Spin effects in molecular quantum cellular automata

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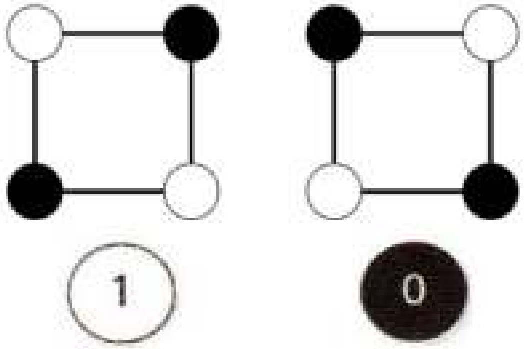
Quantum cellular automata based on mixed valence molecules (clusters)

❑ **M**olecular **Q**uantum **C**ellular **A**utomata (QCA) - (Craig S. Lent et al)

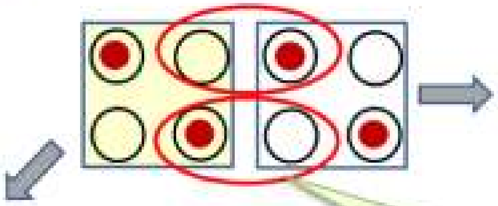
The main idea of QCA is to encode binary information in charge distribution in two-electron mixed-valence molecular square



The cell charge "polarization" encodes the binary information:

binary **"1"** **and** binary **"0"**

Transmitting binary information via the intercell Coulomb interaction

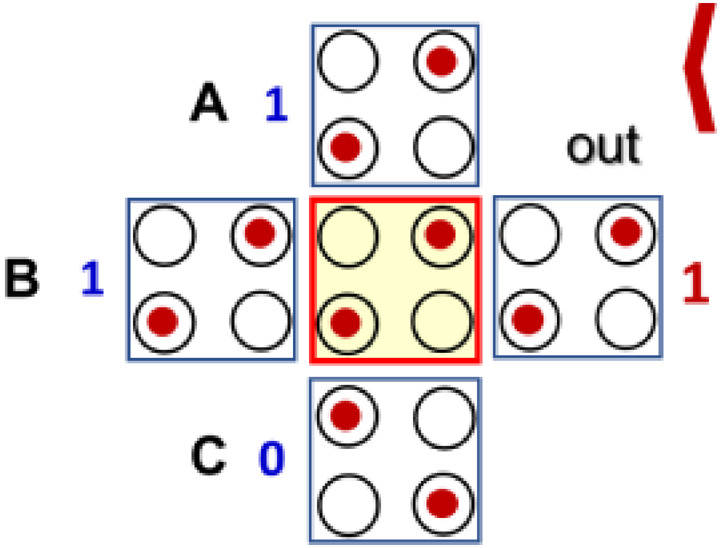


Working cell accepting the same polarization

Polarized "driver-cell"

Minimum Coulomb repulsion

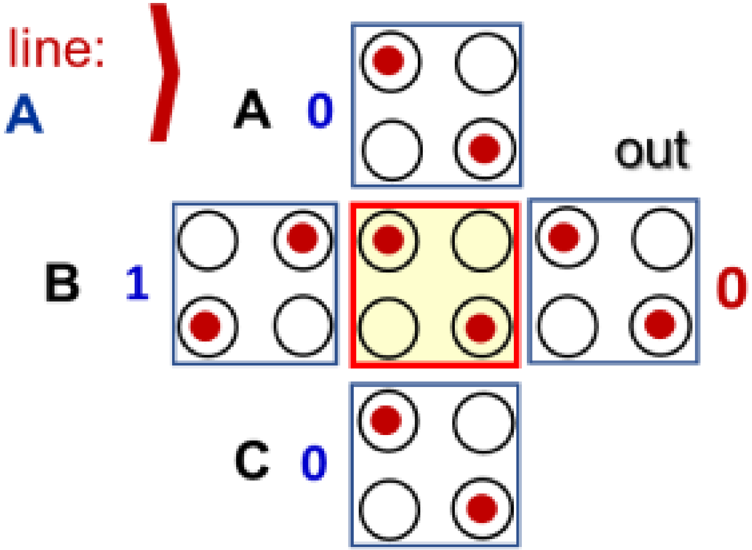
QCA logic gates: majority gate functioning as AND and OR



