather than just a single DQD molecule. A concept output circuit is shown in Figure 3.16a. Here, the mobile charge is not shown, but the dots are drawn with different sizes to indicate the asymmetry of each DQD. Upstream calculations result in a particular configuration on cells B and A, which determines the state of cell 0. The bit on cell 0 is copied onto the serpentine output (cells 1, 2, ...). This serpentine circuit provides a larger target for laser illumination and strengthens the desired spectroscopic signal by the proliferation of bit copies. Here, the serpentine path has 8 cells, but it could be modified to include many more cells.

Simulations of a concept output circuit are shown in Figures 3.16b and 3.16c. The ground state of the circuit is calculated and visualized. Cells A and B are treated as driver molecules, providing a potential for the output circuit (cells 0, 1, 2, ...). For the non-negative integer k, the k-th output cell is a two-state system. In the basis $\{|0\rangle, |1\rangle\}$, cell k has a free Hamiltonian $\hat{H}_k = -\gamma \hat{\sigma}_x + (\Delta_0 + \Delta(k)) \hat{\sigma}_z/2$ characterized by electron transfer coupling integral γ , natural detuning Δ_0 , and external bias $\Delta(k)$. $\hat{\sigma}_x$ and $\hat{\sigma}_z$ are Pauli operators. The total circuit Hamiltonian is $\hat{H} = \sum_k \hat{H}_k + \hat{H}_{int}$, where \hat{H}_{int} is the interaction term between the cells forming the circuit. \hat{H}_{int} is diagonal in a basis $|X\rangle = |x_0\rangle |x_1\rangle |x_2\rangle \cdots$, where $x_k \in \{0, 1\}$ denotes a localized state of the mobile charge on dot x_k of cell k. The diagonal elements of $\hat{H}_{int}, \langle X|\hat{H}_{int}|X\rangle$, are calculated directly from the electrostatic potential energy of assembly for the system of point charges modeling each cell. Here, the serpentine output simulated has 14 cells. The serpentine output circuit correctly copies the bit on cell 0 to all of its member cells. As a target for illumination, a multi-cell circuit may provide an superior Raman SNR to that of a single molecule.



Figure 3.16: A fanout circuit provides multiple bit copies to enhance the spectroscopic signalto-noise ratio. (a) Upstream calculations determine the states of cells B and A, which determine the state of cell 0. The bit from cell 0 is copied directly to the remainder of the serpentine fanout circuit (cells 1, 2, ...). The two dots of a molecule are drawn with different radii to indicate the asymmetry of the molecule and that one dot may be preferred over the other dot by the mobile charge. (b) A circuit-level model of the circuit of subfigure (a) copies a bit over all cells (0, 1, 2, ...) in the serpentine output circuit. The mobile charge is depicted as a red sphere on the gray spheres (quantum dots). (c) The circuit model also supports the opposite output bit from the case of (b). In these circuits, a = 1 nm, and $\Delta_0 = 10$ meV. Courtesy: Peizhong Cong.

This concept also could be extended from the asymmetric two-dot QCA molecules shown here to asymmetric three-dot molecules that support the latching of bits through clocking [36, 81]. Thus, an output bit could be latched onto many molecules in an output circuit. The state of the circuit could be held on the clocked circuit for the duration of a measurement.

Conclusion

Ab initio calculations presented here show that it is possible to design asymmetric, mixed-valence QCA molecules that allow device switching and spectroscopic state readout. Molecular quantum dots should be designed to be dissimilar so that different configurations of the mobile charge have distinct Raman spectra. Differences should be minimized to keep the bias toward any particular device state well below the driving potential applied by a neighboring molecule.

The molecules presented here illustrate the proof-of-principle for the spectroscopic readout of simple, cationic QCA molecules with C=C-based dots. Organometallic molecules with metallocene dots may provide more stable devices and should be explored, in both theory and experiment. Additionally, asymmetric designs of zwitterionic three-dot molecules are of interest, since these will support clocking, and no counter-ions are produced in their synthesis [17, 18].

CHAPTER FOUR

Designing Boron-cluster-centered Zwitterionic Y-shaped Clocked QCA Molecules

N. Liza, Y. Lu, and E. Blair, "Designing boron-cluster-centered zwitterionic Y-shaped clocked QCA molecules," Nanotechnology 33, 465201 (2022).

Abstract

Clocked control of QCA provides power gain to boost weakened signals, as well as quasi-adiabatic device operation for minimal power dissipation in QCA devices and circuits. An applied electric field may be used to clock molecular QCA. A zwitterionic, Y-shaped, three-dot molecule may function as a field-clocked QCA cell. In this work, we focus on the design of a counterion built into the center of a zwitterionic molecular QCA cell. *Ab initio* computations demonstrate that choice of counterion determines the number of mobile charges for encoding the device state on the three quantum dots. We use $B_5H_5^{2-}$ or $B_4CH_5^{-}$ as the central counterionic linker for two different Y-shaped, three-dot QCA molecules. While both molecules support the desired device states, the number of trapped charges in the counterion determines the number of mobile holes on the molecular quantum dots. This, in turn, determines whether the device state is encoded by a hole or an electron. This choice of encoding determines how the molecular QCA cell responds to a clocking field.

Introduction

In molecular QCA scheme, synchronous control of QCA circuits through clocking is important, since this enables quasi-adiabatic operation, defines the direction of information flow and calculations, and provides power gain to boost degraded signals[40, 82, 36]. Ionic molecular QCA candidates have been synthesized and stable device states have been observed using STM microscopy, and field-driven switching has been observed [13, 14, 15], even in individual molecules [43]. Most of these mixed-valence complexes are positively charged cations or negatively charged anions. Counterions are produced during their chemical oxidation or reduction. These external counterions tend to achieve charge balance in QCA circuit and disrupt the molecular QCA circuit operation. One natural solution is to use charge-neutral, MV, zwitterionic molecules, since the synthesis of such molecules does not produce counterions. [16, 17]. In these molecules, counterions are covalently built into molecules. While MV, zwitterionic molecules have been synthesized [18], stable device states have not yet been observed experimentally in these molecules using STM imaging. No sample of theses molecules are known to exist for further testing. New candidates must be designed and synthesized to accelerate the developments in realizing molecular QCA.

Here, we explore the design of zwitterionic QCA candidate molecules, focusing specifically on the use of a central boron cage as the counterion. The boron cage traps fixed neutralizing electrons, which are donated by functional groups that also act as quantum dots. To demonstrate the concept, three allyl groups are used as dots, in a Y-shaped arrangement about the boron cage. We use allyl groups for simpler quantum dots, and the focus is on different counterions. It is predicted through *ab initio* modeling that such molecules could function as QCA, and that the boron cage may be selected in order to engineer a particular molecular response to the clocking field.

The choice of the central counterionic cage plays a defining role in the molecular device characteristics. The counterion may be designed for a specific number of trapped electrons. This determines the number of mobile charges on the three allyl dots. This, in turn, affects the device characteristics, since the unique dot encodes the device state. If there are two mobile holes on three allyl dots, then a single electron neutralizes one of the three dots, defining the device state. If only one mobile hole is used, its location encodes the device state. This choice of encoding (electron versus hole) significantly affects the molecule's device characteristics, especially its response to a clocking electric field. We explore the device ramifications of changing the counterion.

Methods

All *ab initio* computations in this work were performed with the Q-Chem 5.2 software package [83]. Geometry optimizations of molecule **1** and **2** were performed to obtain three logical device states, 0, Null and 1. The restricted open-shell Hartree-Fock (ROHF) method was employed for all computations to avoid spin contamination [60]. The 6-31g* basis set was used for all atoms (H, B, C, N) of molecule **1** and **2** for all the computations. The clocking field values for appropriate switching of the molecules were determined by examining a series of applied field values. To test the electronic bistability of each molecule, the dipole moment of a target molecule induced by the dipole moment of a nearby driver molecule was calculated. The neighbor molecule was simulated by two external point charges. Computations with a point charge driver and electric-field clocking were performed without nuclear relaxation.

Results

Molecule 1

A Y-shaped, mixed valence zwitterionic molecule $B_5(CN)_2(C \equiv CC_3H_4)_3$ (molecule 1, Figure 4.1a) functions as a clocked QCA cell. The optimized geometry of the neutral molecule is shown in a ball-and-stick diagram, and a device schematic depicts the dots as black circles. Three allyl groups, each having a low-lying, non-bonding π orbital, provide three outer quantum dots, labeled "0," "Null," and "1." Allyl groups are chosen for their chemical simplicity, which minimizes the molecule's computational



Figure 4.1: Molecule 1 provides a three state QCA cell. (a) Three allyl groups of molecule 1 (left) function as three quantum dots. These three dots (0, Null and 1) are represented schematically by circles (right). (b) Three stable charge configurations of 1 based on localized mobile holes provide three logical device states, 0, Null and 1. These three charge states are shown by calculated electrostatic potential surfaces (upper) and schematic diagrams (lower). The presence of a mobile hole on a dot is represented by a blue circle. Two red circles on the boron cage shows the presence of two fixed electrons. The red and blue surfaces in the electrostatic potential surface plots represent presence of negative and positive charge respectively (colors are displayed in the online version only).

cost. The pentaborate cage serves as a central dot that links the three outer dots. The cage is further functionalized with two electron-withdrawing CN groups that raise the central linker's electronegativity.

Geometry optimizations for neutral **1** result in the three degenerate, zwitterionic device states of Figure 4.1b. An electrostatic potential (ESP) plot (top row of diagrams) is mapped onto the electron density plot for each of the device states, and a corresponding schematic shows the electronic configuration of the mobile charge on the system of quantum dots. The ESP color scheme is blue for positive potential, red for negative, and green for neutral. In the schematic representations (bottom row), blue dots represent a mobile hole, and red dots represent trapped electrons.

The electron-deficient boron cluster $(B_5H_5^{2-})$ traps two electrons at the center of the molecule. Any pair of the outer dots may be occupied by one mobile hole each, leaving one neutral dot to determine the state. Then, the device state corresponds to the direction of the x-component of the molecular dipole as follows: states "0" and "1" have dipoles in the positive and negative x directions, respectively; and the null state has $\mu_x = 0$. The two states "0" and "1" encode a bit and are called "active" states. The "Null" state does not encode any information. The device may be driven to the null state using an externally-applied electric field, and the symmetry between the active states may be broken by the dipole moment of a neighboring molecule.

Device State	Property	Dot 0	Dot Null	Dot 1
"O"	Bond angle	121.7	113.8	113.8
0	Charge	0.030	0.748	0.748
"NI.111"	Bond angle	113.8	121.7	113.8
INUII	Charge	0.748	0.030	0.748
"1"	Bond angle	113.8	113.8	121.7
1				

0.748

0.748

0.030

Charge

Table 4.1: The C-C-C bond angles (in degrees) and the Mulliken charge analysis of the dots (allyl groups) of optimized molecule $\mathbf{1}$ for the three device states obtained at ROHF/6-31G^{*}.

