Jahn-Teller effect in molecular electronics: quantum cellular automata

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Abstract. The article summarizes the main results of application of the theory of the Jahn-Teller (JT) and pseudo JT effects to the description of molecular quantum dot cellular automata (QCA), a new paradigm of quantum computing. The following issues are discussed: 1) QCA as a new paradigm of quantum computing, principles and advantages; 2) molecular implementation of QCA; 3) role of the JT effect in charge trapping, encoding of binary information in the quantum cell and non-linear cell-cell response; 4) spin-switching in molecular QCA based on mixed-valence cell; 5) intervalence optical absorption in tetrameric molecular mixed-valence cell through the symmetry assisted approach to the multimode/multilevel JT and pseudo JT problems.

Keywords: Jahn-Teller effect, quantum-dot cellular automata, vibronic interactions, quantum computing, molecular electronics, mixed-valency, magnetic polyoxometalates, electron transfer, adiabatic approximation

1. Introduction

Nowadays one can observe a fast growth in computing speed in conformity with the well known "Moore's law" according to which the computer chips double their density approximately every two years. The technical challenges in manufacturing microelectronic devices and natural limit of the size (a single molecule) indicates that the age of the "Moore's law" goes to the end. A central idea of quantum computing is that a quantum spin ½ (or more generally, any two-state quantum system) can serve as a carrier of information. The most serious obstacle in the realization of quantum computing is the decoherence which should be sufficiently long or, at least, not shorter than duration of the gate logical operation. The conclusion of [1] (see exhaustive discussion by Winpenny [2]) is that, in principle, one could reach a decoherence time in a molecular magnet that would permit quantum information processing. Nevertheless, practical realization of quantum computing has not been reached yet mainly due to the conceptual obstacle related to decoherence. That is why an alternative route to proceed in this fundamental problem draws close attention of researchers and engineers working in microelectronics and quantum computing. This route exploits the principles of quantum computing based on the paradigm of QCA employing quantum dots or/and especially on molecular implementation of QCA, a new revolutionary computing paradigm which was proposed by Lent et al [3] as a physical implementation of an automaton at nano-scale using QCA (see development of the field in Refs. [4-15]). 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.

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 idea of a four-dot QCA cell is schematized in figure 1. The cell consists of the four quantum dots occupied by two extra electrons (or holes) which can tunnel between the sites or, alternatively, it can be a
tetranuclear mixed-valence (MV) molecule. The information is encoded in the two antipodal charge configurations of the cell 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 (figure 1). The arrays of the cells compose logical devices such as wires, majority gates, invertors, etc. from which more complex circuits can be designed. The architectures of these circuits had been proposed in underlying papers [3,4] and then discussed thoroughly [5-13].

Recently much attention has been paid to the role of the vibronic JT and pseudo JT interactions in functionality of such logical devices (see references in the text). Particularly it has been demonstrated that the vibronic coupling produces considerable self-trapping effect which significantly influences such key characteristic of the QCA as cell-cell response function. Hereunder we briefly discuss this and other related effects caused by the vibronic JT coupling in QCA.

2. Molecular quantum-dot cellular automata

Recently the idea of using molecular systems as QCA units has been proposed and discussed [9]. Molecular QCA offer promise of nanometer-scale devices with accompanying ultra-high device densities operating at room temperature and, providing at the same time options to control the key properties of the molecule by chemical means. A molecule acting as structured charge containers acceptable as a molecular QCA 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.

As single molecule implementation of QCA, Lent and Tougaw [9, 16] proposed to use 1,4-dialyl butane radical cation consisting of butyl bridge linking two allyl groups accommodating electron. Then other attractive candidates for molecular cells have been proposed and discussed [9].