If input **A** = 1

Maj(**A,B,C**) → Gate **OR**

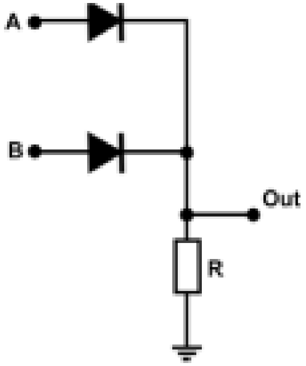
program line:
input **A**



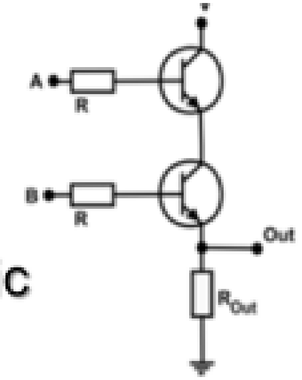
If input **A** = 0

Maj(**A,B,C**) → Gate **AND**

Diode OR gate



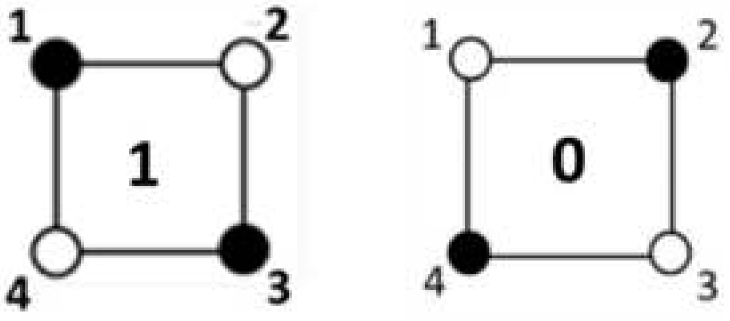
Transistor AND gate



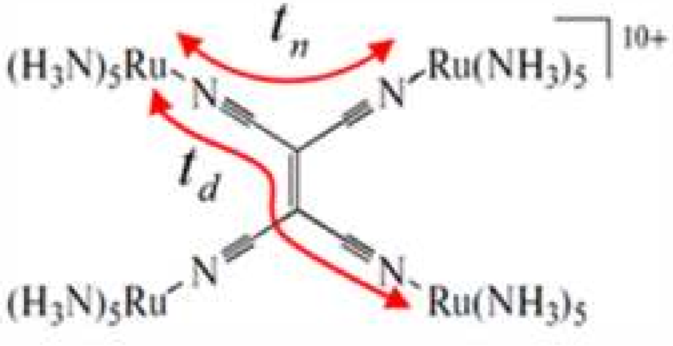
Equivalent electronic devices

QCA cell based on two-electron mixed-valence molecular square – key interactions

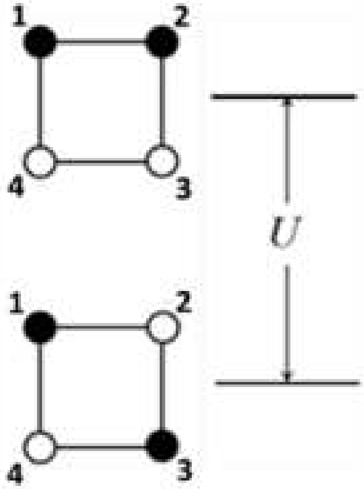
Diagonal-type electronic distributions can be used to encode binary information



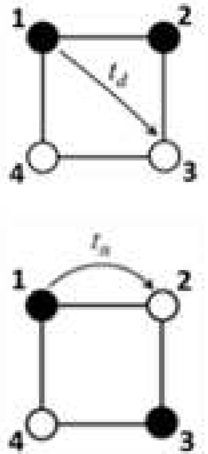
Example of molecular square cell – Creutz-Taube derivative



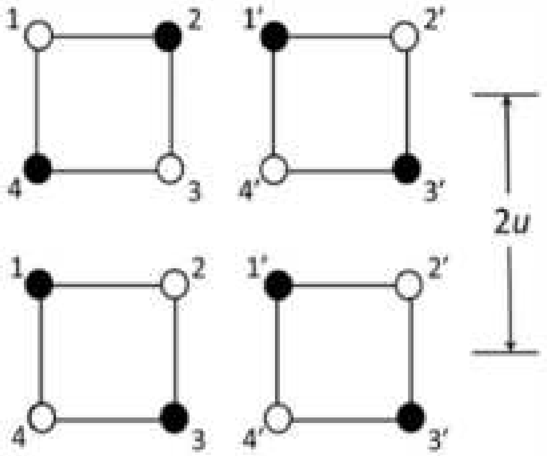
Intracell interelectronic Coulomb repulsion



