MOLECULAR QUANTUM DOT CELLULAR AUTOMATA:
LOCALIZATION AND CELL-CELL RESPONSE IN TETRAMERIC
MIXED-VALENCE UNITS

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Abstract

Our interest in this article is prompted by the vibronic problem of charge polarized states in the four-dot molecular quantum cellular automata (mQCA), a paradigm for nanoelectronics, in which binary information is encoded in charge configuration of the mQCA cell. The polarization of the cell is evaluated and we show how the partial delocalization caused by the joint action of the vibronic coupling and electron transfer processes influences polarization of a four-dot cell. The results obtained within the adiabatic approach are compared with those based on the numerical solution of the dynamic vibronic problem. The Coulomb interaction between the cells is considered and the influence of the vibronic coupling on the shape of the cell-cell response is revealed.

1. Introduction

According to the Moore’s low during more than two decades the number of computing units on a chip was doubled every 18 months approaching nowadays to a natural physical limit of practical implementation restricted by the level of heat release and quantum effects. A new revolutionary computing paradigm was proposed by Lent et al. [1] as a physical implementation of an automaton at nano-scale using quantum-dot cellular automata (QCA) [2]. This discovery gave a strong impact to the development of the new multidisciplinary field of nanotechnology that combines physics, chemistry, material science, computer science, and electrical engineering [2-15]. The metal-based and semiconductor-based QCA have been realized as micron scale as metal dots composing wires and majority gates on a silicon substrate (see, for review ref. [12]). The electronic QCA devices consuming extremely small amounts of electrical power and very small heat release are capable of performing computation at very high switching speeds.

The cell consists of the four dots occupied by the two extra electrons (or holes) which can tunnel between these dots. The binary information is encoded in the two antipodal charge configurations of the cell which are energy beneficial and transferred via Coulomb interaction between the neighboring cells. Just these two quasi-stable charge distributions that conventionally are referred to as cell polarizations $P = -1$ and $P = +1$ encode the binary information 1 and 0. The grids of the cells compose logical devices such as wires, majority gates, funout, invertors, etc. from which complex circuits can be designed. The
architectures of these circuits had been proposed in underlying papers [1-5] and then discussed thoroughly [6, 10-17].

Recently the idea of using molecular systems as QCA (mQCA) units has been proposed and discussed [18-25]. This proposal marked a new landmark towards further miniaturization of microelectronic devices while receiving a substantial increase of their advantages compared to the conventional ones. In fact, molecular mQCA promise nanometer-scale units with accompanying ultra-high device densities as well as room-temperature operation and provide at the same time options to control the key properties of the active molecules by chemical means. A molecule acting as structured charge containers acceptable as a mQCA cell should have two or more positions in which the electrons occupying the nonbonding orbitals can be localized mimicking the dots and tunnel among these positions. Attractive candidates for molecular cells have been proposed and discussed in detail in Ref. [18-31]. The proposal [13] to realize QCA cells by MV molecules [32-48] seems to be especially promising because they naturally have two or more metal sites with different oxidation degrees forming specific charge configurations while the electron-lattice interaction can lead to the self-trapping and consequently to the barrier between these localized configurations.

In this article we consider the levels of the delocalized electronic pair and vibronic interaction in a tetranuclear MV systems that can be exemplified by the tetaruthenium complexes $2\text{Ru(II)}^+\ 2\text{Ru(III)}$ in which two holes are delocalized over four metal sites. The mQCA implementations are closely related to the localization/delocalization features of the named compounds and therefore the vibronic coupling proves to be one of the key factor defining the stability of the charge configurations, response to the varying electric field of the driver and switching period in QCA. As it was mentioned in ref. [13] the MV ruthenium complexes are representatives of Robin and Day classes I, II, and III [49-51] and therefore the vibronic coupling is needed for the adequate description of the magnetic characteristics and profiles of the intervalence optical bands.

2. The main interactions

To model the molecular systems suitable for use as four dot mQCA we will consider the structures exemplified by the tetaruthenium MV complexes suggested in Ref. [13] to encode the binary information. These MV species consist of the two Creutz-
Taube complexes assembled in the center-bridged and side-bridged square-planar tetramers within which two holes are shared among the four sites. The four sites A, B, C and D will be enumerated as shown in Fig. 1. The following consideration is applicable to the both cases delocalized holes or electrons and for the sake of definiteness we will refer to the electrons. The Hamiltonian of the system is assumed to consist of three terms:

\[ H = H_e + H_v + V. \]

Here \( H_e \) is the electronic (Hubbard type) Hamiltonian, including all interactions between electrons and ions provided that the reference configuration of the ions is fixed to the full-symmetric one (\( D_{4h} \)). The next two terms are the Hamiltonians of the free vibrations (\( H_v \)) and the electron-vibrational interaction \( V \). The vibronic interaction [49,50] is known to produce bistability in MV system which leads to a barrier between the two charge distribution and therefore acts as one of the key factors in the mQCA action.