The proposal [13] to realize QCA cells by MV molecules is especially promising because they naturally have two or more sites with different oxidation degrees forming specific charge configurations while the electron-lattice interaction (vibronic coupling) can lead to the self-trapping and consequently to the barrier between localized configurations. This refers to a variety of MV systems studied in molecular magnetism, such as dimers, and mainly to large scale MV systems, like biologically important metal clusters and reduced polyoxometalates (e.g., Keggin and Wells-Dawson systems) accommodating two or several electrons delocalized over a metal network (see review articles [17-19]).

Three examples of such molecules are shown in figure 2. These are the MV tetra–ruthenium complexes (figure 2, left), $[2 \times 2]$ Fe grid [20] and the tetra-ferrocene units coupled to the central cyclobutadiene which is bonded to Co fragment [21]. The last system contains two high-spin and two low-spin ferrous ions at opposite corners of the rhombic arrangement featuring thus matrix-like array that are most suitable for molecular implementation of the QCA concept.

A great potentiality of molecules as the leading candidates to be implemented in QCA is based on the following substantial advantages: (a) unlike cells composed of quantum dots, molecular cells of specified composition are identical and therefore have identical physical characteristics (electron
Figure 2. Molecular QCA cells: (a) two types of the tetra-ruthenium complexes exhibiting different electron networks of the transfer pathways for the electronic pair; (b) molecular structure of MV complex [MeL₄Fe⁴⁺]⁴⁺ proposed in Ref. [20] as [2x2] Fe grid for QCA; (c) four ferrocene units coupled to the central cyclobutadiene which is bonded to Co fragment [21].

transfer integrals, vibronic parameters, etc.); (b) they can be engineered to have desired controlled characteristics with the use of chemical tailoring; (c) molecular cells are relatively large (but still nanoscale!) objects, much larger than ions and, thus, much easier for individual addressing while processing the information; (d) such molecules can be attached to different types of platforms by grafting clusters on solid surfaces, grafting monolayers, etc.

3. Jahn-Teller model of mixed-valence molecular cell
We will consider MV complexes assembled in the center-bridged and side-bridged square-planar tetramers as schematically shown in figure 3. The following consideration is applicable to the both cases of the geometric structure of the bridging ligands directly related to the electron transfer pathways.

Figure 3. Left: schematic quantum cellular automata cell composed of four metal sites. Right: coulomb configurations (a), Coulomb energies (b) of a MV tetrameric system with two delocalized electrons and the group-theoretical assignment of the electronic terms (c).

The adopted molecular coordinate system is shown in figure 3, left. The Hamiltonian of the system is assumed to consist of three terms describing the main relevant interactions in MV system containing two electrons delocalized over four sites:

\[ H = H_e + \sum_i \hbar \omega_i \left( Q_i^2 - \frac{\partial^2}{\partial Q_i^2} \right) + V. \]
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 operator of free vibrations and the electron-vibrational interaction Hamiltonian $V$. The vibronic interaction [22-24] is known to produce bistability in MV system which leads to a barrier between the two charge distributions and, therefore, it acts as one of the key factors in the QCA action. The main electronic interactions contributing to the Hamiltonian $H_e$ are the following [25, 26]:

1. Coulomb repulsion between the two itinerant electrons which depends on whether these electrons are instantly localized at the adjacent sites (along the sides of the square) or they occupy the remote sites (antipodal positions) as shown in figure 3. The Coulomb repelling forces tend to keep the electrons as far as possible from each other in order to minimize the energy, i.e. on the sites located at opposite vertices. These two localized configurations will be referred to as distant pairs belonging to the ground manifold. The difference in the energies of the Coulomb repulsion between the distant pairs and the neighboring ones (d- and n-pairs, the last have four possible configurations) will be denoted as $U$ as illustrated in figure 3. The charge configurations in the two lowest states are assumed to encode the binary information in molecular QCA.

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 $t_i$ and $t_j$ correspond to the jumps between the distant and adjacent sites respectively (figure 3). The parameters of the isotropic exchange interaction acting within the localized configurations are normally smaller than the transfer integrals in MV compounds and therefore such magnetic exchange will be neglected.