Two types of one-electron transfer processes



Intercell Coulomb interaction



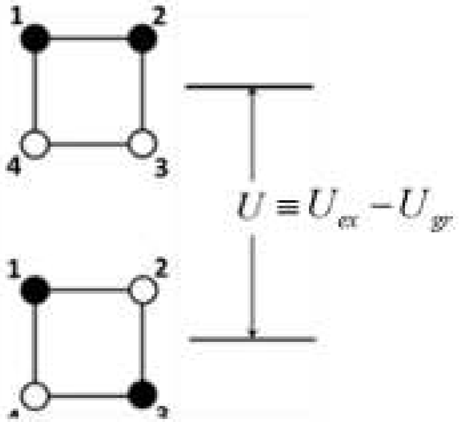
Pseudo-Hubbard-type Hamiltonian of the free cell and its eigenvalues

$$\boxed{\hat{H}_C = \sum_{i>j} U_{ij}\, n_i n_j + \sum_{i>j} t_{ij} \sum_{\sigma} \left(c^{+}_{i\sigma} c_{j\sigma} + c^{+}_{j\sigma} c_{i\sigma} \right)}$$

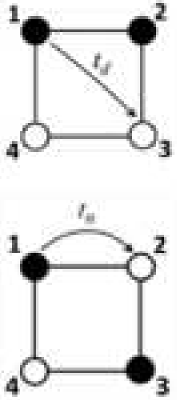
$$U_{13} = U_{24} \equiv U_{gr}, \quad U_{12} = U_{23} = U_{34} = U_{14} \equiv U_{ex},$$

$$t_{13} = t_{24} \equiv t_d, \quad t_{12} = t_{23} = t_{34} = t_{14} \equiv t_n$$

Intracell interelectronic Coulomb repulsion



Two types of one-electron transfer processes



Spin-singlets

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

$$E\left[{}^1B_{2g}(n)\right] = E\left[{}^3A_{2g}(n)\right] = U - 2t_d,$$

$$E\left[{}^1E_u(n)\right] = U,$$

$$E_{\pm}\left({}^1A_{1g}\right) = \frac{1}{2}(U + 2t_d) \pm \frac{1}{2}\sqrt{(U + 2t_d)^2 + 32\, t_n^2}\,,$$

Spin-triplets

$$E\left[{}^3B_{1g}(n)\right] = U + 2t_d,$$

$$E_{\pm}\left({}^3E_u\right) = \frac{U}{2} \pm \frac{1}{2}\sqrt{U^2 + 16\, t_n^2}\,.$$

- **For t_d=0 ground state always possesses S=0;**
- **For $t_d \neq 0$ the ground state can have either S=0 or S=1 depending on t_d, t_n *and* U.**

Effect of electrostatic field induced by polarized driver-cell

Limit of strong Coulomb repulsion

$$U >> |t_n|, |t_d|$$

Weak non-linear Stark effect for "delocalized" orbital singlets with *S*=0

$$E_{\pm}^{S=0}(P') = -\frac{4t_n^2}{U}\left(1-2\frac{t_d}{U}\right) \pm \sqrt{\left[\frac{4t_n^2}{U}\left(1-2\frac{t_d}{U}\right)\right]^2 + (P'u)^2},$$

$$E_{\pm}^{S=1}(P') = -\frac{4t_n^2}{U} \pm P'u.$$

Strong linear Stark effect for "localized" orbital doublets with *S*=1

$P' = \frac{\rho_{1'3'} - \rho_{2'4'}}{\rho_{1'3'} + \rho_{2'4'}}$ – **polarization of "driver-cell"**

$P = \frac{\rho_{13} - \rho_{24}}{\rho_{13} + \rho_{24}}$ – **polarization of "working cell"**