The optimized geometries of the device states of molecule 1 show that a single hole occupation affects the C-C-C bond angle in the allyl groups. These C-C-C bond angles are listed in Table 4.1 for the three device states. When occupied by a mobile hole, the cationic allyl group's C-C-C angle is about 114°. The charge neutral allyl radical group has a C-C-C bond angle of about 122°. These values are consistent with the cationic and neutral allyl bond angles reported in the literature [41].

An analysis of the molecular orbitals in the three device states of **1** shows that two unpaired allyl π electrons are doped into the *closo*-pentaborate cluster. Figure 4.2 shows the frontier orbitals for the "0", "Null" and "1" states of molecule **1**. For each state, the highest occupied molecular orbital (HOMO) is occupied by a single, unpaired π electron on the neutral allyl group. The lowest unoccupied molecular orbital (LUMO) and the LUMO+1 are unoccupied degenerate π orbitals on the cationic allyl



Figure 4.2: Frontier molecular orbitals of Molecule 1 for the "0", "Null" and "1" states. The lowest unoccupied molecular orbital (LUMO) and the LUMO+1 are localized on the cationic allyl groups. The HOMO-1 orbital localizes on the pentaborate cage and demonstrates self-doping for zwitterionic MV molecular QCA cell.

groups. These two orbitals are unoccupied because the unpaired electron from each allyl is transferred to the pentaborate cage, stabilizing the boron cluster in accordance with Wade's rule [84]. These stabilizing electrons for the central cage are found in the HOMO-1 orbital. These results are consistent with the ESP plots of Figure 4.1b. Additionally, the Mulliken charge analysis of Table 4.1 reflects these results.

A clocked QCA candidate must be able to (1) switch between an active state and the null state under an applied external clocking field, and (2) switch between its active states when driven by neighboring molecule(s). This may be tested by calculating the molecule's response to a nearby distribution of charge, which simulates a driver molecule, as shown in Figure 4.3a. Let a be the dot-to-dot distance of molecule 1. The dots are equidistant because of the molecule's symmetry, with an inter-dot distance a = 9.05 Å. A pair of point charges Q and 1 - Q separated by a simulates the dots of a driver molecule. This distribution is placed at a distance d = a away



Figure 4.3: Molecule 1 supports clocking using an external electric field and the dipole moment of a nearby molecule switches the molecule between the active states, "0" and "1". (a) Two point charges, Q and 1-Q, simulate a driver molecule close to a molecule immersed in a clocking field \vec{E} . (b) The *x* component, μ_x , of the molecule's dipole moment responds to the clocking electric field ($E_y = -1 \text{ V/nm}$) and the dipole moment, $\mu_{x,\text{drv}}$, of the simulated driver molecule. (c) The molecular dipole moment, μ_x is calculated as a function of the electric field E_y and the driver dipole moment, $\mu_{x,\text{drv}}$. The yellow area corresponds to the molecule in the "0" state and the blue area corresponds to the molecule in the "1" state. The green area corresponds to the "Null" state.

from the test molecule so that the driver dots and the molecule's active dots form a square. The value of Q is varied over [0, 1], and the electronic structure of **1** is calculated at the transition-state geometry, which is the average of state "0", "Null" and "1" geometry. At this geometry, the molecule does not favor any device state. A local electric field in the y-direction is applied as a clock that can drive the molecule into an active ("0" or "1") state or the "Null" state. A negative clocking field $(E_y \hat{y}$ with $E_y < 0$) drives one mobile hole to the Null dot so that the molecule takes an active state. Neighbor interactions may bias the mobile hole toward one of the active dots. When a positive clocking field is applied $(E_y > 0)$, both mobile holes are driven to occupy the upper two dots, resulting in the "Null" state.

Molecule 1 demonstrates bistable charge switching under the influence of the field $E_y \hat{y}$ and a distribution of point charges simulating a neighboring driver molecule. In Figure 4.3b the induced *x*-component of the molecule's dipole moment, μ_x , is plotted as a function of the driver dipole moment, $\mu_{x,drv}$. For this computation, a clocking field of $E_y = -1$ V/nm is applied. Each value of the driver dipole induces an opposing dipole in the target molecule, resulting in a symmetric, non-linear cell-cell response plot. This shows that the Coulomb field from the driver charge distribution is sufficient to localize the molecule's mobile charge and select a device active state.

Figure 4.3c shows the induced molecular dipole moment μ_x as a function of both the clocking electric field, E_y , and the driver dipole moment, $\mu_{x,drv}$. For fields smaller than about 0.3 V/nm, the molecule is either in "0" (yellow area) or "1" state (blue area). This response is similar to the plot shown in Figure 4.3b and the molecule is said to be in an active state. For $E_y \gtrsim 0.65$ V/nm both mobile holes are forced to occupy both of the active dots, and the molecular dipole moment, μ_x , is zero for all values of the driver dipole moment $\mu_{x,drv}$ (green region). The molecule is clocked to the null state regardless of the charge configuration of the driver.



Figure 4.4: (a) Molecule **2** provides a three state clocked QCA cell (left). Three allyl groups of this molecule function as three quantum dots. Schematic representation of molecule **2** is shown by circles (right). (b) Three different charge configurations based on localized mobile holes provides three logical device states, 0, Null and 1. The device states are shown using calculated electrostatic potential surfaces of the three states (upper) and schematic diagrams (lower). The presence of a hole on an allyl group is represented by a blue circle and a red circle at the center represents the presence of a negative charge.

Molecule 2

In molecule 2, $B_4C(CN)_2(C\equiv CC_3H_4)_3$, we employ a *closo*-carbaborate cage as the central linker between three allyl groups, as shown in Figure 4.4a. Unlike the linker from molecule 1, which traps two electrons, this electron-deficient boron cluster traps only one electron at the center of the molecule. This results in only a single mobile hole on one of the three allyl groups. This creates three stable, degenerate charge configurations and provides three localized device states ("0", "Null" and "1") encoded in the location of the hole. Figure 4.4b shows the calculated ESP plots (upper row) of the three device states. The device state, "0", "Null" or "1," corresponds to the *x*-component of the molecular dipole as in the case of 1, but having the opposite direction. In the ESP plots, the blue surface coloring (positive ESP) indicates the presence of the mobile hole, and red surface (negative ESP) at the center indicates the electron trapped by the central boron cage.

Device State	Property	Dot 0	Dot Null	Dot 1
"0"	Bond angle	115.0	122.6	122.6
0	Charge	0.814	0.093	0.093
"Null"	Bond angle	122.6	115.0	122.6
INUIT	Charge	0.093	0.814	0.093
((1))	Bond angle	122.6	122.6	115.0
1	Charge	0.093	0.093	0.814

Table 4.2: The C-C-C bond angles (in degrees) and the Mulliken charge analysis of three dots (allyl groups) of optimized molecule 2 for the three device states obtained at ROHF/6-31G^{*}.

The C-C-C bond angles and Mulliken charges calculated for the allyl groups are consistent with the cationic and neutral allyl bond angles reported in the literature [41]. The C-C-C bond angles are listed in Table 4.2 for optimized geometries in the three device states. For the dot occupied by the mobile hole (cationic allyl group), the C-C-C bond angle is about 115°. The other two charge neutral allyl radical groups (unoccupied dots) have C-C-C bond angles of 122.6°.



Figure 4.5: Frontier molecular orbitals of Molecule **2** for the "0", "Null" and "1" states. The bistable charge configuration is shown by the lowest unoccupied molecular orbital (LUMO) orbitals. A single mobile hole determines the device state.



Figure 4.6: Molecule **2** responds to the dipole moment of a neighboring molecule and the applied local field. (a) The dipole moment of a nearby charge configuration drives molecule **2** to the "0", "Null", or "1" states under an applied electric field, E_y . The molecular dipole moment, μ_x , of **2** is calculated as a function of the driver dipole moment, μ_x , of **2** is calculated as a function of the driver dipole moment, μ_x , of **2** is calculated as a function of the driver dipole moment, μ_x , of **2** is calculated as a function of the driver dipole moment, μ_x , of **2** is calculated as a function of the driver dipole moment, μ_x , of **2** is calculated as a function of the electric field E_y and the driver dipole moment, $\mu_{x,drv}$. The yellow area corresponds to the "1" state, and the blue area corresponds to the "0" state. The green area corresponds to the molecule in the "Null" state.

Molecular orbital analysis of Molecule 2 is consistent with the electrostatic potential plots of Figure 4.4b. Figure 4.5 shows orbitals from the HOMO-2 up to the LUMO. These orbitals indicate that the unpaired allyl π electron from the cationic (hole-occupied) dot is doped into the carbaborate cluster. For each state, the HOMO and HOMO-1 are both singly-occupied orbitals. The LUMO is localized on the cationic allyl group. The LUMO is empty because the electron (unpaired allyl π electron) that would otherwise occupy this dot is trapped on the carborate cage in the HOMO-2 orbital.

Molecule 2 exhibits bistability when driven by a near-by charge distribution and immersed in an applied clocking field. Figure 4.6a shows a symmetric, non-linear QCA cell-cell response plot for Molecule 2. Each value of driver dipole moment, $\mu_{x,drv}$ induces an oppositely-oriented dipole moment, μ_x , in the molecule. For this computation, a driver setup similar to that of Figure 4.3a is employed. An average of the device state geometries is used, and a clocking field of 1 V/nm is applied in +y-direction.

In this case, a negative clocking field $(E_y < 0)$ drives the mobile hole to occupy the Null dot, resulting in the "Null" state. When a sufficiently positive E_y is applied, the mobile hole is pushed into one of the upper two dots, establishing the molecule in the active state determined by neighbor interactions. Figure 4.6b shows the xcomponent of the induced molecular dipole moment μ_x as a function of both the clocking electric field, E_y , and the driver dipole moment, μ_{drv} . For $E_y \gtrsim 0.5$ V/nm, the molecule is either in the "0" (blue area) or the "1" state (yellow area). This response is similar to the plot shown in Figure 4.6a and the molecule is said to be in active state. For $E_y \lesssim 0.07$ V/nm, the dipole moment of the molecule, μ is zero for all values of the driver dipole moment. The molecule is then in the "Null" state: the clocking field always drives the mobile hole to the Null dot, regardless of the neighbor dipole. This demonstrates clocked control of molecule **2** for QCA operation.

Conclusion

Three allyl groups were attached to a central cage to obtain a Y-shaped, threedot QCA molecule. Two molecules were considered, each with a different anionic boron cage as the central linker. Ab initio electronic structure computations were used to explore the response of these molecules as devices. In each case, the boron center traps unpaired electrons from one or more allyl groups. Each molecule demonstrated the three, desired charge configurations for three device states. The molecules both responded to a charge distribution modeling a neighboring QCA molecule in the presence of an applied clocking electric field, $E_y \hat{y}$.