The main factors controlling the electronic spectrum are the following:

1. Coulomb repulsion between the two itinerant electrons which can be instantly localized either at the adjacent sites (along the sides of the square) or at the remote sites (antipodal positions). The Coulomb repelling forces of electrons tend to localize them at opposite vertices. These two localized configurations which will be referred to as distant (\( d \)) pairs form the ground manifold. The difference in the energies of the Coulomb repulsion \( U_2 \) between the distant pairs and the neighboring (\( n \)) ones \( U_1 \) will be denoted as \( U = U_1 - U_2 \) which is the only Coulomb parameter. The charge configurations in the two lowest states are assumed to encode the binary information in nQCA.

2. The transfer of the two electrons among the four sites. Only the one-electron transfer processes will be taken into consideration. The electron transfer parameters \( t_n \) and \( t_d \) correspond to the jumps between the distant and adjacent sites respectively (Fig. 1). The parameters of the isotropic exchange interaction acting in the localized configurations are normally smaller than the transfer integrals in MV compounds and therefore the magnetic exchange will be neglected.

3. Electronic levels in the limit of strong Coulomb repulsion

The energy levels are labeled by the irreducible representations (irreps) of the point group D\(_{4h}\) of the molecule and by the quantum number of the full spin of the system (\( S=0 \) and \( S=1 \) for two electrons). Group-theoretical classification (see [53]) of MV clusters enables to classify the allowed terms with due account of the Pauli principle and point symmetry prior explicit evaluation of the wave-function and energy levels. In this way one can find the following spin-singlet and spin-triplet terms for the \( d \)-configurations \( ^1B_{1g}(d), ^1A_{1g}(d), ^3E_u(d) \) (the low-lying group of levels) and \( n \)-configurations (excited states) \( ^1B_{2g}(n), ^1E_u(n), ^1A_{1g}(n), ^3A_{2g}(n), ^3B_{1g}(n), ^3E_u(n) \) (symbols \( d \) and \( n \) are indicated). Using the well developed technique [54] the wave functions for the allowed multiplets can be expressed in terms of bi-electronic determinants.

Let us consider a region of a strong inter-site Coulomb repulsion \( U \), assuming thus that the Coulomb repulsion \( U \) exceeds considerably both transfer parameters, \( U >> |t_n|, |t_d| \). This is most likely the realistic case just actual for utilization of the system as mQCA cell. Qualitatively, it is clear that in the opposite case of a weak Coulomb
repulsion and/or strong transfer, the isolated cell would have two distinct polarizations which is unfavorable for the QCA performance. Within the “strong $U$ approximation” the energy levels are divided in two groups accordingly to their attribution to the different Coulomb multiplets ($d$ and $n$). The groups of the levels are well insulated from each other (by a large gap $\propto U$) and the energies can be represented as series in terms of small parameters $|t_n|/U$, $|t_d|/U$. The levels belonging to $d$-configurations, whose properties are important in view of the mQCA applications, can be approximately expressed as:

$$
E\left(1B_{1g}(d)\right) = 0,
$$

$$
E\left(1A_{1g}(d)\right) = -\frac{8t_n^2}{U} + \frac{16t_n^2t_d}{U^2} \equiv -\Delta ,
$$

$$
E\left(3E_u(d)\right) = -\frac{4t_n^2}{U} \equiv -\Delta_1 .
$$

Let us focus on the low lying group of levels which are stabilized and split due to mixing of $d$- and $n$-configurations via the transfer processes. The energy pattern involves two orbitally non-degenerate levels with $S = 0$ and the orbital doublet $3E_u$

![Fig. 2. Scheme of the low lying levels of the electronic pair providing strong Coulomb repulsion: (a) $t_d = 0$; (b) $t_d > 0$](image)

(with $S = 1$) between them. The $d$-levels of interest are shown in Fig 2 in which the absolute values of the gaps are denoted as $\Delta$ and $\Delta_1$. The main contribution to the gaps is produced by the $t_n$- transfer which is active in the two virtual steps (corresponding to the 2nd order perturbation theory) switching between the two $d$-localizations of the pair. For this reason the corresponding splitting ($\propto t_n^2$) is independent of the sign of $t_n$.

