A New Molecular Implementation in Quantum Cellular Automata: Quantum Inverter in One Molecule

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Abstract

Here we discuss a new concept within the general trend of molecular implementation of quantum cellular automata (QCA). We propose to employ complex polyoxometalate (POM) anion [\(\text{V}^{IV}_8\text{V}^{V}_4\text{As}_8\text{O}_{40}(\text{H}_2\text{O})]\)\(^4\)– (briefly V\(_{12}\)) as a quantum inverter. As distinguished from previous ideas on the molecular QCA, in which a molecule was supposed to act as a quantum cell, the proposal reported here employs POM V\(_{12}\) as a logical gate. We estimate the Coulombic forces in the different electronic distributions within the mixed-valence \(\text{V}^{IV}_8\text{V}^{V}_4\) network, reveal the role of the electron transfer processes and vibronic coupling. Finally, we plot the adiabatic picture of the switching cycle and the non-linear cell-cell response function.

1. INTRODUCTION

The main idea of quantum dot cellular automata [1-16] is demonstrated in Fig. 1. The quantum dots are supposed to be arranged in a square-planar cells. The two electrons are shared among four sites and mainly localized on the opposite vertices of the square in order to minimize the Coulomb repulsion between the electrons. The electrons can tunnel between the two antipodal positions but they are unable to tunnel between different cells. This configuration allows to encode the binary 1 and 0 as shown in Fig. 1. The logical devices, like majority gates can be designed as arrays of

![Fig. 1. Scheme of two polarization of the cell in quantum-dot cellular automata representing binary 1 and 0](image)

the cells. For example, Fig. 2 illustrates the binary wire which transmit the input 1 though the linear arrays of the cells coupled by the Coulomb forces, so that \(\text{In}=1\) results in the output \(\text{Out}=1\) at the other end of the wire. The QCA work at very high frequencies and extremely small heat release providing at the same time an unique possibility to create large density of the logical gates. These advantages becomes much more pronounced in QCA when the dots are replaced by molecules which are capable to store binary information. Unlike quantum dots, the molecular system of a specified chemical composition are absolutely identical and therefore have identical physical characteristics. By a proper chemical synthesis the molecular clusters can

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be engineered to have desired physical characteristics that can be controlled by the due choice of the metal ions, ligands, etc. Finally, molecules can be attached to different types of platforms by grafting individual clusters or monolayers on solid surfaces.

**Fig. 2.** Scheme of quantum binary wire composed of four-dot cells

The cell in molecular QCA is usually represented by a tetrameric square planar mixed-valence molecule containing electronic pair which is shared among four sites. The role of dots accommodating electrons play the redox centers in the molecule [9]. Then molecular cells can be arranged in order to design logical gates whose architectures are quite similar to those composed of quantum dot cells. A new concept proposed in this article is to go beyond the idea of molecular cell and use a molecule as a logic gate. We will see that the molecular structure of POM $[\text{V}^{IV}_8\text{V}^{V}_4\text{As}_8\text{O}_{40}(\text{H}_2\text{O})]^{4-}$ allows to employ it as a quantum inverter composed of two cells.

2. MOLECULAR STRUCTURE OF V$_{12}$

The metal core of the $[\text{V}^{IV}_8\text{V}^{V}_4\text{As}_8\text{O}_{40}(\text{H}_2\text{O})]^{4-}$ anion consists of twelve vanadium ions arranged in three strongly distorted rectangular units (Fig. 3.). The central square involves four $\text{V}^{IV}$ ions in which four electrons localized on the four sites, so that only the magnetic exchange (relatively weak) is active. In contrast, the external squares (see Fig. 3) can be designated as $\text{V}^{IV}_2\text{V}^{V}_2$, (two $d^1$ centers and two $d^0$ centers) so that each square represents a mixed-valence rectangle with the delocalized electronic pair (more detailed description of the structure and physical properties of this POM can be found in Refs. [17]). Each rectangle can be considered as a molecular cell so that this system can model two molecular cells in the structure of V$_{12}$.

**Fig. 3.** Molecular structure of the POM $[\text{V}^{IV}_8\text{V}^{V}_4\text{As}_8\text{O}_{40}(\text{H}_2\text{O})]^{4-}$: general view, view from $C_4$ axis and external (see text) mixed-valence $\text{V}^{IV}_2\text{V}^{V}_2$ rectangular moiety.
3. QUALITATIVE DISCUSSION OF THE INVERTER FUNCTIONALITY

The scheme of the quantum dot inverted is illustrated by Fig. 4. Let us assume that the input cell is set to the binary state 1. The Coulomb repulsion forces tend to polarize the neighboring cells which get the polarization 1. As one can see that the array of the quantum dot cells in Fig.4 inverts the input 1 so that the output becomes 0. This scheme of the inverter is widely used as a component of the circuits in complex electronic devices.