Taking into account the interactions so far mentioned the electronic Hubbard-type Hamiltonian $H_e$ of the cell can be represented as:

$$H_e = U_n \sum_{i,j} \sum_{\sigma, \sigma'} n_{i,\sigma} n_{i+1,\sigma'} + U_d \sum_{i,j} \sum_{\sigma, \sigma'} n_{i,\sigma} n_{i+2,\sigma'} + I_n \sum_{i,j} \sum_{\sigma} \left( a_{i,\sigma}^+ a_{i+1,\sigma} + a_{i+1,\sigma}^+ a_{i,\sigma} \right)$$

$$+ I_d \sum_{i,j} \sum_{\sigma} \left( a_{i,\sigma}^+ a_{i+2,\sigma} + a_{i+2,\sigma}^+ a_{i,\sigma} \right),$$

(2)

where $a_{i,\sigma}^+$ ($a_{i,\sigma}$) creates (annihilates) an electron occupying active orbital at the site $I$ with spin projection $\sigma$, so that $n_{i,\sigma}$ are the occupation number operators. The summation in equation (2) is performed over the pairs of the neighboring sites ($1^{\text{st}}$ and $3^{\text{rd}}$ terms) and over the pairs of the distant sites ($2^{\text{nd}}$ and $4^{\text{th}}$ terms). The first term in equation (2) describes the interelectronic Coulomb repulsion ($U_n$) between the adjacent sites, while the second term ($U_d$) is that for the remote sites. The diagonal terms of the type of $n_{i,\sigma} n_{i,\sigma}$ responsible for the intra-site repulsion, are excluded. The last two terms describe the two types of the relevant one-electron transfer processes (figure 2a).

One can find the following spin-singlet and spin-triplet terms for the d-type configurations $^1B_{1g}(d), ^3A_{1g}(d), ^3E_u(d)$ (the low-lying group of levels) and the n-type configurations (excited Coulomb states) $^1B_{2g}(n), ^1E_u(n), ^3A_{1g}(n), ^3A_{2g}(n), ^3B_{1g}(n), ^3E_u(n)$ as shown in figure 3. The explicit expressions for energy levels are found in Ref. [25]. The electron transfer processes in a bi-electron system separate spin-triplets and spin-singlets, thus resulting in an effective magnetic interaction between the electrons. This kind of the effective magnetic exchange caused by electron delocalization has been recognized in our earlier consideration of MV double reduced polyoxometalates with Keggin and Wells-Dawson structures, and allowed us to explain the unusual diamagnetism of these
compounds [27-29]. As to the MV square planar cell, it was shown that the energy pattern is symmetric with respect to the sign of $t_n$ but it does depend on the sign of $t_d$.

It is reasonable to employ the vibronic model for MV systems formulated by Piepho, Krausz and Schatz [22] (conventionally referred to as PKS model), which deals with the independent “breathing” displacements of the ions around the sites of the electron localization. This model is simple but it properly reflects the main features of the vibronic coupling in MV systems, in particular, the presence of the potential barrier separating localized configurations. With the use of the group-theoretical classification [30], one can prove 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 $D_{4h}$: $A_g, B_{1g}, E_u$. One can obtain the following expressions for the PKS coordinates for a square-planar tetrameric system belonging to this point group:

$$Q_{A_g} = \frac{1}{2}(Q_A + Q_B + Q_C + Q_D), \quad Q_{B_{1g}} = \frac{1}{2}(Q_A - Q_B + Q_C - Q_D).$$

$$Q_{E_u,x} = \frac{1}{\sqrt{2}}(Q_A - Q_C), \quad Q_{E_u,y} = \frac{1}{\sqrt{2}}(Q_B - Q_D).$$

(3)

In equations (3) $Q_{\alpha}$ ($\alpha = A_g, B_{1g}, E_u,x, E_u,y$) 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 $(i=A, B, C, D)$ as shown in figure 3. In the case of the MV system under consideration, the linear vibronic interaction can be represented in the matrix form as follows:

$$V = \sum_{\alpha} \nu_{\alpha} O_{\alpha} Q_{\alpha},$$

(4)

where the parameters $\nu_{\alpha}$ are the vibronic constants and the matrices $O_{\alpha}$ are given in Ref. [25].