4. Vibronic model for a bi-electron mixed-valence square-planar species

In the full Hamiltonian the second term describes the free vibrations of the system which is represented by the set of the harmonic oscillators. We shall employ the conventional vibronic model for MV systems formulated by Piepho, Krausz and Schatz [49, 50] (PKS model) which deals with the independent “breathing” displacements of
the ions around the sites of the electron localization. One can prove [53] that in the case under consideration the PKS coordinates form the four-dimensional space which can be attributed to the bases of the following irreps of the point group D_{4h}: A_{1g}, B_{1g}, E_u. Using the projection operator [53, 54] one can obtain the following explicit expressions for the PKS coordinates for a square-planar tetrameric system belonging to the point group D_{4h}:

\[ Q_{B_{1g}} = \frac{1}{2} (Q_A - Q_B + Q_C - Q_D), \]
\[ Q_{E_{x,y}} = \frac{1}{\sqrt{2}} (Q_A - Q_C), \quad Q_{E_{x,y}} = \frac{1}{\sqrt{2}} (Q_B - Q_D). \]  

In Eq. (3) \( Q_\alpha (\alpha = B_{1g}, E_u x, E_u y) \) are the symmetry adapted PKS coordinates (actually, the normal coordinates of the system in the PKS model) composed of the four “breathing” vibrations \( Q_i \) associated with the sites \((i=A, B, C, D)\). The PKS coordinates (or, alternatively, the so-called reaction coordinates ) will be denoted as \( Q_{B_{1g}} = Q, Q_{B_{1g}} = Q, Q_{E_y} = Q_y \). In the case of the MV system under consideration the vibronic coupling can be represented in the matrix form as following:

\[ V = \sum_\alpha \nu_\alpha O_\alpha Q_\alpha. \]  

In Eq. (4) \( \nu_\alpha \) is the coupling parameter (having dimension of energy) of the “extra” electrons with the vibrational mode \( \alpha (\alpha = B_{1g}, E_u x, E_u y) \). The coupling with the full-symmetric mode \( (A_{1g}) \) is eliminated by a due shift of the equilibrium position. The matrices \( O_i \) are defined in the basis of the electronic wave functions for spin triplet and spin singlet terms. Within the PKS model the frequencies and the vibronic parameters prove to be equal for all active vibrations and will be denoted as \( \nu \) and \( \omega \) correspondingly.

5. Vibronic trapping and spin effects

Under the condition of strong Coulomb repulsion the vibronic problem can be restricted to the ground manifold and therefore is reduced to the \( (^1B_{1g} + ^1A_{1g}) \otimes b_{1g} \) and \( ^3E_u \otimes b_{1g} \) subtasks. This means that a pair of the \( S=0 \) levels \( ^1B_{1g} \) and \( ^1A_{1g} \) are mixed with the only vibration \( b_{1g} \) and the same vibration is active in the \( S=1 \) term \( ^3E_u \).

Using the vibronic matrices and the explicit expressions for the energy levels one can find the two following effective Hamiltonians acting within the low lying spin-singlet and spin-triplet manifolds:

\[ H_1 = \left( \begin{array}{cc} -\Delta & 0 \\ 0 & 0 \end{array} \right) + \hbar \omega \left( \begin{array}{c} \frac{1}{2} \frac{\partial^2}{\partial Q^2} - \nu \sigma_x Q \end{array} \right), \]  

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\[ H_2 = -\Delta_1 + \frac{\hbar \omega}{2} \left( Q^2 - \frac{\partial^2}{\partial Q^2} \right) - \nu \sigma_z Q. \]  \quad (6)

The Pauli matrix \( \sigma_x \) is defined in the basis \(^1A_{1g}(d),^1B_{1g}(d)\) while \( \sigma_z \) is related to the basis \(^3E_u(x(d),^3E_u(y(d))\). One can find the expressions for the adiabatic potentials:

\[ \varepsilon_{\pm}(Q) = -\frac{\Delta}{2} + \frac{\hbar \omega}{2} Q^2 \pm \frac{1}{2} \sqrt{\Delta^2 + 4\nu^2 Q^2}, \]

\[ \varepsilon_{x,y}(Q) = -\Delta_1 + \frac{\hbar \omega}{2} Q^2 \pm \nu Q. \]  \quad (7)