$P(P')$ – **"cell-cell response function"**

Electric field effect is spin-dependent

⇒ such cells can be regarded as single-molecule magnetoelectrics

A. Palii, , B. Tsukerblat, J. M. Clemente-Juan, E. Coronado, *J. Phys. Chem. C*, **120**, 16994 (2016).

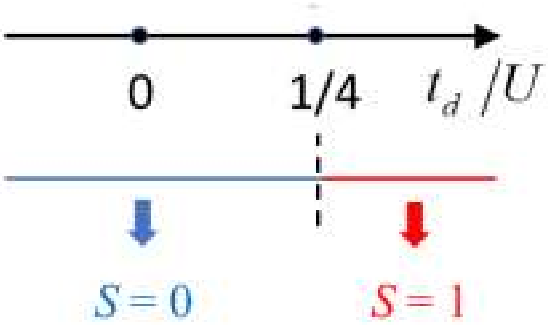
Limits of zero and strong electric field and possibility of spin-switching

$P'u = 0$

$$\varepsilon_-^{S=0} = -\frac{8t_n^2}{U}\left(1-2\frac{t_d}{U}\right),$$

$$\varepsilon_+^{S=0} = 0,$$

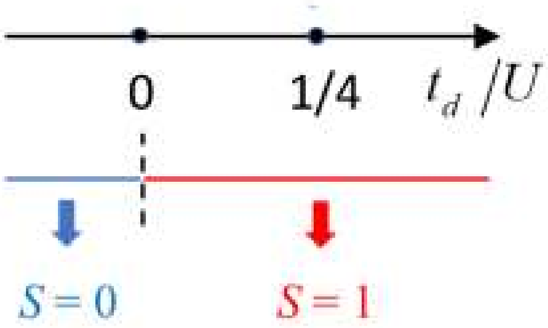
$$\varepsilon_\pm^{S=1} = -\frac{4t_n^2}{U}$$



$|P'|u \gg \frac{4t_n^2}{U}\left|1-2\frac{t_d}{U}\right|$

$$\varepsilon_\pm^{S=0}(P') \approx -\frac{4t_n^2}{U}\left(1-2\frac{t_d}{U}\right) \pm P'u,$$

$$\varepsilon_\pm^{S=1}(P') = -\frac{4t_n^2}{U} \pm P'u.$$



$t_d/U < 0$ – ground state is always that with $S=0$

$t_d/U > 1/4$ – ground state is always that having $S=1$

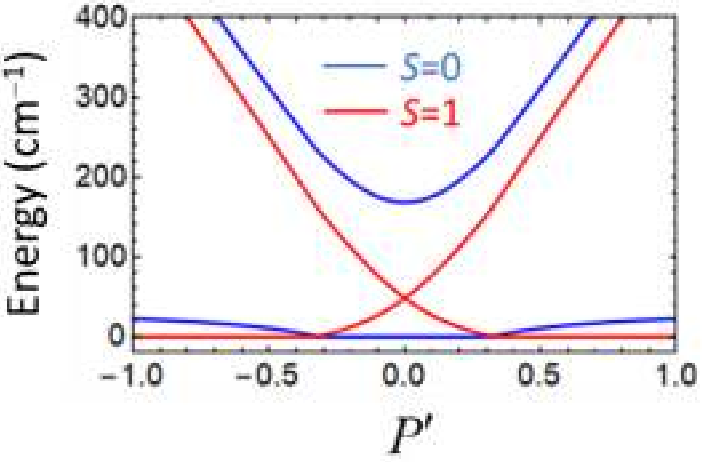
$0 < t_d/U < 1/4$ **– ground state can be switched from $S=0$ to $S=1$**

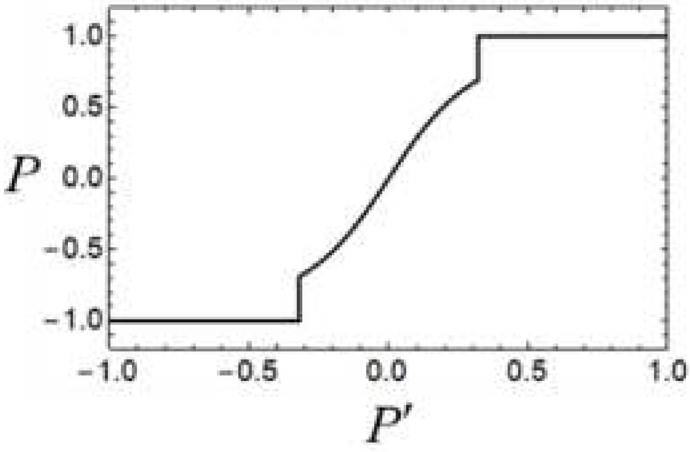
Spin-switching in the working cell induced by electric field of polarized driver-cell