Taking into account the assignment of the electronic states, one can formulate the independent combined JT and pseudo JT vibronic problems, which can be symbolized as follows: $(1B_{1g} + 2A_g + B_{2g} + E_u) \otimes (h_{1g} + e_u)$ for spin-singlets and $(1A_g + 2B_{1g} + 2E_u) \otimes (h_{1g} + e_u)$ for spin-triplets terms, where the small letters are used for the vibrational irreps. One can see that the JT effect (see books and review articles [31-34]) is an inherent ingredient of the description of the quantum cell in QCA.

Figure 4. Pictorial representation of the symmetry adapted vibrational coordinates ($Q_{\alpha} > 0$) of a MV square-planar unit in PKS model. The balls mimic the sites, i.e. the metal ion and ligand surrounding: large green ball-expanded site, small blue ball-compressed site, medium grey balls-reference configuration (full-symmetric vibration $Q_{A_g}$ is not shown).

4. Vibronic self-trapping and spin effects in mixed-valence molecular cell

Action of the cell as a unit keeping binary information assumes that the charges should be presumably localized at the antipodal sites. This is possible if the Coulomb repulsion suppresses considerably the
transfer processes which are responsible for the delocalization of the electrons. Under the condition of strong Coulomb repulsion \( (U \gg |t_n|, |t_d|) \), the full vibronic problem can be restricted to the ground manifold being thus reduced to one-mode \( (E_n + A_g) \otimes b_{1g} \) and \( E_n \otimes b_{1g} \) subtasks [25]. This means that a pair of the levels with \( S=0 \) (\( B_{1g} \) and \( A_{1g} \)) are mixed through the only vibration \( b_{1g} \) and the same vibration is active in the \( S=1 \) term \( E_n \). One thus arrives to the JT and pseudo JT problems for spin-triplets and spin-singlets correspondingly. One can see that in the framework of the PKS model the \( e \)- modes do not act within the ground manifold because they mix the ground Coulomb configurations of \( d \)-type with excited \( n \)-type configurations. The vibronic pseudo JT problem proves to be one-dimensional and therefore is essentially simplified. The adiabatic potentials are found to be:

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

\[
\varepsilon_{x,y}(Q) = -A_1 + \frac{\hbar \omega}{2} Q^2 \pm \nu Q.
\]

In equation (5) the functions \( \varepsilon_+(Q) \) and \( \varepsilon_-(Q) \) represent the two branches of the adiabatic potential for the \( (E_n + A_{1g}) \otimes b_{1g} \) pseudo JT problem, while \( \varepsilon_{x,y}(Q) \) is adiabatic surfaces for the static JT problem \( E_n \otimes b_{1g} \). The following notations are used:

\[
\frac{8r_n^2}{U} - \frac{16t_n^2}{U^2} = -\Delta, \quad \frac{4t_n^2}{U} = A_1.
\]

Within the PKS model, the frequencies and the vibronic coupling parameters prove to be equal for all active vibrations (because they originate from the couplings of the same strength with the breathing modes at the equivalent centers). Depending on the interrelation between the gap \( \Delta \) and the strength of the vibronic coupling \( \nu \), the lower sheet \( \varepsilon_-(Q) \) can have a single minimum at \( Q_\pm = 0 \), providing weak coupling (or/and small gap \( \Delta \)), \( \nu^2 < \Delta \hbar \omega / 2 \) (figures 5a-c), or two minima at the points \( Q_\pm \):

\[
Q_\pm = \pm \sqrt{\frac{\nu^2}{\hbar^2 \omega^2} - \frac{\Delta^2}{4 \nu^2}}.
\]