In Eq. (7) the functions \( \varepsilon_{\pm}(Q) \) are the two branches, \( \varepsilon_{\pm}(Q) \) and \( \varepsilon_{-}(Q) \), of the adiabatic potential for the \((^1B_{1g} + ^1A_{1g}) \otimes b_{1g}\) pseudo JT problem which is mathematically equivalent to that for an one-electron dimer [45], while the \(^3E_u \otimes b_{1g}\) coupling leads to the two intersecting parabolas \( \varepsilon_{x,y}(Q) \) which is peculiar for the static JT effect. Figure 8 shows the composition of the adiabatic potentials \( \varepsilon_{\pm}(Q) \) and \( \varepsilon_{x,y}(Q) \) for some qualitatively different cases. Depending of the interrelation between the gap \( \Delta \) and the strength of the coupling \( \nu \) the lower sheet \( \varepsilon_{-}(Q) \) can have the only minimum, \( Q_\pm = 0 \) providing weak coupling (or/and large gap \( \Delta \)), \( \nu^2 < \Delta \hbar \omega/2 \) or two minima in the points

\[ Q_\pm = \pm \sqrt{\frac{\nu^2}{2\hbar^2 \omega^2} - \frac{\Delta^2}{4\nu^2}} \]  \quad (8)

under the condition of strong coupling (or/and small gap \( \Delta \)), \( \nu^2 > \Delta \hbar \omega/2 \). The energy of the only minimum of \( \varepsilon_{-}(Q) \) in which the electronic pair is fully delocalized is just the electronic energy \(( -\Delta )\) while the energies of the two equivalent minima located at \( Q_\pm \) are the following:

\[ \varepsilon_{-}(Q_-) = -\frac{\nu^2}{2\hbar \omega} - \frac{\Delta}{2} - \frac{\Delta^2 \hbar \omega}{8\nu^2}. \]  \quad (9)

The potential curves \( \varepsilon_{x,y}(Q) \) represent two intersecting parabolas and exhibit two minima irrespectively of the value of the vibronic coupling (static JT effect) which are disposed at \( Q_x = -Q_y = \nu/\hbar \omega \) and have the energies \(-\Delta_1 - \nu^2/2\hbar \omega\). These two minima correspond to the localization of the electronic pair in the antipodal positions along the molecular \( X \) and \( Y \) axes (“broken symmetry” states). In this case of the static JT effect the tunneling between the minima is forbidden so that the electronic pair is fully localized in each of the two minima irrespectively of the strength of the vibronic coupling. It is convenient to introduce a dimensionless parameter \( \kappa = (2\Delta_1 - \Delta)/\Delta_1 \) which is expressed through \( t_d \) as \( \kappa = 4t_d/U \) and serves as a measure of the position of the spin-triplet \(^3E_u\) within the gap.
between two spin-singlets $^1B_g$ and $^1A_g$ (providing $\kappa = 0$ the spin-triplet is located just in the middle of this gap).

Fig. 3. Adiabatic potentials of a square planar MV unit for the low lying levels belonging to the $d$-configuration of the electronic pair: $\varepsilon_0(Q) = \varepsilon(Q)/\hbar\omega$-dimensionless adiabatic energy, $\nu_0 = \nu/\hbar\omega$, $\Delta/\hbar\omega = 4$.

The most interesting case of strong vibronic coupling is illustrated in Figs. 3d-e. In the limit of strong coupling ($\nu/\hbar\omega = 3.0$ in Figs. 3d-f) providing $\kappa = 0$ (Fig. 3d) the minima for the spin-singlet and spin-triplet states become degenerate. These minima correspond to the full localization of the charges along the diagonals of the square for both spin configurations. This is a result of the full quenching of the $t_n$ processes by a strong vibronic interaction which leads to the localization of the electronic pair and consequently to the paramagnetic ground state.

Providing $t_d < 0$ the minima of spin-singlet states are deeper than those for the spin-triplet states although the singlet-triplet gap in the electronic spectrum (at $Q = 0$) is reduced. In the case of $t_d > 0$ the strong enough vibronic coupling leads to the spin-crossover of the levels so that the spin-triplet state becomes the ground one. In the last case the system is locked in the minima. One can see that the magnetic properties of the
system are closely related to the interrelation between the two relevant transfer parameters and qualitatively in quantitatively affected by the vibronic coupling. In general, the vibronic interaction produce the barrier between the two charge distribution and therefore acts as a key factor defining switching period in QCA.

