

The Circuit Paradigm in Modeling Coupled Nanomechanic-Nanoelectronic Dynamics

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Abstract — In this paper molecular arrays performing fast electronic switching combined with slow mechanical nuclear vibrations and switching are studied. Coherence is restricted to the internal dynamics of the molecules. Equivalent circuits for molecules performing optically induced electron- and proton transfer will be presented. The circuit paradigm is applied to study signal processors composed of arrays of molecules performing coupled nanomechanic and nano-electronic dynamics.

I. INTRODUCTION

Metal contacted molecules as nanoelectronic components have been proposed, and their voltage-current characteristics have been demonstrated. However, so far no viable technology for large-scale integration has been suggested. Coulomb-coupling of devices as an alternative approach for nanodevice integration has been proposed and demonstrated [1].

The intermolecular forces in a natural environment (e.g. forces between molecules in certain polymer chains) are Coulomb-forces between the dipole and quadrupole moments of the molecules.

In a recent paper [2] we have proposed equivalent circuits for arrays composed of Coulomb-coupled molecules. The internal electronic dynamics of the molecules are described by quantum Markovian master equations [3], describing the dynamics of the devices as irreversible evolution of an open quantum system coupled to a heat bath. The state of the nuclei is characterized by classical state variables such as position and momentum. The introduction of equivalent circuits has been based on mixed quantum-classical nonlinear dynamics. Equivalent circuit models for Coulomb-coupled arrays subject to a close-to-resonance external electromagnetic field have been introduced.

In this presentation we focus on the mixed quantum-classical dynamics of molecular arrays. We still assume that the molecules are far enough apart from each other that the overlap between their quantum-wave functions can be ignored, thus coherence is restricted to the internal dynamics. However, additional to the internal dynamics and electron transfer, studied earlier, we explore nuclear vibrations and switching as well. We study coupled 'nanomechanic' and 'nano-electronic' dynamics of Coulomb-

coupled molecules as potential devices and circuits performing signal processing.

We envisage an array of molecules subject to a sequence of electromagnetic pulses of well-defined frequency, shape of envelope, and length. The idea that this array, in principle, can do computing is not new. It has been suggested [4] to induce parallel logic in arrays of quantum dots through selective driving of resonances. A 'potentially realizable quantum computer' has also been proposed [5], [6] by subjecting an array of weakly coupled quantum systems to a sequence of pulses. We also studied an optically pumped computing architecture [7]. However, none of the former studies looked at the impact of the nuclear vibrations and switching on the behavior of molecular arrays performing signal processing.

II. EQUIVALENT CIRCUIT OF A TWO-STATE MOLECULE WITH ONE DIMENSIONAL VIBRATION

In this paper we assume that the molecules in the array can be considered to be two-electronic-state quantum systems with one degree of freedom of vibration. We also assume that the potential energy surfaces of the electronic states are given, as well as the parameters of the damping channels are known. We note that the generalization for more than two electronic states and for more than one mechanical degree of freedom is straightforward.

In case of a two-state molecule, $\{ | \phi_1 \rangle, | \phi_2 \rangle \}$, with one nuclear degree of freedom R , the Hamiltonian matrix \mathbf{H} of an isolated molecule depends on R as

$$\mathbf{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{bmatrix} = \begin{bmatrix} E_1(R) & G(R) \\ G(R) & E_2(R) \end{bmatrix}. \quad (1)$$

The mixed quantum-classical dynamics of each molecule can be described by a three dimensional quantum-coherence-vector, $\vec{\lambda}(t) = [\lambda_1(t), \lambda_2(t), \lambda_3(t)]$, representing the 2×2 density-matrix of the two electronic states, and by the distance between the two nuclei, $R(t)$, together with their momentum, $P(t)$. The Bloch equation describes the dynamics of the coherence vector

$$\gamma \frac{d\vec{\lambda}(t)}{dt} = \mathbf{\Omega} \cdot \vec{\lambda}(t), \quad (2)$$

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where \hbar is the Planck constant, and \mathbf{U} is the Bloch matrix

$$\mathbf{Q} = \begin{bmatrix} 0 & -H_{22} + H_{11} & -j(H_{12}^* - H_{12}) \\ H_{22} - H_{11} & 0 & -H_{12} - H_{12}^* \\ j(H_{12}^* - H_{12}) & H_{12} + H_{12}^* & 0 \end{bmatrix} \quad (3)$$

If the nuclear vibration has only one degree of freedom, for example as in the case of a diatomic molecule, the mechanics can be characterized by two classical dynamic equations

$$\begin{aligned} \frac{d}{dt}R(t) &= \frac{1}{M}P(t), \\ \frac{d}{dt}P(t) &= \left\langle \Psi \left| -\frac{\partial}{\partial R}(V_{nn} + V_{en}) \right| \Psi \right\rangle, \end{aligned} \quad (4)$$

where R and P are the position and momentum of the vibration, M is the vibrating mass, and V_{nn} , V_{en} are the nucleus-nucleus and electron-nucleus potential energies, respectively. They are determined by the potential energy surfaces (PES).

We assume that the far Coulomb-field of a molecule is characterized by $e\lambda_3(t)$ only. The nuclear position $R(t)$ has just an indirect effect. Thus only $(H_{22} - H_{11})$ depends on the state of the neighbors. The external electromagnetic field adds a time-varying term to $(H_{12} - H_{12}^*)$ according to the interaction between the electric field and the multipole moments of the molecule.