under the condition of strong coupling (or/and large gap \( \Delta \)), \( \nu^2 > \Delta \hbar \omega / 2 \) (figures 5d-f). The energy of the single minimum of \( \varepsilon_-(Q) \) in which the electronic pair is fully delocalized is just the electronic energy \( (-\Delta) \). 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 \( Q_\pm = -Q_y = \nu / \hbar \omega \) 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 (“broken symmetry” states). In the case of static JT effect, the tunneling between the minima is forbidden (at least up to third order of perturbation theory with respect to electron transfer), and so the electronic pair is fully localized in each of the two minima irrespectively of the strength of the vibronic coupling.
To distinguish different physical situations in figure 5 we use the dimensionless parameter \( \kappa = (2\Delta_1 - \Delta) / \Delta \), which is expressed through \( t_d \) as \( \kappa = 4t_d/U \) and serves as a measure of the position of the spin-triplet \( ^3E_c \) within the gap between two spin-singlets \( ^1B_{1g} \) and \( ^1A_{1g} \) in the electronic spectrum (providing \( \kappa = 0 \) the spin-triplet is located just in the middle of this gap). Figures 8a-c show that weak vibronic coupling (\( \nu / \hbar \omega = 1.0 \)) effectively reduces the singlet-triplet gap (\( ^1A_{1g} \), \( ^3E_c \)). The most interesting case of strong vibronic coupling is illustrated in figures 5 d-e. In the limit of strong coupling (\( \nu / \hbar \omega = 3.0 \)) and providing \( \kappa = 0 \), the minima for the spin-singlet and spin-triplet states become practically 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 at the minima.
5. “Intercommunication” between molecular cells: cell-cell response function within the Jahn-Teller model

In the previous section we have considered the electronic and vibronic properties of the isolated molecules which play role of the cells in QCA. Implementation of the logically significant OCA arrays or circuits requires consideration of the “intercommunication” between the molecular cells. It is essential that the charge configuration of the input cell is able to dictate the charge configuration of the two output

![Diagram of interacting cells](image)

**Figure 6.** Left: geometry of interacting cells. Right: cell-cell response function calculated for different values of the vibronic coupling parameters and $\Delta = 800 \text{ cm}^{-1}$, $h\omega = 200 \text{ cm}^{-1}$, $\kappa = -0.52$, $\nu = 310 \text{ cm}^{-1}$, $b = 3.5 \text{ Å}$, $c = 6 \text{ Å}$.

cells. In the simplest case of a QCA wire one has to solve the non-stationary problem of the case of a QCA wire one has to solve the non-stationary problem of the signal propagation from the input cell in a definite state (binary “1” or “0”) to the output. In a QCA fanout circuit an input signal is transformed into two or more output signals. Providing different cellular automata architectures one should assume that the state of a cell should 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 neighboring cell. To characterize this kind of highly non-linear behavior of a bistable cell the use of the cell-cell response function has been proposed [35]. Since the vibronic coupling produces a trapping effect, it is expected to produce substantial influence on the cell-cell response function. Let us consider the polarization of the cell, a scalar quantity $P$ introduced by Lent et al (see [3, 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-site cell:

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

(8)

where $\rho_i$ are the electronic charges on the sites. If the sites $B$ and $D$ are empty ($\rho_B = \rho_D = 1, \rho_A = \rho_C = 0$) the cell is fully polarized along $AC$ and so $P = -1$. Alternatively, if the electrons occupy sites $B$ and $D$, polarization $P = +1$. From the qualitative arguments one can conclude that in MV systems the effective electronic charges are the results of the competitive effects of the vibronic (JT and pseudo JT) coupling and transfer processes. The geometry of the interacting cells is shown in figure 6. One can introduce the values $U_{AC}$ and $U_{BD}$ which 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 \( P_2 \). The electronic densities are calculated in Ref. [25] within the quantum-mechanical (dynamical) approach to the vibronic problem. The vibronic coupling strongly modifies the cell-cell response function whose idealized (sharp step) view is shown in figure 1. From figure 6 (right) one can observe 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 \( \nu \) 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 (reducing their mobility) and, therefore, it decreases polarization of the cell. More detailed consideration, in particular, estimation of the parameters for some MV clusters is given in Ref. [25].