We have demonstrated that the central linking group may be chosen to engineer the device behavior in a neutral, mixed-valence, Y-shaped QCA molecule. For molecule **1**, a *closo*-pentaborate linker traps two electrons at the center of the
molecule, creating two mobile holes that occupy two of the three allyl dots. In molecule **2**, a *closo*-carborate monoanion traps one electron, establishing one mobile hole on the three allyl dots to define the device state. The number of mobile holes in the QCA cell, in turn, determines the device's response to applied electric fields. For **1**, a clock $E_y > 0$ is required to drive both mobile holes to the active dots, establishing $\mu_x = 0$ and clocking the molecule to the "Null" state. For **2**, on the other hand, $E_y < 0$ drives the single mobile hole to the null dot, establishing $\mu_x = 0$. Thus, **1** and **2** respond to the clock in opposite ways. This is analogous to the behavior of a conduction channel in NMOS and PMOS transistors: in these two cases, opposite gate voltages are required for a conduction channel to exist.

CHAPTER FIVE

Ab Initio Studies of Counterion Effects in Molecular QCA

Abstract

A practical limitation of using ionic MV molecules in QCA circuit is uncontrolled effects posed by external neutralizing counterions. Counterions localize randomly near molecules that are chemically oxidized or reduced to form ionic QCA cells. These randomly-placed counterions can bias the device states of the molecules, producing incorrect computational results. External counterions also may affect device properties in unpredictable ways. In this work, we investigate the effects of counterions on QCA molecules using first-principles calculations. Complete active space self consistent field (CASSCF) computations are used to show that nearby counterions may degrade device states by causing mobile charge to localize in undesirable ways on the molecule. The placement of nearby counterions also can affect the electron tunneling (ET) matrix element and the inner-sphere reorganization energy of the molecules, changing device operating characteristics. These undesirable and random complications may be avoided by using zwitterionic MV QCA molecules, in which the counterion is built into the molecule itself. In zwitterionic molecules, positive and negative charges reside at well-defined locations, and the molecule is charge neutral. This design approach avoids the formation of randomly-placed counterions near the QCA devices. In this paper, we design and model two zwitterionic QCA candidate molecules. First-principles calculations demonstrate the desired device states. Predicted device characteristics are compared to the characteristics of ionic QCA molecules. Zwitterionic device behaviors may be engineered by building different counterions into the central linker between working dots.

Introduction

To realize device states, most previously-studied molecules require chemical oxidation or reduction to a cationic or anionic state. External counterions are created during this preparation. One challenge of using these ionic molecules in QCA circuit is the effects of external counterions on the QCA devices which may introduce complications in the circuit [13]. In this work, we study how nearby counterions may affect the electronic properties of QCA molecules. In particular, we analyze the electron transfer (ET) matrix element, inner-sphere reorganization energy and charge distribution of the molecules. We design simple ionic QCA candidate molecules and evaluate their device properties with and without the presence of external counterions. Ab initio calculations show how a counterion near a QCA molecule affects the localization of the mobile charge in the molecule as well as its electronic properties. These effects will be irregular and unpredictable in an environment of randomly placed counterions. Results also show that using a zwitterionic QCA molecule with a built-in counterion in QCA circuit can overcome the unpredictable effects from external counterions. In zwitterionic molecules, the counterion is covalently built into the molecule and positive and negative charges reside at well-defined locations, while the molecule itself is charge neutral [85, 17]. A neutral MV zwitterionic QCA candidate molecule based on two ferrocene groups and a nido-carborane cage was synthesized and tested [18].

In molecular QCA, Coulomb interaction between neighboring molecules drives transitions between device states via inter-dot, intra-molecular electron transfer (ET). Nuclear relaxation of the QCA molecule may enhance the charge localization. An excessively-strong nuclear reorganization energy, λ , may trap mobile charge so that the driving electric field from a neighboring molecule may be unable to switch the device states. In this case, a molecule may become 'stuck' in one state. The inner sphere reorganization energy, λ , involves change in structure of bond lengths and angles of a QCA molecule upon an electron transfer event. The electron transfer (ET) matrix

element, H_{AB} , also known as tunneling energy or hopping energy, describes how easily an electron can tunnel from one dot to the other. ET matrix element, H_{AB} , also referred as γ in literature, is the coupling between the diabatic states of a molecule. A larger value of H_{AB} results in easier tunneling and strong communication between dots. This may lead to charge delocalization and weak bit values. A smaller value H_{AB} means weak electronic communication which may enable charge localization by neighboring molecules via Coulomb interaction and provide strong QCA bit values. ET matrix element is highly dependent on the electronic structure of the quantum dots, interaction between them, and the nature of the bridge between the dots in a molecule [86, 48, 4, 87]. H_{AB} and λ relate molecular structure, electronic properties and QCA functionality of MV molecules in a QCA circuit. We calculate these parameters to explore how nearby ions affect a QCA molecule's device behaviors. We investigate the change in ET matrix element and inner-sphere reorganization energy of QCA molecules and analyze the effect on mobile charge localization in presence of nearby counterions. We also analyze how the localization of the mobile charge in the molecule is affected by the Coulomb interaction between the external counterion and the molecule.

Finally, we propose the use of zwitterionic molecules as QCA candidates. MV zwitterionic QCA molecules have well-defined positions for the counterions and mobile charges which can overcome the complications created by random counterions. We design two types of zwitterionic neutral molecules: (1) one with a built-in positive counterion and a mobile electron and (2) a negative counterion built into the molecule and a mobile hole. We observe a significant change in ET matrix element and reorganization energy of the zwitterionic molecules compared to the respective ionic QCA candidate molecules.

In the Methods section, we provide the computational details of *ab initio* calculations performed on the QCA molecules. In the Results section, we conduct CASSCF calculations for simple QCA molecular systems with inter-molecular electron transfer between the dots and also for QCA candidate molecules with intra-molecular electron transfer between the working dots. Even though the counterion effects for the intermolecular electron transfer through space are predictable, the effects become more complex for molecules with electron transfer through bond. We also present design of two zwitterionic neutral molecules by building the counterion into the molecule. By design, the built-in counterion avoids biasing any molecular device state, since it has a well-defined location at the center of the molecule [85, 17]. We analyze ET matrix element and reorganization energy of the zwitterionic molecules. By avoiding the creation of randomly-placed counterions, zwitterionic molecules may offer more consistent and predictable device operation. We finally conclude our work by proposing use of zwitterionic MV molecules as QCA candidates.

Methods

All *ab initio* calculations were performed using the GAUSSIAN 16 software package [78]. Geometry optimizations were performed at the Hartree-Fock level of theory [56]. For each molecule, the ET matrix element, H_{AB} , and the reorganization energy, λ , were calculated from the adiabatic potential energy surfaces (PESs). PESs were obtained from first principles using a state-averaged complete active space selfconsistent field (CASSCF) method [79, 80]. A weighting coefficients of 0.5 was used for both the ground state and the first excited state in the CASSCF state average to mix the two states equally. The active spaces used for CASSCF calculations for different molecules are given in Table 5.1. For molecules **2-8**, adiabatic potential energy surfaces (PESs) were calculated for the electronic ground state, $E_0(q)$, and the first excited state, $E_1(q)$, over several nuclear geometries R(q). Each R(q) is a linear combination of the geometries R_0 and R_1 , which correspond to states 0 and 1, respectively. The unitless reaction coordinate, q, specifies a unique linear combination of R_0 and R_1 :

$$R(q) = \left(\frac{1+q}{2}\right)R_0 + \left(\frac{1-q}{2}\right)R_1.$$
(5.1)

The ground-state and first-excited-state PESs were used to calculate H_{AB} and λ . H_{AB} is half of the difference between the minima of the excited state $E_1(0)$ and the ground state energy at the transition state geometry (q = 0):

$$H_{AB} = \frac{1}{2} (E_1(0) - E_0(0)) .$$
 (5.2)

The reorganization energy, λ , is found by taking the difference between E_1 and E_0 at a local minimum of $E_0(q)$. The local minima of E_0 occur at $q = \pm 1$ so that

$$\lambda = E_1(\pm 1) - E_0(\pm 1) \tag{5.3}$$

This may be interpreted as cost of switching the molecule's electronic configuration from that of state 0 to that of state 1 (or from state 1 to state zero), but freezing the nuclear coordinates in the geometry of state 0 (or state 1). H_{AB} and λ are illustrated on a pair of adiabatic curves, shown in Figure 5.7.

Molecular structures, orbitals and electrostatic potential (ESP) surfaces presented here are visualized using GaussView 6, a part of the Gaussian 16 software suite [78]. The 6-31g* basis set was used for all atoms (H, C, P) for molecules 1-5 and 7 in all calculations. The 6-311++G(2d,2p) basis set was used for molecule 6. The 6-311g* basis set was used for all atoms (H, C, B, F, Cl) for molecules 8-9 in all calculations. MATLAB was used for modeling the simpler 1D system of an electron in a double well potential [88].

Results

Electron Tunneling through Space

In this section, we analyze simple molecular dimer systems where the electron tunnels from one dot to the other through space. We use *ab initio* modeling to cal-

Molecule	Active space	Molecule	Active space
1a	CAS(1,2)	4	CAS(3,4)
$1\mathrm{b}$	CAS(3,2)	5	CAS(7,6)
2a	CAS(3,4)	7	CAS(7,6)
2b	CAS(5,4)	8	CAS(1,2)
3a	CAS(5,6)	9	CAS(1,2)
3b	CAS(7,6)		

Table 5.1. Active spaces for molecules **1a-9**, used for the CASSCF Calculations.

culate the effect of nearby counterions on molecular properties such as ET matrix element, H_{AB} and reorganization energy, λ .

Hydrogen molecular cation H_2^+ , Molecule **1a**. The hydrogen molecular cation H_2^+ has only one electron and is the simplest possible QCA molecular model when the inter-atomic distance *a* is large (≥ 4 Å) [4]. For this H_2^+ system in vacuum with a = 4 Å, the mobile charge tunnels through space between the two dots (two H atoms) with $H_{AB} = 58.2$ meV.

To investigate the effect of a counterion on the value of tunneling energy, H_{AB} , we calculate H_{AB} for the dimer in the presence of a counterion having charge Qplaced at distance d away from the dimer. Specifically, d is the distance from Q to the midpoint between dots. In this case, Q = -1, and H_{AB} is calculated as d is varied from 4 Å to 0 Å. This molecule-counterion setup is shown in Figure 5.1. The results are shown in Table 5.2 (column **1a**). As the charge Q = -1 approaches the center of the double quantum dots, H_{AB} decreases. The approaching counterion suppresses the electronic wave function in the region between the two atoms (dots), reducing the electron transfer integral $\langle \psi_0 | \hat{H} | \psi_1 \rangle$. This may be interpreted as raising the inter-dot barrier and reducing the inter-dot communication, causing H_{AB} to decrease.

To illustrate and illuminate this phenomenon, 1D modeling was performed using an analogous system: an electron in a finite double-well potential system, as shown in



Figure 5.1: A point charge, Q, mimics an external counterion, separated from the center of a QCA molecule by a distance, d. The value of Q is -1 for cationic molecular system and +1 for an anionic molecular system. The distance between two molecular quantum dots is a.