$t_d/U < 0$ – ground state is always that with $S=0$

$t_d/U > 1/4$ – ground state is always that having $S=1$

$0 < t_d/U < 1/4$ – **ground state can be switched from $S=0$ to $S=1$**





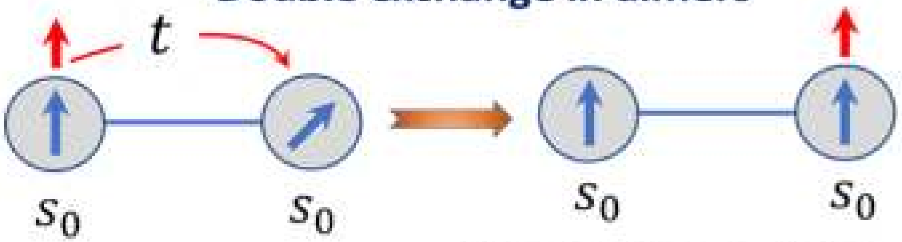
$$t_n^2/U = 30\,\mathrm{cm}^{-1}, \quad t_d/U = 0.15, \quad u = 250\ \mathrm{cm}^{-1}$$

In addition to QCA function additional spin-switching function appears due to magnetoelectric effect

Clusters with double exchange as another example of spin-switchable QCA cells

d^2-d^2-d^1-d^1

Double exchange in dimers



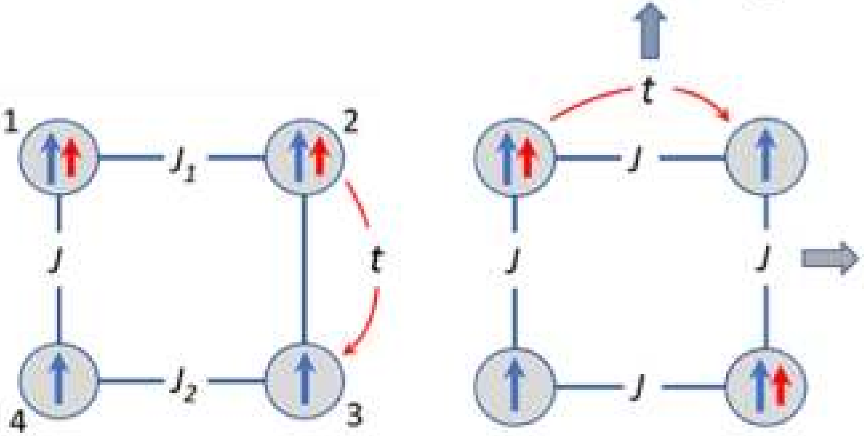
Zener, De Gennes, Anderson& Hasegawa

$$E_{\pm}(S) \equiv \pm t \frac{S + 1/2}{2s_0 + 1}$$

Double exchange

Excess electron polarizes the spin-cores tending to stabilize ferromagnetic spin alignment