6. Polarization of the cell within the adiabatic vibronic model

Let us consider polarization of the cell which is a scalar quantity $P$ introduced by Lent et al [1,9] as a normalized measure of the degree to which the electron densities are localized in antipodal positions along the diagonals ($AC$ or $BD$) of a square planar four dot cell:

$$P = \frac{(\rho_A + \rho_C) - (\rho_B + \rho_D)}{\rho_A + \rho_C + \rho_B + \rho_D},$$

where $\rho_i$ are the electronic charges on the sites. If the sites $B$ and $D$ are the empty ($\rho_B = \rho_D = 1$, $\rho_A = \rho_C = 0$) the cell is fully polarized along $AC$ and $P = +1$. Alternatively, if the electrons occupy sites $B$ and $D$, polarization $P = -1$. There is no preference of a certain site population in a symmetric system and therefore in the stationary electronic states of the system the polarization of the isolated cell vanishes. When the nearby cell is present the electrostatic perturbation leads to an additional polarization and highly non-linear response function [1,9]. In general, the vibronic coupling in an isolated cell results in the “broken symmetry” quasi-stationary states in the wells of the potential minima. It is to be noted that the full localization (for which $\rho_i$ are either 0 or 1 and consequently polarizations $P_{-1} = +1$ or $P_{+1} = -1$) is reached only in the strong coupling limit while, in general, the vibronic localization is partial. At the same, it is important to note that the conditions of the vibronic trapping are spin dependent, and in particular the potential minima for the spin-triplet states (orbital doublet) are stable irrespectively of the vibronic coupling and therefore the system can possess only two discrete polarizations $P = +1$ or $P = -1$. That is why we focus on spin-singlet states. The electronic densities can be explicitly expressed in terms of the involved parameters as follows:

$$\rho_A^- = \rho_C^- = \frac{1}{2} \left[ 1 + \sqrt{1 - \left( \frac{\hbar \omega \Delta}{2 \nu^2} \right)^2} \right], \quad \rho_B^- = \rho_D^- = \frac{1}{2} \left[ 1 - \sqrt{1 - \left( \frac{\hbar \omega \Delta}{2 \nu^2} \right)^2} \right],$$

$$\rho_A^+ = \rho_C^+ = \rho_B^- = \rho_D^- = \frac{1}{2} \left[ 1 + \sqrt{1 - \left( \frac{\hbar \omega \Delta}{2 \nu^2} \right)^2} \right], \quad \rho_B^+ = \rho_D^+ = \rho_A^- = \rho_C^-.$$

The electronic densities are determined by the only dimensionless parameter of delocalization $\hbar \omega \Delta / 2 \nu^2$ which reflects the competitive roles of the vibronic coupling and transfer processes. It can be seen that the vibronic coupling leads only to a partial localization at which the magnitudes $\rho_i$ are different from 0 or 1. One can see that, in general, the localization is incomplete, so that in the left minimum the electronic density is
is mainly ($\rho_A = \rho_C < 1$) concentrated along the diagonal $AB$ while a residual density still remains on the sites $B$ and $D$. The modified expressions for polarizations $P_{-1}, P_{+1}$ which take into account the effect of partial vibronic trapping can be found:

$$P_{\pm 1} = \mp \sqrt{1 - \left( \frac{\hbar \omega \Delta}{2 \nu^2} \right)^2}. \quad (12)$$

One can see also that polarization vanishes providing $\hbar \omega \Delta / 2 \nu^2 = 1$, which is actually the condition of instability of the symmetric configuration and charge distribution when the two minima of lower sheet of the adiabatic surface merge. In spin-triplet states the system is always fully polarized due to the static character of the JT effect. The incomplete polarization of the cell essentially affects the response function of the cell to the external perturbations from the neighboring cells.

8. Cell-cell response function within the vibronic model

In this Sections we apply the vibronic approach to consideration of the interacting cells. To use the cellular automata architectures one should assume that the state of a cell must be strongly influenced by the state of the neighboring cell (or cells) so that a slight polarization of a cell would induces nearly complete polarization of a neighbor. To characterize this kind of highly non-linear behavior of a bistable cell Lent et al [8] proposed to use the cell-cell response function. Since the vibronic coupling produces the trapping effect it should substantially the cell-cell response function.

In this Section we will evaluate the cell-cell response function of square planar cell on the basis of the vibronic model so far discussed.