Figure 5.4a. The blue line shows an unperturbed double-well. Each well corresponds to a molecular quantum dot and the separation between the dots provides an inter-dot barrier. When a negative point charge, Q = -1 was placed near the wells, the barrier height between the wells increased (dashed yellow lines). On the other hand, when a positive point charge, Q = +1, approached the system, the barrier height decreased (red dotted line).

The probability densities $|\psi_s|^2$ of states $s \in \{0, 1\}$ of the electron localized on dot s are plotted in Figure 5.4b. The states $\psi_s(x)$ are obtained by applying a bias between the two wells (not shown in Figure 5.4a). The waveforms $|\psi_0|^2$ and $|\psi_1|^2$ are repelled from or attracted to the center (x = 0) under the influence of a nearby anion or cation, respectively. Attraction toward x = 0 leads to greater overlap between the wave functions $\psi_s(x)$ (see the Q = 1 case in Figure 5.4a). This corresponds to an increase in $H_{AB} = \langle \psi_0 | \hat{H} | \psi_1 \rangle$. Likewise, repelling the mobile charge from x = 0 reduces the overlap between the wave functions $\psi_s(x)$, reducing H_{AB} . H_{AB} was calculated for different distances d of the counterion from the double-well system.

$\frac{d}{(\text{\AA})}$	1a , <i>Q</i> =-1	$\mathbf{1b},\ Q=+1$	2 Q=	a, =-1	2 Q=	$\mathbf{b}, =+1$	3 Q=	a , =-1	3 Q=	$\mathbf{b}, =+1$
	H_{AB}	H_{AB}	H_{AB}	λ	H_{AB}	λ	H_{AB}	λ	H_{AB}	λ
∞	58.2	113.0	44.4	333.5	64.0	600.7	40.7	151.9	54.6	214.6
5	57.2	114.4	43.5	330.7	65.0	598.7	40.1	155.2	55.7	212.0
4	56.4	115.7	42.8	328.9	65.8	597.3	39.5	157.4	56.5	209.6
3	54.5	118.6	41.2	325.5	67.6	595.0	38.2	161.2	58.2	206.0
2	48.6	127.5	37.0	319.1	71.9	592.4	35.2	166.3	62.0	203.3
1	30.6	155.2	26.9	308.9	80.7	592.5	30.5	169.2	68.2	204.7
0	11.8	183.8	18.3	302.8	87.5	594.4	28.6	166.2	69.9	203.0

Table 5.2: ET matrix element, H_{AB} , and reorganization energy, λ for molecules **1a-3b** for different molecule - counterion distances, d, are calculated with CASSCF method. Value for the external counterion, Q, is shown for each molecule. All values of H_{AB} and λ are in meV.

Results are shown in Figure 5.5, and the results are consistent with the discussion provided for molecule **1a**.

Hydrogen molecular anion H_2^- , Molecule 1b. We also investigate the effect of a counterion on tunneling energy for H_2^- system in space. For a simple H_2^- system with inter-atomic distance, a = 4 Å, the tunneling energy $H_{AB} = 113$ meV. When a counterion, Q = +1 approaches the system, H_{AB} increases as shown in Table 5.2 (column 1b). This is because the inter-dot barrier is now lowered: the nearby cation draws electron density to the region between the dots, increasing inter-dot communication, H_{AB} .

Cationic Ethylene dimer $C_4 H_8^+$, Molecule 2a. The cationic ethylene dimer system (2a) of Figure 5.2(a) has two ethene groups separated by a distance a = 5Å. Each ethene molecule serves as a quantum dot, and through-space ET enables device switching. $H_{AB} = 44.4$ meV and $\lambda = 333.5$ meV were calculated for 2a. When a counterion of charge Q = -1 approaches 2a, both H_{AB} and λ decrease. Table 5.2 (column 2a) shows this trend. Anionic Ethylene dimer $C_4 H_8^-$, Molecule 2b. For an anionic ethylene dimer $C_4 H_8^-$ (molecule 2b) with a = 5 Å, we calculated $H_{AB} = 64$ meV and $\lambda = 600.7$ meV. An approaching counterion of charge Q = +1 raises H_{AB} by lowering the inter-dot barrier. λ decreases as the charge approaches the system. The values of H_{AB} and λ are listed in Table 5.2 as functions of distance d from the cation.

Cationic and anionic allyl dimer (**3a** and **3b**). Figure 5.2(b) shows similar tests for both cationic and anionic dimer systems **3a** and **3b**. The tunneling energy is 40.7 meV and 54.6 meV for the cationic and anionic dimers, respectively. H_{AB} decreases when a charge Q = -1 approaches the cationic system and increases when a charge Q = +1 approaches the anionic system. The reorganization energy, λ , for molecules **3a** and **3b** is $\lambda = 151.9$ meV and 214.6 meV, respectively. For **3a**, λ increases when a counterion, Q = -1, approaches. λ for molecule **3b** decreases as a counterion, Q = +1 approaches the system. These values are listed in Table 5.2 (columns **3a** and **3b**).



Figure 5.2: (a) An ionic ethylene dimer system with inter-molecule distance, a = 5 Å provides a two-dot QCA system. (b)An ionic allyl dimer system with inter-molecule distance, a = 5 Å provides a two-dot QCA system.

Through-bond Electron Transfer

Next, we study the influence of ions in the vicinity of bridged double-dot QCA systems with through-bond tunneling. Through-bond ET is not as simple as tunneling



Figure 5.3: Counterion effects are predictable for the systems with electron tunneling through space in molecules 1-3. (a) For cationic molecular systems, when a counterion, Q=-1 approaches the system, H_{AB} decreases as distance decreases. (b) For anionic molecular systems, when a counterion, Q=+1 approaches the system, H_{AB} increases as distance decreases.

through space. In this case we are calculating the tunneling energy for intra-molecular charge transfer. Nearby charges affect not only the charge distribution on the dots, but also the distribution in the linker, leading to more complex changes in the QCA device.

Molecule 4, 1,8-nonadiene cation . In a 1,8-nonadiene cation (molecule 4 of Figure 5.6 (a)), two ethene groups each provide a quantum dot [44]. Localized states of the mobile hole on the quantum dots provide the binary device states of the DQD QCA cell (Figure 5.6 (b)). In the absence of nearby ions, $H_{AB} = 97.2$ meV and $\lambda = 554.5$ meV were calculated for 4.

When a counterionic point charge (Q = -1) approaches the DQD system as in Figure 5.1, the ion depletes the linker of negative charge, causing a net positive charge density in the linker. This lowers the inter-dot barrier for the electron occupying the HOMO, increasing overlap between the ψ_0 and ψ_1 states. The result is a larger H_{AB} . λ also increases as the negative charge approaches the molecule. Table 5.3 lists the



Figure 5.4: (a) A finite double-well potential in one dimension represents a two dot QCA system. Presence of a point charge nearby, affects the barrier height of the double well system. When an electron, Q=-1 approaches the system, the barrier height increases. This is shown by the yellow dashed line. When a hole, Q=+1 approaches the system, the barrier height decreases, as shown by the red dotted line. (b) Probability densities of localized states 0 and 1 are also affected by the presence of a point charge. The ET matrix element, H_{AB} can be calculated from the overlap between two waveforms.



Figure 5.5: Presence of an external counterion affects the ET matrix element, H_{AB} of a QCA molecule with through-space ET. When a positive charge, Q = +1 approaches the system described in Figure 5.4a, H_{AB} increases as the barrier height decreases. When Q = -1 approaches the system, H_{AB} decreases as the barrier height between the wells increases.

values of H_{AB} , λ , and Mulliken charges on different atom groups for different distances of the counterion from the molecule.

Table 5.3: ET matrix element, H_{AB} and reorganization energy, λ in molecule **4** for different molecule-counterion distance, d calculated at CASSCF(3,4)/6-31G* level. The counterion is Q = -1. The charge in the central C atom, and in the dots are also shown. As d gets smaller, H_{AB} and λ increases, the central C atom becomes more positive, dots become less positive.

d	H_{AB}	λ	Mulliken (Charge a	at $q{=}0$
(Å)	(meV)	(meV)	Central C	Dot 0	Dot 1
∞	97.2	554.5	-0.32	0.37	0.37
4	110.4	603.4	-0.31	0.36	0.36
3	120.5	632.2	-0.29	0.34	0.34
2	145.2	688.0	-0.15	0.32	0.32
1	169.0	728.3	+0.56	0.29	0.29

Molecule 5, 1,3 - Diallyl Propane radical anion. Molecule 5 is a 1,3 - diallyl propane radical anion, which provides a QCA molecule with two dots. Two allyl groups function as two quantum dots, and a propyl bridge mediates electron transfer, as shown in Figure 5.8(a). One allyl group of this molecule is neutral and other allyl



Figure 5.6: Molecule **4** provides a two-state QCA cell. (a) Two ethene groups each provide a quantum dot. (b) A localized mobile hole provides two logical device states, 0 and 1. The device states are shown using Lowest Unoccupied Molecular Orbitals (LUMO) (upper) and schematic diagrams (lower). The blue circles in the schematic diagrams represent the presence of a mobile hole.



Figure 5.7: The potential energy surfaces of ground state E_0 and the first excited state E_1 of Molecule 4 are plotted against reaction coordinate, q. The ground state has two local minima which is consistent with the bistable nature of the molecule. ET matrix element, H_{AB} and reorganization energy, λ is calculated from this adiabatic plot.



Figure 5.8: Molecule 5: 1,3-Diallyl Propane radical anion provides a two-state QCA cell. (a) Two allyl groups each provide a quantum dot. (b) A localized mobile electron provides two logical device states, 0 and 1. The device states are shown using Highest Occupied Molecular Orbitals(HOMO) (upper) and schematic diagrams (lower). The red circles in the schematic diagrams represent the presence of a mobile electron.



Figure 5.9: The potential energy surfaces of 1,3-Diallyl Propane radical anion molecule demonstrates the bistable charge localization driven by nuclear reorganization. ET matrix element, H_{AB} and reorganization energy, λ is calculated from E_0 and E_1 as a function of q.

group is anionic. The molecule has two degenerate ground-state conformations, with an electron localized on either allyl groups. The localized mobile electron provides two logical device states, 0 and 1. The highest occupied molecular orbital (HOMO) is shown in 5.8(b) for state 0 and 1. The red circles in the schematic diagrams indicate the presence of a mobile electron.