6. Spin-switching in molecular quantum cellular automata based on mixed-valence cell

The main efforts in the area of QCA have been focused on the analysis of electronic charge density distribution within the cell and its change due to polarization (electric quadrupole moment) induced by the Coulomb field of the neighboring cells. Much less attention has been paid on the role of spin effects in QCA. At the same time, there is a strong correlation between the molecular spin and the degree of localization in mixed valence clusters.

In Ref. [26] we focused on the study of spin-effects in a single square-planar MV cell comprising two electrons and in coupled molecular cells for QCA. Using the vibronic model it was demonstrated that the polarizabilities of the cell are different in spin-singlet and spin-triplet states of the electronic pair. Based on this inference the concept of spin-switching in molecular QCA has been proposed and the conditions under which this effect is feasible have been derived. In order to reveal these conditions we have performed a series of quantum-mechanical calculations of the vibronic energy levels of the isolated cell and of the cell subjected to the external polarizing field. To present the results in a descriptive way they are qualitatively discussed in terms of the adiabatic potential curves illustrating spin effects in switching cycle during operation in QCA. The spin-switching effect stemming from the theoretical model is shown to be dependent on the relative strength of the intra-cell electronic interactions (Coulomb repulsion energies and electron transfer parameters) and the vibronic coupling. This is expected to suggest a route for observation of spin-switching in which the non-magnetic vibronic ground state of the cell is changed to the magnetic one due to polarization induced in this cell by the neighboring one. The spin switching is shown to produce a significant effect on the cell-cell response function leading to the unusual stepwise shape of this function. Figure 7 shows the switching cycle of a cell subjected to the Coulomb field of the neighboring cell. The cycle is presented by plotting the adiabatic potentials for cells 1 and 2 calculated for different \( S \) values. Figure 7 shows only the lowest sheet \( \varepsilon_s^{0\rightarrow}(Q) \) of the adiabatic potential for \( S = 0 \). Depending on the spin-state of the polarized cell, one can distinguish two cases. Figure 7a shows the case in which the cell retains spin-singlet state when it becomes polarized. Figure 7b demonstrates a possibility of spin-switching. Thus, for a negative value of \( \kappa \), \( \kappa = -0.5 \) (that is \( t_d < 0 \) ) the polarization of cell 2 is unable to change the ground spin state of cell 1 (figure 7a), and so this state always remains nonmagnetic. It is worth to mention that the gap between the lowest levels with \( S = 0 \) and \( S = 1 \) is reduced due to partial vibronic localization of the system. On the contrary, in case of positive \( \kappa \) the polarization of cell 2 leads to the change of the ground spin state of cell 1 as shown in figure 7b for \( \kappa = 0.5 \). One can see that the system switches from a non-magnetic state \( (S_g = 0 \text{ at } P_2 = 0) \) to a magnetic one \( (S_g = 1 \text{ at } P_2 = \pm 0.5) \). This example demonstrates that for some ranges of parameters the spin-switching in the cell can be induced by the polarization of the neighboring cell.
Figure 7. Adiabatic potentials of the cell 1 calculated at different $P_2$: $8t_n^2/U = 600 \text{ cm}^{-1}$, $\nu = 250 \text{ cm}^{-1}$, and $\kappa = -0.5$ (a), $\kappa = 0.5$ (b); $S = 1$ – red lines, $S = 0$ – blue lines.