Let us suppose that the cell 2 (input) is initially polarized and nearest neighbor cell 1 (Fig. 4) is affected by the Coulomb forces from the cell 2. The most typical geometry of two-cell system is shown in Fig. 4, the size of each square cell will be denoted by $b$ (intra-cell distance) and the distance between the nearest neighboring cells by $c$ (cell-cell distance). Let’s assume that $U_{AC}$ and $U_{BD}$ are the Coulomb interaction energies of cell 1 in the two antipodal localizations of the electronic pair with the cell 2 having a certain polarization $P_2$. In the arbitrary polarized cell 2 the sites $A'$ and $C'$ are assumed to possess the charges $\rho e$ while the charges on the sites $B'$ and $D'$ are $(1-\rho)e$ where $0 \leq \rho \leq 1$ and $e$ is the electronic charge. Providing $\rho = 1$ and $\rho = 0$ the cell 2 has polarizations $P_2 = 1$ and $P_2 = -1$ respectively, while when $\rho = 1/2$ the cell 2 is unpolarized ($P_2 = 0$). One can find the Coulomb energy $U_{AC}$ of the arbitrary polarized cell 2 with the cell 1 in which the charges localized in the position $AB$ as follows:

$$U_{AC} = e^2 \left[ \frac{2\rho}{b+c} + \frac{\rho}{\sqrt{(2b+c)^2 + b^2}} + \frac{\rho}{\sqrt{b^2 + c^2}} + \frac{2(1-\rho)}{\sqrt{(b+c)^2 + b^2}} + \frac{1-\rho}{2b+c} + \frac{1-\rho}{c} \right]. \quad (13)$$
The Coulomb energy $U_{BD}$ (providing the same polarization of the cell 2) can be found by substitution $\rho \rightarrow 1 - \rho$ in the expression for $U_{AC}$.

According to the definition, one can write down the polarization $P_2$ as $P_2 = 2\rho - 1$ and hence $\rho = (1 + P_2)/2$. It is convenient to represent the matrix Hamiltonian $H_1$ in the basis of the fully localized electronic states with $S = 0$, and to use the basis $3E_u x(d) \equiv \psi_{AC}^1(r)$, $3E_u y(d) \equiv \psi_{BD}^1(r)$ in $H_2$. The wave-functions of the two configurations (expressed in terms of Slater determinants) localized configurations are different in the two orbitals and therefore the off-diagonal matrix elements of the one-electron operators connecting these configurations vanish. For this reason the interaction of electrons of the cell 1 with the electric field produced by the polarized cell 2 does not have non-vanishing off-diagonal matrix elements in the basis so far indicated.

The matrix Hamiltonians of cell 1 acting within the low lying the spin-singlets and spin-triplet manifolds of this cell can be written as follows:

$$
H_1 = -\frac{\Delta}{2} \left( 1 + \sigma_x \right) + \begin{pmatrix} U_{AC} & 0 \\ 0 & U_{BD} \end{pmatrix} + \frac{\hbar \omega}{2} \left( Q^2 - \frac{\partial^2}{\partial Q^2} \right) - \nu \sigma_z Q,
$$

$$
H_2 = -\Delta_1 + \begin{pmatrix} U_{AC} & 0 \\ 0 & U_{BD} \end{pmatrix} + \frac{\hbar \omega}{2} \left( Q^2 - \frac{\partial^2}{\partial Q^2} \right) - \nu \sigma_z Q
$$

Let us first apply the adiabatic approximation an imaginative picture. One can find the expression for the two branches of the adiabatic potentials of the cell 1 for $S = 0$ subjected to the Coulomb field of the cell 2 (we keep the same notations as for the free cell):

$$
\varepsilon_\pm(Q) = \frac{1}{2} (U_{AC} + U_{BD} - \Delta) + \frac{\hbar \omega}{2} Q^2 \\
\pm \frac{1}{2} \sqrt{(U_{AC} - U_{BD})^2 - 4(U_{AC} - U_{BD})\nu Q + 4\nu^2 Q^2 + \Delta^2}.
$$

For the spin $S = 1$ potentials one can find:

$$
\varepsilon_x(Q) = U_{AC} - \Delta_1 - \frac{\nu^2}{2\hbar \omega} + \frac{\hbar \omega}{2} \left( Q - \frac{\nu}{\hbar \omega} \right)^2
$$

Fig. 4. Geometry of interacting cells and charge distributions: $P_2 = 2\rho - 1, \ P_1 = 1$. 