Table 5.4: ET matrix element, H_{AB} and reorganization energy, λ in anionic molecule **5** for different values of molecule-counterion distance, d calculated at CASSCF(7,6)/6-31G* level. The external counterion here is Q = +1. The Mulliken charges in the central C atom, and the dots are also shown. As the counterion approaches the molecule, d gets smaller, H_{AB} decreases, λ increases, and the central C becomes more negative, dots become less negative.

d	H_{AB}	λ	Mulliken (Charge a	t $q=0$
(A)	(meV)	(meV)	Central C	Dot 0	Dot 1
∞	20.4	249	-0.28	-0.43	-0.43
5	18.8	240	-0.28	-0.43	-0.43
4	17.8	242	-0.28	-0.42	-0.42
3	15.7	250	-0.30	-0.41	-0.41
2	13.8	258	-0.35	-0.40	-0.40
1	6.3	307	-1.35	-0.33	-0.33

The calculated adiabatic PESs for molecule **5** are shown in Figure 5.9. These yield $H_{AB} = 20.4$ meV and $\lambda = 249.7$ meV for the unperturbed DQD system

When a positive charge (Q = +1) approaches the DQD, excess negative charge density is induced around the center C atom of the molecule. This excess negative charge in the linker increases the inter-dot barrier height for the mobile frontier-orbital electron and reduces the inter-dot communication. The mobile electron also is drawn toward the linker by the external cation so that the dots become less negative as d decreases. While H_{AB} decreases with decreasing d in a straight-forward manner, further study is required to explain the trend of decreasing λ with decreasing d. This analysis is summarized in Table 5.4.

The approach of a counterion has different results for through-bond ET in the cationic 4^+ and in the anionic 5^- DQD systems. This highlights the added complex-

ity in the counterion effects for the through-bond ET case. Furthermore, since the location of nearby counterions cannot be precisely controlled, this can lead to unpredictable and undesirable effects in QCA devices and circuits. We may eliminate these unpredictable effects by designing zwitterionic molecules, which incorporate the counterion into the molecule covalently.

Molecule 7, Zwitterionic 1,3-Diallyl, 2-dimethyl Phosphorus . To eliminate device variability due to randomly-placed counterions, we propose molecule 7. Here we replace the central C atom of molecule 5 with a P atom. Now the molecule is zwitterionic, with its built-in counterion localized in a predictable way. The central P atom provides a fixed positive charge. Either of the allyl groups can be negatively charged based on the electron localization, providing two bistabe device states, 0 and 1. The molecule in its ground state geometry and the total density plots of state 0 and 1 are shown in Figure 5.10 (b). The color of the total density surface plots also encodes the electrostatic potential (ESP).

Here we explore the device behavior of a mixed valence zwitterionic molecule with negative charge centers as the quantum dots. A zwitterionic molecule based on mono-cationic phosphorus cluster $[Ph_2P_5]^+$ might be ideal to design for this purpose, since this phosphorus cluster already has been synthesized and has demonstrated stability at room temperature [2, 3]. We designed molecule **6** with $[Ph_2P_5]^+$ as the central linking counterion and two allyl groups as two quantum dots as shown in Figure 5.11. Calculations show **5** exhibits two stable states, each with the mobile electron localized on one allyl dot or the other. The fixed hole always occupies the central cluster. For computational simplicity, however, further calculations are performed for molecule **7**, which is a simpler prototype of MV molecules with negative charge centers. Here, the phosphorous cluster of **6** is replaced by a single *P* atom.



Figure 5.10: (a) Molecule 7 (1,3-Diallyl, 2-dimethyl phosphorus) provides a zwitterionic three-state QCA cell. The built-in counterion here is a single P atom, much simpler than the $[Ph_2P_5]^+$ of 6. Two allyl groups and the central P atom provide one quantum dot each, and the central P atom provides one fixed hole. (b) A localized mobile electron provides two logical device states, 0 and 1. The device states are shown using calculated electrostatic potential surfaces (upper) and schematic diagrams (lower).



Figure 5.11: (a) Zwitterionic molecule **6** provides a three-state QCA cell. Two allyl groups and a central mono-cationic phosphorus cluster $([Ph_2P_5]^+)$ provide a total of three dots. The central $[Ph_2P_5]^+$ provides one fixed hole[2, 3]. A mobile electron can occupy any dot. (b) The mobile electron provides two logical device states, 0 and 1. A surface plot (upper) shows the electrostatic potential (ESP) for each state, and schematic diagrams (lower) shows the location of the fixed hole and mobile electron on the three-dot system. The red and blue coloring on ESP surfaces indicates negative and positive ESP, respectively. The red circles in the schematic diagrams indicate the mobile electron, and the blue circles indicate the fixed hole (colors are displayed in the online version only).



Figure 5.12: The potential energy surfaces of zwitterionic molecule 7 demonstrates the bistable charge localization driven by nuclear reorganization. ET matrix element, H_{AB} and reorganization energy, λ is calculated from E_0 and E_1 as a function of q.



Figure 5.13: A C \rightarrow P substitution in the anionic molecule **5** provides zwitterionic molecule **7**. The adiabatic potential energy surfaces for molecule **7** show significant increase in λ and only a marginal increase in H_{AB} , compared to molecule **5**. The built-in positive charge provided by the P atom in between two negative charge centers (allyl groups) in molecule **7** lowers the barrier between the dots, which results in an increased H_{AB} .

For 7, we computed $H_{AB} = 36.9$ meV and $\lambda = 703.9$ meV. A comparison of the H_{AB} and λ values between molecules 5 and 7 shows a significant change in both energies (See Figure 5.13). The increase in H_{AB} in 7 can be explained by placing a negative point charge near anionic molecule 5. The negative point charge will draw positive charge density to the center of anionic molecule 5. This positive charge will mimic the central P atom of molecule 7. When the external negative point charge is close enough, negative charge is repelled from the linker, uncovering positive charge on the central C atom. This lowers the potential on the linker for the mobile electron, with a corresponding increase in H_{AB} . This is shown in Table 5.5, which explains the reason for the increasing H_{AB} in molecule 7. Further investigation is needed to explore why λ increases.

Molecule 8 cation. Molecule 8 shown in Figure 5.14(a) provides a double-dot cationic QCA cell with a mobile hole. Two tetra-methyl-allyl groups function as two quantum dots. A mobile hole can occupy either dot. Occupation of the mobile hole by the dots determines two device states 0 and 1, as shown by the lowest unoccupied molecular orbitals (LUMO) in Figure 5.14(b). The blue circles in the schematic diagrams indicate a mobile hole.

d	H_{AB}	λ	Mulliken (Charge a	at $q{=}0$
(Å)	(meV)	(meV)	Central C	Dot 0	Dot 1
∞	20.4	249	-0.28	-0.43	-0.43
5	21.8	259	-0.28	-0.43	-0.43
4	22.4	257	-0.27	-0.44	-0.44
3	23.3	250	-0.25	-0.44	-0.44
2	25.4	231	-0.11	-0.46	-0.46
1	34.9	194	+0.84	-0.51	-0.51

Table 5.5: ET matrix element, H_{AB} and reorganization energy, λ in anionic molecule **5** for different values of distance of a negative charge, d, calculated at CASSCF(7,6)/6-31G* level. Here, Q = -1. The Mulliken charges in the central C atom, and in the dots are also shown.



Figure 5.14: Molecule 8 cation provides a two-state QCA cell. (a) Two tetramethyl-allyl groups each provide a quantum dot. (b) A localized mobile hole provides two logical device states, 0 and 1. The device states are shown using Lowest Unoccupied Molecular Orbitals(LUMO) (upper) and schematic diagrams (lower). The blue circles in the schematic diagrams represent the presence of a mobile hole.



Figure 5.15: The adiabatic potential energy surfaces of cationic molecule 8 demonstrates the bistable charge localization driven by nuclear reorganization. ET matrix element, H_{AB} and reorganization energy, λ is calculated from E_0 and E_1 as a function of q.

We calculate the ET matrix element, $H_{AB} = 98.7$ meV and reorganization energy, $\lambda = 475.2$ meV from the adiabatic potential energy surfaces shown in Figure 5.15. When a counterion, Q = -1 approaches the molecule, both H_{AB} and λ increase, as shown in Table 5.6. We calculate the Mulliken charges at the symmetric geometry q = 0, and observe that positive charge is induced at the central C atom of molecule **8** as the negative charge approaches the molecule, which leads to increased H_{AB} . The opposite tendency is observed when a positive charge, Q = +1 is placed near the molecule as shown in Table 5.7. In this case H_{AB} decreases, since the central C atom becomes more negative as the positive charge approaches the molecule. The dots become more positive, as negative charge density is drawn toward the center of the molecule. The reorganization energy, λ also changes in an inexplicable way.

Molecule 9 zwitterion. We substitute the central C atom of molecule 8 with a B atom to design zwitterionic molecule 9 shown in Figure 5.16(a). The central bridge of the molecule provides fixed negative charge and the mobile hole can localize on

d	H_{AB}	λ	Mulliken (Charge a	at $q{=}0$
(Å)	(meV)	(meV)	Central C	Dot 0	Dot 1
∞	98.7	475.2	-0.37	0.48	0.48
5	99.7	485.6	-0.37	0.47	0.47
4	100.9	486.3	-0.36	0.46	0.46
3	104.6	487.5	-0.34	0.44	0.44
2	112.1	493.0	-0.12	0.41	0.41
1	116.1	502.1	+0.66	0.40	0.40

Table 5.6: ET matrix element, H_{AB} and reorganization energy, λ in cationic molecule **8** for different values of distance of a negative charge, d calculated at CASSCF(1,2)/6-311G* level. Here, Q = -1. Mulliken charges in the central C atom and in the dots are also shown.

Table 5.7: H_{AB} and λ , calculated at CASSCF(1,2)/6-311G^{*} level, in cationic molecule **8** decrease with the decrease of the distance, d, between a positive charge, Q = +1 and molecule **8**. The Mulliken charges for the central C, and the dots for each d are also shown.

d	H_{AB}	λ	Mulliken (Charge a	at $q=0$
(Å)	(meV)	(meV)	Central C	Dot 0	Dot 1
∞	98.7	475.2	-0.37	0.48	0.48
5	98.2	464.5	-0.36	0.49	0.49
4	97.9	464.3	-0.36	0.50	0.50
3	96.9	464.6	-0.39	0.52	0.52

either dots. Localization of the mobile hole determines two device states, "0" and "1" as shown in the ESP plots of Figure 5.16(b).

Even though a zwitterionic QCA molecule based on the derivative of the 1carba-closo-decaborate monoanion $[closo-1-CB_9H_{10}]^-$ or 1-carba-closo-hexoborate monoanion, $[CB_5H_6]^-$ would provide more stability and robustness to the molecule [85, 17, 89], here we focus on computational tractibility and design a simpler prototype, molecule **9**.

The calculated ET matrix element, H_{AB} , and reorganization energy, λ , for molecule **9** are 87.6 meV and 618.4 meV, respectively, obtained from the adiabatic PESs of Figure 5.17. When we compare the electronic properties of molecule **8** and molecule **9**, we see a significant change in H_{AB} and λ which is captured by Figure 5.18. The decrease in H_{AB} is consistent with the analysis from Table 5.7. However, the increase in λ is inexplicable and needs further investigation.

Table 5.8: Summary of changes in ET matrix element, H_{AB} , in different ionic QCA molecules, for through-space and through-bond ET, in presence of a nearby approaching counterion.