7. Beyond the Born-Oppenheimer approximation through the symmetry assisted approach
The adiabatic approximation (Born-Oppenheimer paradigm) is valid in the cases of strong vibronic coupling in the JT systems but can lose its accuracy providing moderate vibronic coupling. Moreover, by definition, this approximation (based on classical representation of the ionic movement) fails in the description of the discrete vibronic spectrum and, in particular, in the evaluation of the intervalence optical bands in MV systems. Understanding of limitations of the Born-Oppenheimer approximation gave rise to a new trend at the borderline between physics and chemistry that can be referred to as “Chemical theory beyond the Born-Oppenheimer paradigm” (see very recent book [36] with this indicative title). Alternatively, the quantum-mechanical approach usually leads to a complicated (often practically unsolvable) dynamic problem in multimode systems, especially in cases when several electronic states are coupled to the JT and pseudo-JT modes (see review in [32]). This occurs, for example, in the nanoscopic MV systems, which can be exemplified by polyoxometalates (like Keggin and Wells–Dawson structures [27-29]). Therefore, a precise solution of the quantum-mechanical
vibronic problem is of primary importance for the evaluation of the shapes of the electron transfer optical absorption bands and quantitative analysis of the main parameters of tetrameric quantum cells.

**Figure 8.** Illustration for the ground state of a bi-electronic square planar MV system in the case of $t_d > 0$: (a) singlet-triplet gap $\Delta E_{T-S}$ (in cm$^{-1}$) vs $\nu$ in the case of weak Coulomb repulsion, (b) temperature dependence of $\chi T$ at different values of the vibronic coupling parameter shown in the plot and $|t_n|/U = 2$, $t_d/U = 2$.

To solve the multidimensional JT problem we have recently suggested [37-39] a theoretical tool which has been referred to as “symmetry assisted approach”. The symmetry assisted approach allows to block the vibronic matrices to full extent in accordance with the point symmetry of the systems and thus to make tractable the complicated dynamic problems for these molecular cells. The mathematical details of the approach are described in Refs. [37-39]. These calculations are implemented in a specially designed software (which will be published elsewhere in a more general mathematical formulation). With this tool we also extended the theory of the molecular QCA cell beyond the limit of prevailing Coulomb repulsion in the electronic pair (as described in previous sections). Consequently the general pseudo JT problems for spin-singlet $\left( {^1B_{1g}, {^2}A_{1g}, {^1}B_{2g}, {^1}E_u } \right) \otimes (b_{1g} + e_u )$ and spin-triplet states $\left( {^3A_{1g}, {^3}B_{1g}, {^3}E_u } \right) \otimes (b_{1g} + e_u )$ in a square-planar bi-electronic system has been recently solved [39]. The obtained symmetry adapted electron-vibrational functions have been employed for the calculation of the profiles (shape-functions) of the charge transfer absorption bands in the tetrameric MV complexes and for the discussion of the magnetic properties. In Ref. [39] we presented also the characteristics of the performance of the evaluation which can be referred to as “index of efficiency” defined as the ratio (CPU time for blocked matrix) / (CPU time for full matrix). In particular, use of the symmetry adapted basis leads to a significant reduction of the CPU time, for example for $N= 24$ (number of the unperturbed vibrational levels) the CPU time with the use of symmetry is only 7.1% of the total time without application of the symmetry assisted approach.

To illustrate some results let us consider a particular case of a weak Coulomb repulsion or/and strong transfer, $|t_n|/U, |t_d|/U > 1$, positive $t_d$ ($|t_n| = 2000$ cm$^{-1}$, $t_d = 2000$ cm$^{-1}$). The full sets of the vibronic levels as functions of the vibronic coupling for spin-triplets and spin-singlets in the case of $t_d > 0$ are given in Ref. [39]. Here we mention only that the low lying levels demonstrate spin-crossover (figure 8, left) which manifests itself in the temperature dependences of the magnetic susceptibility $\chi T$ vs $T$ (figure 8, right).
Figure 9. Shape-function of the charge transfer bands as functions of $\nu/\hbar \omega$ in the case of weak Coulomb repulsion and $t_d > 0$ (the same parameters as in figure 7): blue-before spin-crossover ($S=0$ ground state); red-after spin-crossover ($S=1$ ground state).