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\pm \frac{1}{2} \sqrt{(U_{AC} - U_{BD})^2 - 4(U_{AC} - U_{BD})\nu Q + 4\nu^2 Q^2 + \Delta^2}.
$$

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$$
\varepsilon_x(Q) = U_{AC} - \Delta_1 - \frac{\nu^2}{2\hbar \omega} + \frac{\hbar \omega}{2} \left( Q - \frac{\nu}{\hbar \omega} \right)^2
$$
\[ \varepsilon_y(Q) = U_{BD} - \Delta_1 - \frac{v^2}{2\hbar\omega} + \frac{\hbar\omega}{2} \left( Q + \frac{v}{\hbar\omega} \right)^2 \]  

(16)

The adiabatic representation of the switching cycle is shown in Fig. 5 in which the mean energy of the Coulomb repulsion between cells (the term \( U_{AC} + U_{BD} \)/2 in Eq. (15)) is taken as the reference point of the energy. The potential curves are gradually changing as changes the polarization the cell 2 passing from the fully polarized cell 2 in \( P_2 = -1 \) state to \( P_2 = 1 \) one. Correspondingly, the cell 1 gradually switches between two monostable configurations (AB and CD) passing through the bistable state which is achieved when the cell 2 is unpolarized, \( P_2 = 0 \).

The differences between the spin-singlet and spin-triplet states are to be noted. Here we consider a particular case of the ground spin-singlet state of the isolated cell 1 and the case when the cell 1 remains diamagnetic in course of variation of the state of the cell 2. At the same time the ground \( S = 0 \) and \( S = 1 \) levels (minima of the potentials) approaches as cell 1 passes to the monostable state. While the polarizing field decrease the barrier between \( S = 0 \) states and finally localize the cell 1 in one of them, the effect of the cell 2 on the \( S = 1 \) is quite different. In fact, the Coulomb field of the cell 2 shifts the two \( S = 1 \) minima up and down keeping the minima at the same positions \( Q_x = -Q_y = v/\hbar\omega \) and retaining the exact crossing of the potentials. The last means the JT effect in the cell 1 remain static and consequently polarization of the cell 1 in a spin-triplet state remains constant when changing the polarization of the cell 2.

More precise results can be obtained within the exact (in the framework of the model) quantum-mechanical evaluation. By diagonalizing the matrices of the Hamiltonians in the basis composed of the products \( \psi_{AC}(S)\chi_n(Q) \) and \( \psi_{BD}(S)\chi_n(Q) \) of the localized electronic states and harmonic oscillator wave-functions one obtains the vibronic energy levels \( \varepsilon_S^\xi \) of cell 1 and the corresponding vibronic wave-functions

\[ \psi_S^\xi(Q) = \sum_n \left[ c_{AC}^\xi (S) \psi_{AC}(S) + c_{BD}^\xi (S) \psi_{BD}(S) \right] \chi_n(Q). \]  

(17)

The eigenvalues of the Hamiltonian \( H_2 \) can be also obtained directly as follows:

\[ \varepsilon_n^{AC} (S = 1) = U_{AC} - \Delta_1 - \frac{v^2}{2\hbar\omega} + \frac{\hbar\omega}{2} \left( n + \frac{1}{2} \right), \]  

(18)

\[ \varepsilon_n^{BD} (S = 1) = U_{BD} - \Delta_1 - \frac{v^2}{2\hbar\omega} + \frac{\hbar\omega}{2} \left( n + \frac{1}{2} \right). \]

The example of the spin-vibronic energy levels of cell 1 as functions of the polarization of cell 2 is shown in Fig. 6. At \( P_2 = 0 \) (that is at \( U_{AC} = U_{BD} \)) the vibronic energy levels with \( S = 1 \) are double degenerate with respect to the localization of the electronic pair: \( \varepsilon_n^{AC} (S = 1) = \varepsilon_n^{BD} (S = 1) \), while at \( P_2 \neq 0 \) these orbital doublets are split into two sublevels with definite localizations. As to vibronic spin-singlets they represent the mixing of the states with two localizations. The energy pattern is symmetric with respect to the sign of polarization \( P_2 \) and at a given set of the parameters shown in the caption...
Fig. 5. Adiabatic picture of the switching cycle in a tetrameric bistable cell.
Fig. 6. Vibronic energy levels of cell 1 as functions of polarization of cell 2 calculated with $\Delta = 800 \text{cm}^{-1}$, $h\omega = 200 \text{cm}^{-1}$, $\kappa = -0.52$, $\nu = 310 \text{cm}^{-1}$, $b = 3.5 \text{ Å}$, $c = 6 \text{ Å}$. (S = 0 – blue lines, S = 1 –red lines).