Tunneling type	Molecule type	Change in H_{AB}
Through	Cation	Decreases
space	Anion	Increases
Through	Cation	Increases
bond	Anion	Decreases

Conclusion

We have studied several QCA molecules in presence of external counterions. The effects of external counterions on QCA molecular systems where electron tunnels through space are straight-forward. The ET matrix element, H_{AB} , decreases when a counter-anion approaches a cationic molecular system (molecules **1a**,**2a**,**3a**), since the barrier height between two working dots is increased and inter-dot communication is reduced. For an anionic molecular system (molecules **1b**,**2b**,**3b**), when a counter-



Figure 5.16: Zwitterionic molecule **9** provides a three-state QCA cell. (a) Two methyl-allyl groups and the central B atom provide one quantum dot each. The central B atom provides one fixed electron. (b) A localized mobile hole provides two logical device states, 0 and 1. The device states are shown using calculated electrostatic potential surfaces (upper) and schematic diagrams (lower). The red and blue surfaces in the electrostatic potential surface plots represent presence of negative and positive charge respectively. The red circles in the schematic diagrams represent the presence of a fixed electron. The blue circles in the schematic diagrams represent the presence of a mobile hole (colors are displayed in the online version only).



Figure 5.17: The adiabatic potential energy surfaces of zwitterionic molecule **9** demonstrates the bistable charge localization driven by nuclear reorganization. ET matrix element, H_{AB} and reorganization energy, λ is calculated from E_0 and E_1 as a function of q.



Figure 5.18: Comparison of ET matrix element, H_{AB} and reorganization energy, λ for Molecule 8 and Molecule 9. A C \rightarrow B substitution turns a cationic molecule 8 into a zwitterionic molecule 9. The adiabatic potential energy surfaces for the zwitterionic molecule 9 show significant increase in λ and only a marginal decrease in H_{AB} , compared to molecule 8. The built-in negative charge provided by the B atom in between two positive charge centers in molecule 9 minimizes the communication between the dots and results in a smaller H_{AB} .

cation approaches the system, the inter-dot barrier is lowered, and tunneling energy increases. However, there is no observed pattern for the change in inner-sphere reorganization energy, λ for these simple molecular systems as the counterion approaches the molecules.

For QCA molecules with intramolecular electron transfer between dots, effect of counterion on the ET matrix element, H_{AB} and reorganization energy, λ is not straightforward. Rather, change in the charge distribution in different parts of the molecule is observed because of coulomb interaction between the molecule and counterion. Opposite charge is induced in the molecule based on the position of the external counterion. Charge is drawn toward the center of the molecule from the working dots, which may lead to inaccurate device properties. For the cationic molecules **4** and **8**, when a counter-anion approaches the molecules, H_{AB} increases, as the positive charge induced at the center of each molecule lowers the inter-dot barrier. When an external cation approaches cationic molecule **8**, H_{AB} gets smaller, as negative charge density induced at the center of the molecule raises the inter-dot barrier. For the anionic molecule **5**, when a counter-cation is placed near the molecule, H_{AB} decreases, as negative charge is induced at the center of the molecule leads to weaker communication between the dots. When an external anion approaches the same molecule, H_{AB} increases, as positive charge is induced at the center of the molecule leads to stronger communication between the dots. The inner-sphere reorganization energy for the molecules also changes due to presence of counterion near the molecules. However, the change in the inner-sphere reorganization energy does not follow any particular pattern.

To eliminate the inconsistent device characteristics due to randomly placed external counterions, we propose zwitterionic molecules as QCA candidates and we modeled two simple zwitterionic molecules. Use of zwitterionic molecules as cells in QCA circuit will eliminate the detrimental counterion effects. We analyzed the changes in electronic properties and device behavior of the designed molecules. Both H_{AB} and λ change significantly in the designed zwitterionic molecules. When a positive charge is incorporated as the central counterion of zwitterionic molecule **7**, H_{AB} and λ both increase. When a negative charge is used as the central built-in counterion in zwitterionic molecule **9**, H_{AB} decreases but λ increases. While the trend in H_{AB} for the zwitterionic molecules is well understood, further investigation is required to understand the significant increase in reorganization energy, λ of these designed zwitterionic molecules.

CHAPTER SIX

Iterative Design and Modeling of Ferrocene-based Zwitterionic QCA Molecules

Abstract

A major obstacle in realizing molecular QCA is lack of synthesized candidate molecules for theoretical and experimental testing. Zwitterionic mixed valence QCA molecules are desirable because of their charge neutrality and by using them in QCA circuit as cells, external counterion effects can be eliminated. Design and *ab initio* modeling of stable, metallocene based zwitterionic molecules may lead to synthesis of new QCA candidate molecules with stable device states. In this chapter we design and theoretically test new QCA candidate molecules with Ferrocene dots that can be synthesized by collaborating chemists in University of Notre Dame. We present an iterative design and modeling process that may lead to synthesis and testing of novel QCA devices. *Ab initio* calculations demonstrated that the designed molecules are chemically stable.

Introduction

Zwitterionic three-dot mixed-valence molecules are ideal candidates for QCA as they support clocking and no counter-ions are produced in their synthesis [17, 18]. Organometallic molecules with metallocene dots have been studied in literature as potential QCA candidates. Molecules based on Ferrocene, $Fe(C_5H_5)_2$ are particularly suitable for molecular QCA and have been focus of investigation for a long time because of their unique geometry and stability. Ionic diferrocenylacetylene (DFA) molecule and charge neutral zwitterionic mixed valence diferrocenyl carborane molecule for QCA have been synthesized and studied using scanning tunneling microscopy (STM) [42, 18]. Even though charge localization and device switching was observed in the ionic diferrocenylacetylene (DFA) molecule, stable device states of the synthesized zwitterionic Diferrocenyl Carborane molecule was not identified using STM imaging. So, design, synthesis and testing of new stable zwitterionic QCA candidate molecules are desirable to fully realize molecular QCA. In this chapter we focus on designing zwitterionic stable diferrocenyl QCA molecules and explore their properties in using *ab initio* methods so that they can be synthesized by chemists and can be tested both theoretically and experimentally.



Figure 6.1: This scheme shows the oxidation of an anionic precursor (left) of the proposed candidate molecule 1 to a neutral, MV molecule (right). Molecule 1 consists of two Fc groups as the two active dots and a diphenyl-boron linker with two acetylene groups as the built-in counterion. Courtesy: Dr. Emily Tsui, University of Notre Dame.

Firstly, we investigate the candidate molecule 1 designed by our collaborator, Dr. Emily Tsui from Univrsity of Notre Dame (see Figure 6.1). During synthesis, the molecule was not stable as a neutral compound and dissociated during chemical oxidation from the anionic species. We find out the reason behind this unstable behavior is the removal of an electron from the central B atom of the molecule rather than from one of the ferrocenes. When B atom looses one electron, the octet rule is dissatisfied and the molecule becomes unstable and dissociates. We hypothesize that this dissociation happens because the ionization potential of the linker is lower than that of the ferrocene groups. Based on this hypothesis, we propose multiple solutions to solve this problem and we design molecule 2, 3 and 4. We run several *ab initio* calculations and test the molecules theoretically. All the proposed and modeled QCA molecules demonstrate stable behavior and are potential candidates for synthesis and further testing.

Computational Methods

For molecule 1 and 2, all *ab initio* computations were performed with the Q-Chem 5.2 software package [83]. The restricted open-shell second order Møller-Plesset (ROMP2) theory was employed for all computations to avoid spin contamination [60, 65, 64]. Resolution of the Identity (RI) method was used for all the ROMP2 calculations to reduce computational time [90]. The def2-TZVPD basis set and RIMP2def2-TZVPD auxiliary basis set were used for all atoms (H, B, C, Fe, F) of molecule 1 and 2 for all the computations. For molecule 3 and 4, all *ab initio* calculations were performed using GAUSSIAN 16 software package[78]. For each molecule, geometries were calculated at the Hartree-Fock level of theory [56]. The LANL2DZ basis set was used for all atoms of molecules 3 and 4.

Results

Molecule 1

Molecule 1, $(Fc-C\equiv C)_2 B(C_6H_5)_2$, consists of two Fc groups as two active dots. The central linker is two Acetylene groups connected to diphenyl-boron. The anionic precursor of the molecule was successfully synthesized by Dr. Tsui's group, but the molecule dissociated while obtaining the neutral species by chemical oxidation. To investigate the reason for this unstable nature of neutral molecule 1, we carry out *ab-initio* calculations for both anionic and the neutral compound. We analyze the charge distribution and ionization energies for each fragment of the molecule. We also calculate the frontier molecular orbitals.

Molecular orbital analysis of anionic precursor of Molecule **1** from Figure 6.2 shows that the highest occupied molecular orbital (HOMO) is largely centered on the



Figure 6.2: (a) Anionic structure of Molecule $\mathbf{1}$ was obtained at RI-ROMP2/def2-TZVPD level. (b) Calculated electrostatic potential (ESP) surface of $\mathbf{1}$ shows that B atom and the central linker between two Fc groups is negatively charged (red surface). (c) Frontier molecular orbitals of $\mathbf{1}$ shows that the HOMO localizes on the central linker.

boron and the linker. When the molecule is oxidized, one electron is removed from the B atom. As a result, the octet rule for B is not satisfied and the molecule is destroyed which can be seen from Figure 6.3. The Mulliken charge analysis for the neutral structure of molecule 1 in Table 6.2 shows that the linker between two ferrocenes has a negative charge, q=-0.45. One Fc group is slightly more positive than the other and has q=+0.26 and q=+0.19 respectively. This is not the expected charge localization for a neutral zwiterionic molecule. For these zwitterionic molecules we expect the positive charge, q=+1 to be on any of the Fc groups and the negative charge, q=-1 should be on the central linker. To find out the reason for this unexpected charge separation, we calculate the ionization energies of each fragment of the molecule: two Fc groups and the linker as shown in Table 6.1. Ionization energy is defined as the minimum energy required to remove the most loosely bound outermost electron of an isolated neutral atom or molecule from the orbital. Calculations show that the

ionization energy of each Fc group is higher than that of the linker. The ionization energy of each Fc is 0.28 Ha, while that of the linker is 0.17 Ha. We hypothesize that, because of the lower oxidation potential of the central linker, one electron is removed from the linker rather than a Fc group during chemical oxidation, which is undesirable and causes the dissociation of the molecule.

Table 6.1: Comparison of the ionization energies for different groups of molecules 1, 2, 3 and 4 shows that the ionization energy of the central linker is increased by $H \rightarrow F$ substitution in the phenyl groups of molecule 1. The ionization energy of the dots are lowered by $H \rightarrow CH_3$ substitution in the Fc groups. The energies are calculated at RI-ROMP2/def2-TZVPD level.

Group	Ionization energy (Ha)
Fc	-0.280
$(\mathrm{Fe}(\mathrm{C}_5(\mathrm{CH}_3)_5)_2$	-0.236
$(H-C\equiv C-H)_2B(C_6H_5)_2$	-0.170
$(H-C\equiv C-H)_2B(C_6F_5)_2$	-0.237

Proposed Solution

We propose three approaches to design three stable zwitterionic molecules.