Double exchange



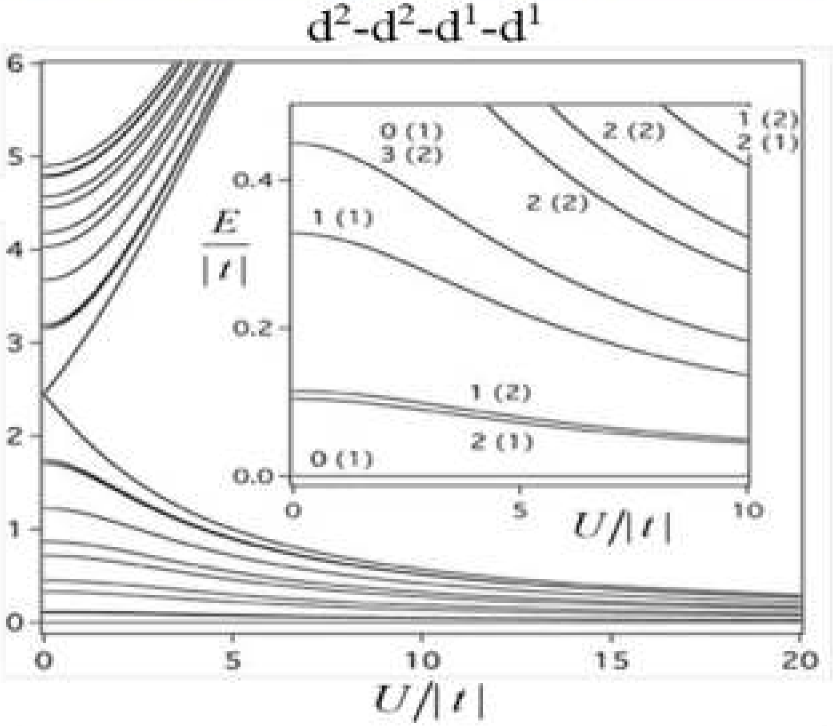
HDVV exchange

A. Palii, J. M. Clemente-Juan, S. Aldoshin, D. Korchagin, A. Rybakov, S. Zilberg, B. Tsukerblat, *J. Phys. Chem. C* **2020**, *124*, 25602-25614.

HDVV – Heisenberg-Dirac-Van Vleck

Effects of double exchange and HDVV exchange

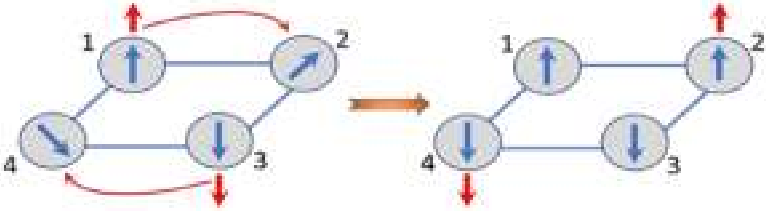
$$\hat{H}_{DE} + \hat{H}_0 = t \sum_{i<k,\sigma} (1 - \delta_{k,i+2})$$
$$\times \left(\hat{c}^{+}_{\psi_i \sigma} \hat{c}_{\psi_k \sigma} + \hat{c}^{+}_{\psi_k \sigma} \hat{c}_{\psi_i \sigma} \right)$$
$$+ \sum_{i<k} U_{ik} \hat{n}_{\psi_i} \hat{n}_{\psi_k}$$



Physical origin of antiferromagnetic effect of double exchange

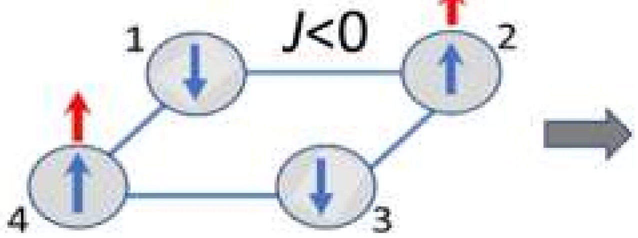
For d^1-d^1-d^0-d^0 – tetramer

$$E_{gr}(S=0) = \frac{1}{2}\left(U - \sqrt{U^2 + 32t^2}\right),$$
$$E_{ex}(S=1) = \frac{1}{2}\left(U - \sqrt{U^2 + 16t^2}\right),$$



Ground state of the double exchange Hamiltonian has S=0.

Ground state of HDVV Hamiltonian has S=1



Double exchange and HDVV exchange produce competitive effects

Combined effect of double exchange and HDVV exchange in the limit of strong Coulomb repulsion

Strong-U – limit (second-order perturbation theory)