![Scheme of quantum dot inverter](image)

Fig. 4. Scheme of quantum dot inverter.

In principle, the same architecture can be designed if the quantum dot cells are replaced by the molecular ones. The central issue is that one can design the quantum inverter by using one POM molecule containing two subunits acting as molecular cell each. This is illustrated by Fig. 5 in which the switching function is shown. Let us assume that the upper square plays role of the input cell which is set to the binary 1. As one can see (Fig. 5) the mobile pair of the electrons in the lower rectangle should be localized to encode the binary digit 0 in order to gain the intercell Coulomb repulsion energy. The lower square can be referred to as output cell and therefore the V12 POM act as the quantum inverter. This qualitative consideration should be supported by quantitative estimations in order to justify the real possibility to design the POM based quantum inverter.

![Scheme of quantum inverter in V12 POM](image)

Fig. 5. Scheme of quantum inverter in V12 POM

4. QUANTITATIVE ESTIMATION OF THE COULOMB REPULSION
To approximately estimate the Coulomb repulsion energies one can use the point charge model for the study of the electron delocalization in complex POM with the Keggin and Wells-Dawson structures. The central vanadium square containing localized electrons does not play active role in the delocalization of the electronic pair in the external mixed-valence vanadium squares. That is why the central square will not be taken into account in the estimation of the Coulomb parameters.

![Fig. 6. Vanadium network in POM V_{12} with the indication of the types of the pairs (from I to V) according to the V-V distances in the external squares and between these squares.](image)

The vanadium network of V_{12} is shown in Fig. 6. Depending on the distances between metal sites one can distinguish five types of the localization of the electronic pair which are denoted by the numbers from I to V. The shortest distance between neighboring sites within the rectangle is 3.43 Å (pair I) while the longest distance 7.53 Å (pair V) corresponds to the remote ions belonging to different rectangles.

![Fig.7. Coulomb energies in the V_{12} POM evaluated in the point charge model.](image)
The results of the estimations of the inter- and intracell Coulomb energies are presented in Fig. 7. One can see that the difference in the Coulomb repulsion in the “eclipsed” and “twisted” ("alternated") intercell charge configurations $K$ is about 2160 cm$^{-1}$, while the difference in the Coulomb energy $U$ of the neighboring and antipodal intracell configurations proves to be about 10,000 cm$^{-1}$. In other words the intracell interaction exceeds considerably the intercell one which reflects the dependences of the Coulomb repulsion upon the metal-metal distances in the $V_{12}$ structure (Fig. 6) This means that the highly excited states with the neighboring configuration of the charges can be eliminated from the consideration when we are dealing with the “eclipsed” and “twisted” types intercell charge distributions. Then, to properly encode the binary information in the two “twisted” configurations which are expected to be able to perform the function of inverter, one should justify the stability of these configurations. The existence of a large energy gap between all intercell and intracell distribution is the necessary condition for that. Along with this condition, one can state that the “twisted” configurations should be significantly lower in energy than the “eclipsed” ones. In fact, the value of the Coulomb energy $K= 2160$ cm$^{-1}$ is to be compared with the effective transfer parameters for the electronic pair facilitating delocalization over the four sites. If these transfer parameters exceed the Coulomb energy $K$ the system is expected to be delocalized over four sites and obviously cannot encode binary information.

5. ELECTRON TRANSFER PROCESSES: QUALITATIVE VIEW

The most significant one-electron transfer processes are unable to switch the system between two “eclipsed” configuration. One can also see that the electronic pair cannot change a certain antipodal configuration of the charges into the second one in one step. This transformation occurs through the virtual excited states belonging to the neighboring charge distributions with the energy $U$. A more detailed consideration shows that the electron transfer pathway for the switching between two

![Diagram](image)

Fig. 8. Scheme of the electron transfer pathways in the two coupled cells modelling quantum inverter.
“twisted” configurations includes four steps as schematically shown in Fig. 8. From the quantum-mechanical point of view this means that the non-vanishing matrix element corresponding to the processes of switching between two “twisted” configurations appears in the fourth order perturbation theory. Therefore this matrix element can be estimated in order of magnitude as $t (t/U)^4$, where $t$ is the transfer parameter corresponding to the one-electron jump between neighboring sites (in this estimation it is assumed that $K<<U$). One can conclude that the transfer processes in V12 probably unable to delocalize the system which is favorable for the inverter functionality. More detailed information can be obtained from ab initio calculations. At the same time the vibronic interaction which is known as localizing factor should be taken into consideration.