Approach 1. One approach to solve this problem and design a stable zwitterionic molecule is to modify the design of molecule **1** by increasing the ionization energy of the central linker. This can be done by adding electron withdrawing group to the phenyl groups. An electron withdrawing group removes electron density from a π system, making the system more electrophilic. The fluoro groups are very electronegative and cause inductive withdrawal of electrons from the carbon atoms of benzene. By replacing H atoms of the phenyl groups of molecule **1** with F atoms, we can achieve an increase in the ionization energy of the bridge. We propose molecule **2** based on this approach. The structure of molecule **2** is shown in Figure 6.4(a).

Approach 2. Another approach is to lower the ionization energy of each ferrocene group. We can do this by adding electron donating groups to the ferrocenes.



Figure 6.3: (a) Neutral structure of Molecule 1 shows two ferrocene groups as two quantum dots. (b) Calculated electrostatic potential surface of 1 indicates that the right ferrocenyl group is slightly positively charged. The mulliken charge analysis shows that Dot 0 has a positive charge, q=+0.26. The bridge/linker between two ferrocenes is negatively charged and has q=-0.230. The charge separation here is not as expected as a zwitterionic molecule. (c) Frontier molecular orbitals of 1 show that the LUMO localizes on dot 0. All the results were obtained at RI-ROMP2/def2-TZVPD.



Figure 6.4: (a) Molecule **2** is proposed based on approach 1. (b) Design of molecule **3** is based on approach 2. (c) Molecule **4** is based on combining approach 1 and 2. The atom symbols on the left are provided for a better understanding of the molecule geometries.

Electron donating groups increase the electron density on aromatic rings making the system more nucleophilic. If we replace the H atoms of the ferroceneyl groups with alkyl substituents like $-CH_3$, the ionization energy of the ferrocenes will decrease. Molecule **3** in Figure 6.4(b) is designed based on this solution.

Approach 3. We can also combine approach 1 and 2 and design molecule $\mathbf{4}$ (see Figure 6.4(c)). This may ensure a significant difference in oxidation potential and may provide better charge localization in molecule $\mathbf{4}$.

Molecule 2

We apply approach 1 to model molecule $\mathbf{2}$, $(Fc-C\equiv C)_2 B(C_6F_5)_2$ by substituting $H \rightarrow F$ in the two phenyl groups attached to B atom of molecule $\mathbf{1}$. Figure 6.5 shows the anionic structure, ESP surface and frontier orbitals of molecule $\mathbf{2}$.



Figure 6.5: (a) Anionic structure of molecule **2** shows the $H\rightarrow F$ substitution in the central linker of **1**. (b) Calculated electrostatic potential surface of **2** indicates the negative charge localization on the linker. (c) Frontier molecular orbitals of **2** obtained at RI-ROMP2/def2-TZVPD, shows that the HOMO is localized on the ferrocene groups, which confirms that an electron will be removed from any of the ferrocene groups during oxidation and the molecule will not dissociate.

The central linker of molecule 2 is negatively charged and the HOMO localizes mostly on the two Fc groups. This ensures that during oxidation process, the electron will be removed from one Fc group and the molecule will not dissociate. This is because the ionization energy of the linker was increased after replacing the H atoms of phenyl groups by F atoms. The calculated ionization energy of this linker is -0.237 Ha. This helps to stabilize the molecule.

Table 6.2: Mulliken charges for various groups in neutral molecules 1 and 2 obtained at RI-ROMP2/def2-TZVPD show more stable and zwitterionic behavior for 2 compared to 1.

Group	Molecule 1	Molecule 2
Linker	-0.45	-1.25
Dot 0	0.26	1.04
Dot 1	0.19	0.21



Figure 6.6: $H \rightarrow F$ substitution in the phenyl groups of **1** raised the ionization energy of the central linker and provides a stable and strong zwitterionic molecule **2** (a) Neutral structure of Molecule **2** was obtained at RI-ROMP2/def2-TZVPD level. (b) Calculated electrostatic potential surface of **2** shows that dot 0 is positively charged while dot 1 is neutral. The linker is negatively charged. The charge separation is as expected as a zwitterionic molecule. (c) Frontier molecular orbital of **2** shows that the LUMO localizes on the dot 0 and HOMO is singly occupied.

We can further prove the stability by mulliken charge analysis, the electrostatic potential surface and frontier orbital analysis of the neutral molecule $\mathbf{2}$ shown in 6.6. The Mulliken charge analysis in Table 6.2 shows that one Fc has charge q = +1.04and the second Fc has charge q = +0.21. The linker has charge, q = -1.25. The charge separation is as expected as a stable zwitterionic molecule. The ESP plot also shows that the left Fc is positively charged(blue) and right Fc is neutral(green). The linker is negative(red). These results for molecule $\mathbf{2}$ demonstrates that by using approach 1, we could enhance the localization of the fixed electron and mobile hole on the linker and ferrocene respectively. This is exactly the criteria of a stable zwitterionic molecule for realization of QCA. This stable, novel molecule is promising candidate for synthesis.

Molecule 3 and 4

Molecule **3**, $(Fe(C_5(CH_3)_5)_2 - C \equiv C)_2 B(C_6H_5)_2$ is modeled by applying approach 2, $H \rightarrow CH_3$ substitution in the Fc groups of molecule **1**. The ionization energy of each active dot, deca-methyl Fc group is lowered to -0.236 Ha. Preliminary Hartree Fock calculations show that the molecule is stable and demonstrate zwitterionic characteristics. The Mulliken charges for three groups of the molecule is shown in Table 6.3. Figure 6.7(a) and (b) shows the neutral structure and the ESP plot of Molecule **3**.

Table 6.3: Mulliken charges for various groups in neutral molecules **3** and **4**, obtained at HF/LANL2DZ level, are consistent with ESP plots of Figure 6.7 and confirms their stability.

Group	Molecule 3	Molecule 4
Linker	-1.020	-1.000
Dot 0	0.945	0.926
Dot 1	0.091	0.074

Molecule 4, $(Fe(C_5(CH_3)_5)_2 - C \equiv C)_2 B(C_6F_5)_2$ is modeled by applying approach 3 on molecule 1. This approach has the largest ionization energy difference of the linker and the dots, as we combine approach 1 and 2 here. As a result, this proposed solution
has the greatest effect on the charge localization. Preliminary HF calculations show that the molecule is stable and demonstrate zwitterionic characteristics. The Mulliken charges for the three groups of molecule **4** are shown in Table 6.3. Figure 6.7(c) and (d) shows the neutral structure and the ESP plot of molecule **4**.



Figure 6.7: Molecules **3** and **4** are based on design principles 2 and 3, respectively, providing improved stability and zwitterionic character over molecule **1**. Additional electron-donating methyl groups are predicted to lower the oxidation potential of the ferrocene working quantum dots, allowing a stable structure (a), and provide better molecular polarization (b) than in molecule 1. Calculated electrostatic potential surface of neutral molecule **3** shows the localization of fixed electron and mobile hole in the central linker and dot 0 respectively. (c) Combination of $H \rightarrow F$ substitution in the two phenyl groups and $H \rightarrow CH_3$ substitution in the Fc groups of molecule **1**, provides strong zwitterionic behavior in neutral molecule **4**. (d) Calculated electrostatic potential surface of **4** shows enhanced localization of positive and negative charges in the molecule. For both molecules, results are obtained at HF/LANL2DZ.

Conclusion

We have designed and modeled three stable zwitterionic QCA candidate molecules based on the molecule **1** provided by our collaborating experimental chemistry research group. We conducted first-principles calculations to validate the chemical stability of these molecules. In our proposed molecule **2**, we engineer the linker between the dots by adding electron withdrawing groups so that the ionization energy of the linker is increased. Molecule 2 demonstrated expected charge localization of a mobile hole and a fixed electron on the active dots and the linker as a zwitterionic molecule. The molecular orbital analysis further confirmed the stability of molecule 2. In molecule 3, we add electron donating groups to the Fc groups so that ionization energy of the Fc groups are decreased. We also add both these approaches to design molecule 4. We have achieved expected charge localization in the active dots and the linker for these molecules using *ab initio* techniques. Even though preliminary calculations for molecule 3 and 4 promises stable neutral zwitterionic structures, more accurate computational approach like RI-ROMP2 is needed. Calculations are in progress for these two molecules. Nonetheless, all the proposed molecules may be very good candidate for synthesis.

CHAPTER SEVEN

Benchmarking a Novel Machine-learning-based Functional for QCA Molecules

Abstract

Machine Learning (ML) has been recognized as a powerful tool for molecular modeling and approximating exchange-correlation functionals for density functional theory (DFT). A newly developed machine-learned functional DeepMind21 (DM21) has been demonstrated to overcome the delocalization error created from traditional DFT functionals. Even though DFT methods have low computational cost, in molecular QCA calculations, DFT methods are avoided because of the delocalization error. In this chapter, we calculate electronic couplings of several QCA molecules using the new machine-learned DM21 functional which has showed more accurate predictions than traditional DFT methods. We compare the results against electronic coupling values calculated with traditional HF methods and DFT functionals and evaluate the performance of DM21 functional in QCA computations. Calculated results show that DM21 performs slightly better than traditional B3LYP functional.

Introduction

In molecular QCA, intra-molecular electron transfer (ET) driven by the Coulomb interaction among neighboring molecules determines the localized device states of a molecule. ET matrix element, H_{AB} , is the electronic coupling between the diabatic states of a molecule which is a measure of how easily an electron can tunnel from one dot to the other. H_{AB} describes the strength of interaction between the chargelocalized states and is highly dependent on the electronic structure of the quantum dots, interaction between them, and also on the nature of the bridge between the dots of the molecule [86, 87]. In Chapter 5, we have briefly discussed the role of ET matrix element in QCA and calculated electronic couplings for different QCA molecules using CASSCF method. In this chapter, we calculate H_{AB} for several QCA molecules including the molecules in chapter 5, using different *ab-initio* methods and benchmark these values. Specifically we use HF method and DFT method with two different functionals: B3LYP and DM21. Our goal is to compare these results with standard CASSCF values, experimental and published values in literature and determine the method with most accurate results.

In Chapter 2, we discussed the background and limitations of HF theory and DFT theory. Even though HF method can approximate charge localization in a molecule properly, this method does not fully incorporate the electron correlation in the calculations. DFT, on the other hand solves this problem by adding an exchange-correlation term in the total energy equation [70, 71]. This term is known as the exchange-correlation functional and often approximated to achieve accurate results. These approximations are called density functional approximations (DFAs) and have shown success in calculation of accurate energies. One of the main obstacles of using DFT in molecule simulations as well as in QCA calculations is the delocalization error, resulting from the deviation of the approximate functional from the exact Kohn–Sham functional [72]. In this error, an electron is delocalized over the two charge centers in a molecule. Because charge localization is a key feature of QCA, DFT is not preferred in molecular QCA calculations where charge configurations are involved.