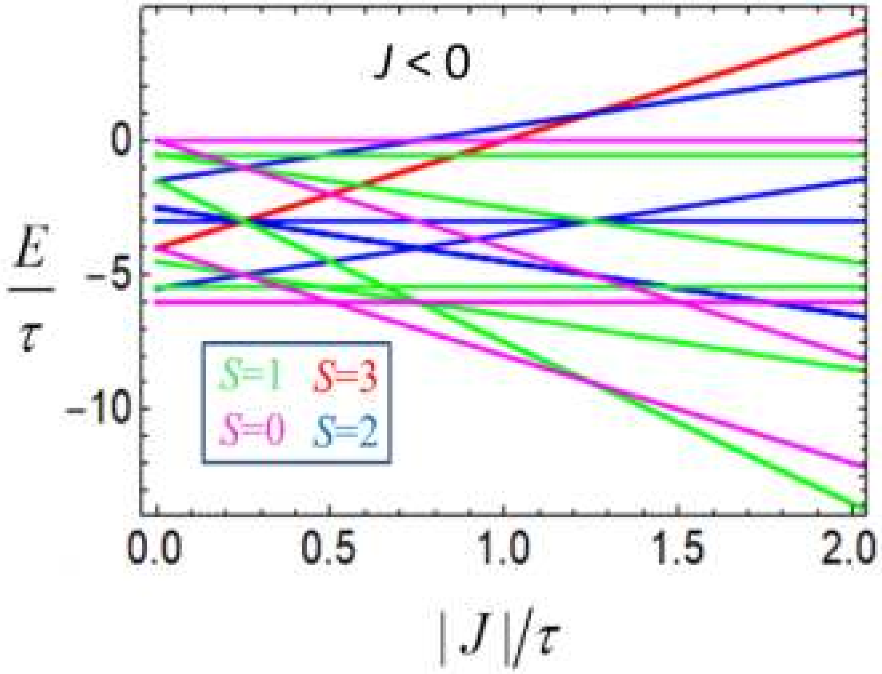
$$\hat{H} = \hat{H}_0 + \hat{V},$$

where

$$\hat{V} = \hat{H}_{DE} + \hat{H}_{HDVV}$$

$$-\hat{P}_0\, \hat{H}_{DE} \hat{P}_1\, \hat{H}_{DE} \hat{P}_0 / U \propto -t^2 / U \equiv -\tau$$ ⇨ *second-order double exchange parameter*

$$\hat{P}_0\, \hat{H}_{HDVV} \hat{P}_0 = -2J\left(\hat{O}_{13} + \hat{O}_{24}\right)\hat{\boldsymbol{S}}_{13}\hat{\boldsymbol{S}}_{24}$$ where $\hat{O}_{kl}\,|k'\,l'\rangle = \delta_{kk'}\,\delta_{ll'}\,|k\,l\rangle$



- **Double exchange in systems comprising two excess electrons results in the antiferromagnetic effect due to opposite spin directions in the subsystem of mobile electrons**
- **In a strong U limit depending on the relative strength of the second order double exchange and HDVV exchange the ground state of the cell can be either spin triplet or one of the two spin-singlets**

Energy levels of the working cell subjected by the quadrupole Coulomb field of the driver-cell

Stark Hamiltonian

$$\hat{H}_{QF} = \frac{1}{2} u P' \left(\hat{n}_2 + \hat{n}_4 - \hat{n}_1 - \hat{n}_3 \right)$$

Total Hamiltonian

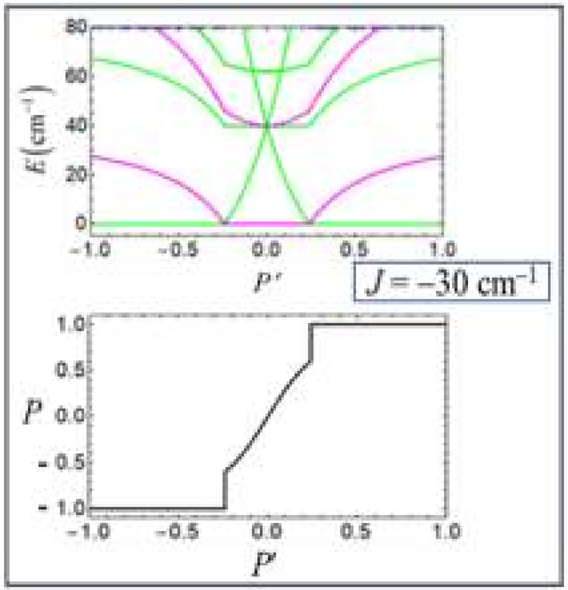
$$\hat{H}_{tot} = \hat{H} + \hat{H}_{QF}$$