For Fig. 6 the spin-singlet remains the ground state which confirms the conclusion of the adiabatic treatment. Using the obtained vibronic wave function one can evaluate the polarization $P_1$ of cell 1 as a function of the polarization $P_2$ of cell 2. Figure 7 shows a family of cell-cell response functions calculated at different values of the vibronic coupling parameters. It is seen that the increase of the vibronic coupling parameter leads...
to the increase of the abruptness of the $P_1(P_2)$-curves, while at smaller values of $v$ the steepness of the curve is less pronounced, and even at $P_2 = \pm 1$ the polarization $|P_1|$ remains smaller than 1. This is evidently due to the fact that the vibronic coupling tends to localize the electrons (that is to reduce the mobility of the electrons). As a result it is more difficult to polarize the cell at stronger vibronic interaction.

9. Conclusion

We have considered the mechanisms of the vibronic self-trapping of charge polarized states in a square-planar MV systems proposed as a charge container in the four-dot mQCA. These systems are exemplified by the two kinds tetra–ruthenium [2Ru(II)+2Ru(III)] clusters (assembled as two coupled Creutz-Taube complexes). We employ the model which takes into account two relevant kinds of the electron transfer processes as well as the inter-site Coulomb repulsive energies in the different instant positions of localization. The electron transfer processes in a bi-electron system separate spin triplets and spin-singlets resulting thus in an effective exchange interaction between the electrons. It is shown that depending on interrelation between the electron transfer parameters in the absence of the vibronic coupling the system can be either diamagnetic or paramagnetic. The vibronic self-trapping is considered within the conventional vibronic PKS model adapted to the bi-electronic MV species with the square topology. The adiabatic potentials are evaluated for the low lying Coulomb levels in which the antipodal sites are occupied, the case just actual for utilization in mQCA. It is essential that the conditions for the vibronic localization are spin dependent. These conditions for spin-singlet and spin-triplet states are revealed in terms of the two actual transfer pathways parameters and strength of the vibronic coupling.

It is demonstrated that the spin-singlet states can be either localized or delocalized while the spin-triplet state always localized and the tunneling between the minima is forbidden. We could demonstrate that the magnetic properties of the system are closely related to the interrelation between the two relevant transfer parameters being at the same time qualitatively and quantitatively affected by the vibronic coupling. In particular, the vibronic coupling leads to the spin-crossover of the adiabatic levels. It was shown that the vibronic interaction results in specific features of the cell polarization. The conclusions of the adiabatic theory have been compared with the quantum-mechanical results. It was shown that the vibronic interaction results in specific features of the cell polarization.

The interrelation between the magnetic nature of the ground vibronic state and the localization/delocalization features can be used for the control of the cell by an external magnetic field. The results so far mentioned are based on a simplified model of strong Coulomb repulsion and adiabatic approximation which allowed us to simplify and visualize the results. In future study we plan to extend the adiabatic model employed in this article beyond the limit of strong Coulomb repulsion. In fact, the vibronic coupling in MV compounds can be strong enough as compare to the Coulomb gap as indicated by the fact of incomplete reduction of the electron transfer in the employed model. Although the adiabatic approximation is an appropriate tool to get insight into the effects of electron correlation and localization vs delocalization this approximation is inapplicable (due to fast non-adiabatic Landau–Zener transitions in the area of avoiding crossing of the adiabatic potentials) to the adequate description of the intervalence optical bands.
Moreover, the discrete structure of the lines which peculiar to the quantum-mechanical description is missed in the semiclassical approach. Therefore, we intend to solve the dynamic JT problem for these systems with the aid of the recently developed approach [55-57]. Finally, the developed model could be a good background for the description of the dissipative dynamics in MV systems [58] closely related the heat release in the switching processes. We hope to discuss this in the forthcoming paper.

Acknowledgments

A.P. acknowledges the University of Valencia for a visiting research grant and the Supreme Council for Science and Technological Development of the Republic of Moldova (project 11.817.05.03A) for financial support. A.P. and B.T. are grateful to COST Action CM1203 “Polyoxometalate Chemistry for molecular Nanoscience (PoCheMon)” for supporting this work.

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