The profiles of the intervalence absorption bands are given in figure 9. The shapes of the bands are given for the two sets of the vibronic parameters, the first one corresponds to the $S=0$ ground state (before spin-crossover point). Therefore, the dynamic pseudo JT vibronic problem in MV tetrers with the delocalized electronic pair is solved with the aid of the powerful symmetry-assisted approach which allows to eliminate the restrictions implied by the Born-Oppenheimer paradigm. The mathematical receipt for the quantum-mechanical treatment of the vibronic eigen-problem is based on the point symmetry consideration and, therefore, the total huge matrix of the JT Hamiltonian is blocked to maximum extent. More careful description of the shapes of the lines and optical bands entire requires consideration of the interaction with the thermal bath and relaxation processes [40].

8. Some new perspectives
Here we briefly indicate a new concept within the general trend of molecular implementation of QCA. It is propose to employ complex polyoxometalate anion $[\text{V}^{IV}_{12} \text{As}_{12} \text{O}_{40} \text{(H}_2\text{O})_4]^4$ (briefly $V_{12}$) [41] as a quantum inverter. The metal skeleton of this polyoxometalate anion involves two mixed-valence squares with two delocalized electrons each as shown in figure 9. The two mixed-valence units can be associated with the two parallel cells coupled within the molecule via Coulomb repulsion. The Coulomb repulsion inside the squares is strong which ensures the antipodal electronic distributions, while the minimal Coulomb repulsion between the electrons in different cells is reached providing twisted configuration of charge distribution in different cells. This architecture of the cells in $V_{12}$ is able to function of molecular quantum inverter as illustrated in figure 10 from which one can see that
in the favorable Coulomb configurations input “1” in one of the cell gives output “0” in the another cell. As distinguished from previous ideas on molecular QCA, in which a molecule was supposed to act as a quantum cell, the proposal reported here employs $V_{12}$ as a logical gate. We estimated the Coulombic forces in different electronic distributions within the mixed-valence $V_{4}^{V_{8}}V_{4}^{V}$ network, revealed the role of the electron transfer processes and vibronic coupling. Estimation of the energies of “twisted” and “eclipsed” charge configurations demonstrates feasibility of the quantum inverter function. More detailed results including ab initio evaluation of the main parameters will be published elsewhere.

9. Concluding remarks
In this short review we have summarized some recent results of the application of the JT vibronic model to the problem of QCA. Many of the systems so far mentioned attracted long lasting attention as molecular magnets for which the peak of studies occurred in the period 2000. The main attention was concentrated on the problem of single molecular magnets with promising applications as memory storage units. Then, these systems, especially MV clusters have been proposed as charge containers suitable for the molecular QCA, which revived interest in the study of these systems and gave rise to the new trends summarized in the present review article. Strong impact on new development has also been given by the new experimental techniques which has allowed to directly observe the key features of MV systems. For example, it is worth to mention the scanning tunneling microscopy (STM) [42] which gave direct access to the distributions of the electronic density in potential wells of the Fe(II)-Fe(III) system. From the theoretical point of view MV systems have been studied as objects in which relaxation processes and environmental decoherence [5,40] caused by the electron-thermal bath are important. This topic is closely related to the energy dissipations for the logic processes, a question of the conceptual significance and practical importance.

In the present review special attention has been paid to the role of the JT and pseudo-JT effects in charge trapping, encoding of binary information in the quantum cell and non-linear cell-cell response. We have also discussed the spin-switching in QCA, and intervalence optical absorption spectra of tetrameric MV square cells evaluated with the aid of the symmetry assisted approach to the multimode/multilevel JT problem. The results of recent studies in the area show that the JT and pseudo JT theory is very efficient at nanoscale and useful for the study of molecular units and corresponding processes in microelectronics. One can express also an optimistic expectation that the developed vibronic approach could be applicable in general problem of molecular information processing which is one of the most challenging problem in a wide field of knowledge ranging from...
molecular electronics down to supramolecular processes occurring in brains (see pioneering papers of Day [43, 44]).

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