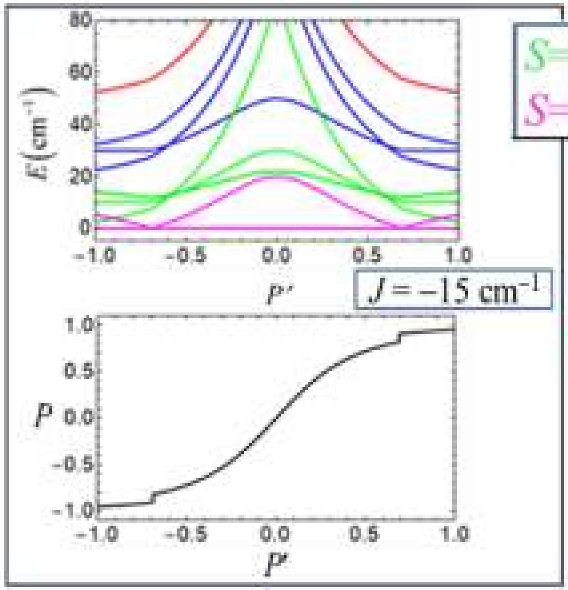
Distribution	S_{13}	S_{24}	S	Energies	
D_1	2	1	3	$-4J - 4\tau - u\,P'$	$S=3$
D_2	1	2	3	$-4J - 4\tau + u\,P'$	
D_1	2	1	1	$(12J - 3\tau - 2uP')/2$	$S=1$
D_2	1	2	1	$(12J - 3\tau + 2uP')/2$	
D_1	1	1	0	$4J - 2\tau \pm \sqrt{4\tau^2 + u^2 P'^2}$	$S=0$
D_2	1	1	0		
D_1	0	0	0	$-3\tau \pm \sqrt{9\tau^2 + u^2 P'^2}$	$S=0$
D_2	0	0	0		

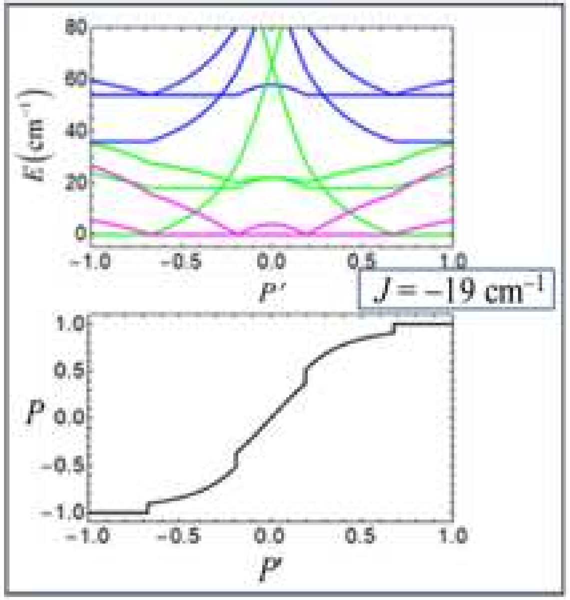
For states with $S=3$ and $S=1$ – strong linear Stark effects

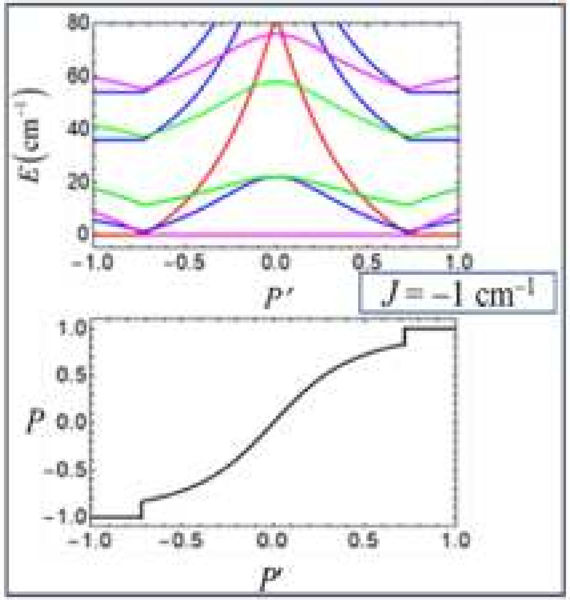
For states with $S = 0$ –weak non-linear Stark effects

Types of switching occurring at u =250 cm^{-1}, τ = 40 cm^{-1} and different J – values









Summary

- **Under some conditions the electrostatic field induced by the polarized driver-cell can induce the spin-switching between the different spin-states.**
- **Spin-switching results in the nonmonotonic behavior of cell-cell response functions due to the fact that different spin-states exhibit different polarizabilities with respect to the quadrupole field induced by the driver-cell;**
- **The performed study allows to considerably extend the class of systems suitable for QCA design and to supply the QCA-based devices with new useful functions, such as spin-switching.**

Acknowledgements

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Thank you

for your attention !