6. VIBRONIC COUPLING

We shall employ the conventional vibronic model for mixed valence systems formulated by Piepho, Krausz and Schatz [18] (conventionally referred to as PKS model) which deals with the independent “breathing” displacements of the ions around the sites of the electron localization. Using the projection operator one can obtain the following explicit expressions for the PKS normal coordinates for a tetrameric system. These coordinates are approximately interrelated with the point group $D_{4h}$, although the actual symmetry is lower. Pictorial representation of the symmetry adapted PKS vibration in mixed-valence square-planar complex is given in Fig. 9.

![Fig. 9. Pictorial representation of the symmetry adapted PKS vibration in mixed-valence square-planar complex.](image)

$Q_+ = Q_{B_1} = \frac{1}{2} (Q_A - Q_B + Q_C - Q_D)$

Fig. 10. Shows the PKS coordinates for the metal network of V12 molecule. One can distinguish the symmetric and antisymmetric collective PKS coordinates corresponding to symmetric and antisymmetric displacements with respect to the

![Fig. 10. PKS coordinates of the metal network in the POM V12.](image)
plane of the system. In general, the electron-vibrational problem in this approximation involves two active modes. From the picture of the ligand displacements (Fig. 10) one can see that only antisymmetric $Q_-$ mode is strongly related to the electron transfer with the change of “twisted” configuration. Just this coordinate is taken into

![Contour plot of the adiabatic energy surface](image)

Fig. 11. Potential surface of the POM V12 in “twisted” configurations of the electronic pair

account in the evaluation of the adiabatic surface corresponding to the functionality of the system as inverter. To evaluate the potential surfaces of the system we employ the model of the linear vibronic interaction (see Ref. [2,3] for the detail). Under some conditions the potential surface has two distinct minima which are shown in the contour plot in Fig. 11 and as a section of the adiabatic potential. The minima correspond two the two “twisted” configurations of the electronic density separated by the barrier. This picture illustrates the fact that the vibronic interaction act as the localizing factor stabilizing In and Out information of the inverter. It is to be emphasized physically different roles of the Coulomb and vibronic interactions in the trapping of different charge configuration. While the Coulomb forces separate the “twisted” and “eclipsed” configurations competing thus with the delocalization processes, the transition between the two “twisted” configuration remains barrierless. On the contrary, the vibronic interaction also competes with the delocalization processes but separates the two twisted configuration by the potential barrier. The last is important for the logic gate because the restrict the clock frequency of the device but at the same time ensures stability of the encoding information.

7. SWITCHING CYCLE AND CELL-CELL RESPONSE IN VIBRONIC MODEL
The vibronic model so far discussed allows to evaluate the main characteristics of the coupled cells. Figure 9 illustrates the adiabatic picture of the switching cycle from which one can see how the polarization of the output cell gradually changes from -1 to 1 when the input cell changes its polarization in the same range. This picture (plotted at some typical parameters) reflects the vibronic nature of the inverter function which has to be taken into account in the evaluation of the main characteristics of the device.

One of the key characteristics of QCA is the cell-cell response function $P_1$ vs $P_2$ ($P_1$ are $P_2$ the cell polarizations) which should be essentially non-linear to ensure the functionality of the devices. The steepness of the cell-cell response function $P_1(P_2)$ is evidently strongly dependent on the degree of electron delocalization, being more pronounced in case of more localized electronic states.

Fig 10. shows a family of cell-cell response functions calculated at different values of the vibronic coupling parameters. One observed that the increase of the

![Diagram](image-url)

**Fig.9.** Adiabatic picture of the switching cycle of the quantum inverter in the vibronic model of V$_{12}$ POM.
vibronic coupling parameter leads to the increase of the abruptness of the $P_1(P_2)$-curves, while at smaller values of $\nu$ the steepness of the curve is less pronounced, and

![Graph showing the relationship between $P_1$ and $P_2$ for different values of $\nu$.](image)

Fig. 10. Cell-cell response function calculated for different values of the vibronic coupling parameters

even at $P_2 = \pm 1$ the polarization $|P_1|$ remains smaller than 1. This is evidently due to the fact that the vibronic tends to localize the electrons reducing thus their mobility.

8. CONCLUDING REMARKS

In this article we proposed a new idea in the area of molecular QCA. It is suggested to use the POM anion as quantum inverted. To justify this idea we have developed a model of V$_{12}$ which takes into account the electron transfer processes and vibronic coupling. The main characteristics of the system are evaluated in the framework of the semiempiric model. These calculations evidence in favor possible functionality of V$_{12}$ as quantum inverter.

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