Recently, machine learning has made significant advances in development of exchange-correlation functionals for DFT. Theoretical studies have shown successful demonstration of training molecular data in designing functionals. These functionals are systematically constructed using accurate density distributions and energies from trained molecules via machine learning. DM21 (DeepMind 21) functional has been developed by training a neural network on molecular data which can describe artificial charge delocalizations correctly. The functional was tested thoroughly for main-group atoms and molecules and showed better performance than traditional functionals [91]. Training of data includes atomization, ionization, and intermolecular binding energies, and electron affinity of small main-group, H-Kr molecules, Fractional charge and spin densities. Some fixed parameters were obtained from popular traditional functionals, methods and literature. The functional has been implemented in the PySCF 2.0 software package [92, 93].

In this chapter, we aim to use this newly proposed DM21 (DeepMind 21) DFT functional to calculate ET matrix element, H_{AB} for several QCA molecules using Koopmans' theorem. We compare these results against H_{AB} values calculated with traditional methods such as HF and DFT method with popular B3LYP functional and state-of-the-art CASSCF method.

Methods

Geometry optimizations of all molecules were performed using the GAUSSIAN 16 software package [78]. HF calculations and DFT calculations with B3LYP functional were also calculated in GAUSSIAN 16. PySCF 2.0 package [92, 93] was used for DFT calculations with DM21 (DeepMind 21) exchange-correlation functionals [91]. Basis sets used for all molecules are shown in Table 7.1. Koopmans' Theorem was used to calculate the ET matrix element, H_{AB} for all molecules [94]. According to Koopmans' Theorem, For a cationic molecule, H_{AB} can be approximated by one-half of the difference in molecular orbital (MO) energy between the highest occupied molecular orbital (HOMO) and the second highest occupied molecular orbital (HOMO-1) of the neutral system. According to this theorem, the ionization potential of HOMO and HOMO-1 can be expressed as the SCF energies and H_{AB} is given by

$$H_{AB} = \frac{1}{2} (E_{HOMO} - E_{HOMO-1})$$
(7.1)

Here, E_{HOMO} and E_{HOMO-1} are the orbital energies of HOMO and HOMO-1 calculated by a single point calculation at the symmetric nuclear geometry. At this symmetric geometry, the mobile charge is delocalized between two dots of the QCA molecule.

Results

We consider the double-dot QCA molecules presented in Chapter 5 and two ferrocene based molecules to calculate their intra-molecular ET matrix elements. The molecules are shown in Figure 7.1. We have already calculated ET matrix element, H_{AB} for molecules **1-5** using CASSCF method in Chapter 5. CASSCF method is the most reliable technique to describe charge distribution in a mixed-valence molecule, and is perfect to calculate H_{AB} accurately for molecules **1-5** because of their small size. H_{AB} values calculated by this method are considered as reference for molecules **1-5**.

Cationic diferrocenyl acetylene (DFA) and diferrocenyl polyene (DFP) molecules have been extensively studied experimentally and theoretically in literature as QCA candidates. These diferrocenyl MV molecules contain two ferrocenyl groups (Fc) acting as two quantum dots linked by $-C \equiv C - \text{ and } -\text{HC}=\text{CH} - \text{ groups respec$ tively as shown in Figure 7.1. These molecules are stable and practical double-dotQCA candidates. DFA has been synthesized, characterized and shown bistable deviceswitching [42]. DFP molecules and their derivatives were also explored experimentallyalong with spectroscopic methods and x-ray crystallography [95, 96]. We chose thesemolecules because of the availability of experimental data to use as reference for ourcalculated values [4, 5].

Here, we calculate H_{AB} for the QCA molecules shown in Figure 7.1 using Koopmans' theorem from equation 7.1. We use HF, CASSCF and DFT methods for the calculations. B3LYP and DM21 functionals are used for DFT computations. Calculated H_{AB} values are compared with the reference values in Table 7.1. H_{AB} values calculated with CASSCF method were obtained from chapter 5. For molecules 1-5,



Figure 7.1: Several QCA molecules were benchmarked in DM21. Electronic parameters of the molecules were computed using DM21 and compared to parameters calculated using conventional methods. The atom symbols on the left are provided for a better understanding of the geometries for molecules 1-5, DFA and DFP cation.

all the methods demonstrate reasonable results. For diferrocenyl molecules DFA⁺ and DFP⁺, The DFT values are closer to the reported experimental values. H_{AB} values calculated using DM21 functional do not improve significantly, even though they are very close to the reference values. However, in most cases, DM21 calculations are more accurate then the B3LYP calculations. For the diferrocenyl molecules, HF methods do not perform well. A bar plot showing percentage of error in calculated H_{AB} values compared to the standard reference values are shown in Figure 7.2. The computational cost of calculating the single point energies using DM21 functional implemented in PySCF software package is high compared to B3LYP. More computational data on H_{AB} values for different QCA molecules may be helpful to evaluate the performance of DM21 functional. Calculations of several other QCA molecules are ongoing.

Table 7.1: ET matrix element, H_{AB} , calculated using Koopmans theorem with HF and DFT(B3LYP, DM21) methods for various QCA molecules are compared with reference values. The reference H_{AB} values for molecules **1-5** are calculated with CASSCF method in Chapter 5. Reference values for molecules **6-7** are obtained from experiment and literature [4, 5]. Basis sets used for each calculation are also given. All H_{AB} values are given in meV.

Molecule	Basis set	ET matrix element, H_{AB}			Reference
		HF	B3LYP	DM21	
1	6-31g*	82.4	72.8	99.3	97.0 (CASSCF)
2	$6-31g^{*}$	20.4	16.3	17.7	20.4 (CASSCF)
3	6-31g*	35.1	35.1	38.1	36.9 (CASSCF)
4	6-311g*	81.5	56.1	57.7	98.7 (CASSCF)
5	6-311g*	62.7	48.6	49.2	87.6 (CASSCF)
	6-31g	691.2	89.8	92.9	199 90 550 4
DFA^+	$6-31g^{*}$	659.9	102.0	104.5	122.29, 009.4 [5]
	LANL2DZ	604.1	110.2	118.5	[0]
	6-31g	652.3	130.8	125.6	61, 100[4],
DFP^+	6-31g*	635.9	130.9	125.2	139.6,
	LANL2DZ	798.7	147.3	107.1	624.4[5]



Figure 7.2: Percent errors in calculated ET matrix element, H_{AB} , with HF and DFT(B3LYP, DM21) methods for various QCA candidate molecules show that DM21 performs slightly better than B3LYP. The percent errors for molecules **1-5** are calculated relative to the H_{AB} values calculated using CASSCF method from Chapter 5 as shown in Table 7.1. For molecules **6** and **7**, reference values are obtained from experimental data and literature [4, 5].

Conclusion

We benchmarked DM21 functional by calculating the electronic couplings of QCA molecules and comparing them against different functionals and methods. The ET matrix element, H_{AB} , calculated using Koopmans' theorem and DFT functional DM21 demonstrated reasonable results. Koopmans' theorem approximates H_{AB} from single-point energy calculations on a neutral molecule. Even though the results calculated with DM21 functional were very close to the reference values and slightly better than B3LYP, there is no significant increase in accuracy of results compared to B3LYP. Exploring more QCA molecules may be helpful for benchmarking DM21 functional against traditional DFT functionals and HF methods. Calculation of H_{AB} for several other QCA molecules are in progress. Improvement of the current functional by training more molecular data, especially QCA molecules might be helpful for QCA calculations. The current implemented DM21 functional on PySCF software package is not compatible to optimize molecules. Modifying its underlying code may improve the functional. The functional can also be incorporated into another existing quantum chemistry software, e.g. Gaussian 16, which may reduce the computational cost. Development of the functional with added features such as optimization and frequency calculations using machine learning might open new path to computationally inexpensive QCA calculations.

CHAPTER EIGHT

Conclusion

This dissertation has focused on the use of *ab initio* molecular modeling to advance the science of molecular QCA. Our objectives here were to design, propose, and characterize novel QCA candidate molecules. Several molecules were presented to study QCA device behavior and device stability. Additionally, we have explored a novel solution to one challenge in implementing molecular QCA computation: the bit read-out problem.

We designed and demonstrated a novel, room-temperature, spectroscopic readout technique for molecular QCA. Several cationic DQD asymmetric molecules were modeled using HF and CASSCF methods. Raman calculations for binary device states of each asymmetric molecule predicted the spectroscopic distinction between the device states. We proposed Tip-enhanced Raman spectroscopy (TERS) to detect the device state of a QCA circuit comprised of several asymmetric QCA molecules at room temperature. Asymmetric metallocene-based QCA molecules may provide more stable devices and should be explored theoretically and experimentally.

We demonstrated that a central counterion may be selected to determine a molecular device's response to the applied clocking electric field. We designed two zwitterionic molecules with different anionic central linkers and explored the roles of the number of fixed and mobile charges in these molecules using ROHF method. Results indicated that the number of the mobile charges in a zwitterionic clocked molecule determine the magnitude and direction of an applied electric field to drive the molecule in the "Null" or "active" states. In a manner analogous to the difference between NMOS and PMOS transistors, the designed molecules showed opposite responses to the clocking electric fields. We have investigated the external counterion effects on an ionic QCA molecule by studying the electronic properties of the molecule. CASSCF calculations showed that randomly-placed external counterions near ionic computational molecules may degrade QCA device operation by affecting the localized charge states of the molecules, and by changing device operating characteristics. We proposed the use of zwitterionic MV QCA molecules in QCA circuits for predictable and controllable device behavior. We designed two types of zwitterionic molecules and their predicted device characteristics were compared to the characteristics of the ionic QCA molecules. Results demonstrated a significant change in the electronic properties of the designed zwitterionic molecules.

We used computer models to improve a QCA candidate molecule proposed by a synthetic chemistry collaborator. We investigated the stability of the proposed QCA molecule by molecular orbital analysis and ionization energy calculations using computationally expensive MP2 method. We designed three stable, zwitterionic, potential QCA candidate molecules for synthesis, modifying the design of the proposed molecule. Synthesis and testing of the proposed molecules hold promise for advancement of molecular QCA in terms of theory and experiment.

Our ongoing work includes exploration of machine-learning-based DFT functionals to achieve QCA calculations with low-cost and high accuracy. We evaluated the performance of a novel, machine-learned DFT functional, DM21, for molecular QCA calculations and benchmarked the functional against traditional *ab initio* methods. Future work includes modification of the neural network used in the development of DM21, training QCA molecular data, and implementation of DM21 in popular quantum chemistry software packages, e.g., Q-Chem, and Gaussian 16 for faster calculations. Acceleration of CASSCF calculations using machine learning and classical algorithm is an active area of interest. Molecular QCA is a revolutionary, post-CMOS classical computing paradigm. The *ab initio* models of molecules demonstrated in this work are important in implementation of molecular QCA. The structural and electronic properties of the nanometer-scale QCA candidate molecules presented here promise ultra-high device densities, ultra-low power dissipation, and room temperature operation, as, at these device scales, bit energies (~ 500 meV) are much larger than $k_BT \sim 26$ meV. The theoretical models presented here will enable solutions to some existing challenges in realization of molecular QCA.

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