The internal electronic dynamics of the molecules, according to the quantum Markovian master equations, is an irreversible evolution of an open quantum system coupled to a heat bath. The simplest model of dissipation relies on three constants of relaxation, on the temperature T , on the electronic (τ), and on the nuclear relaxation (α). Parameters τ and α depend on the specific environment of the molecular array.

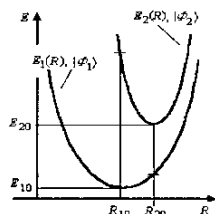


Figure 1 Potential energy surface (PES) of a two-atom molecule

Figure 1 shows the PES of a molecule with electronic states $|\Phi_1\rangle$ and $|\Phi_2\rangle$. In state $|\Phi_1\rangle$ the energy $E_1(R)$ is a function of the distance between the nuclei, and it is minimum at $R = R_{10}$. In electronic state $|\Phi_2\rangle$ the potential energy is minimum at $R = R_{20}$. Note, that in the excited electronic state, i.e. in state $|\Phi_2\rangle$, the nuclear vibration first relaxes to $R_{20} > R_{10}$.

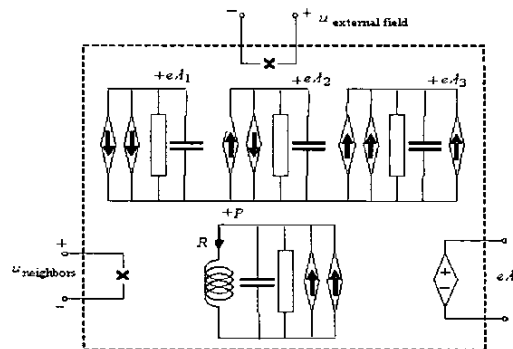


Figure 2 Equivalent circuit of a two-state molecule with one dimensional vibration excited by external electric pulses, and Coulomb-coupled to its neighbors

Figure 2 illustrates the equivalent circuit model of a molecule with two electronic states and a vibration with one degree of freedom. A two-atom molecule with a ground and an excited electronic states, is the simplest example, however, dynamics of larger systems of atoms, switching between two quantum states and vibrating in one dimension, can also be approximated with this model.

The dynamics of the electronic state is characterized by the time-varying charges of three capacitors, charges $e\lambda_1(t)$, $e\lambda_2(t)$, $e\lambda_3(t)$, and the nuclear vibration follows the dynamics of the resonant circuit, in which the capacitor voltage is $P(t)$, and the inductor current is $R(t)$. The electronic and nuclear dynamics are coupled to each other and to the Coulomb field of the neighbors. All couplings are modeled by controlled sources. The molecular array is pumped by an external electromagnetic field. In the equivalent circuit it is represented by a generator, $u_{\text{external field}}(t)$, coupled to the circuit by proper controlled sources. The dissipation caused by the environment is represented with four resistors. Note, that the nonlinear equivalent circuit of the molecule is passive.

III. SELECTIVE SWITCHING BY CHIRPS

If a molecule is in its ground state and the nuclear vibration is negligible, i. e. $R \approx R_{10}$, then a pulse of frequency close-to-resonance

$$\omega_1 = \frac{E_2(R_{10}) - E_{10}}{\hbar} \quad (5)$$

will switch the molecule into its excited state. However, in the excited electronic state the nuclei will be far from R_{20} , thus a vibration will start, which relaxes to $R \approx R_{20}$. Note that during this relaxation the energy difference between the two states has changed significantly, i. e.

$$\omega_2 = \frac{E_{20} - E_1(R_{20})}{\hbar} \neq \omega_1, \quad (6)$$

thus a chirp with frequency ω_1 does not switch the molecule back to its ground state. We need to change the frequency to ω_2 in order to switch the molecule back. Figure

3 illustrates the selectivity of a H₂ molecule, as a switch. We applied a ω_2 -chirp at $t = 500$ fsec. The molecule did not switch. On the other hand, a ω_1 -chirp at $t = 1000$ fsec did switch the molecule from state 1 to state 2. The ω_2 -chirp applied at $t = 2000$ fsec switched the molecule back to state 1.

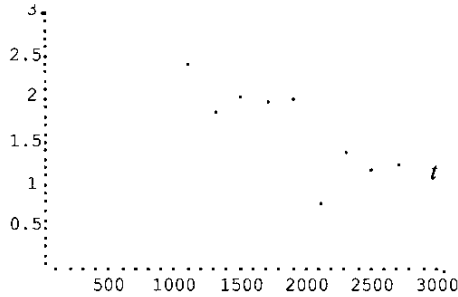


Figure 3 $R(t)$ of a H₂ molecule switched from ground state to excited state by ω_1 -chirp and back by ω_2 -chirp (R in atomic units, t in fsec)

The Coulomb fields of the neighboring molecules perturb the energy differences between the ground and excited states, thus it changes the frequency needed to switch the molecule. The Coulomb field depends not only on the distances but on the state of the neighbors as well. We have studied the effects of the frequency, shape of the envelope, and the length of the chirp on switching. Simulations indicate that in polymer-like molecular chains switching of a molecule can be induced selectively depending on the state of its neighbors. Different frequencies are needed to switch a molecule if (i) both neighbors are in ground states, (ii) one neighbor is in excited state, one is in ground state, and (iii) both neighbors are in their excited states.

Our simulations suggested that chirp-controlled quantum-classical dynamics of molecular arrays can be approximated by simple circuit models. Circuit simulations of examples such as active control of molecular dynamics [9], and proton-transfer-switches [10], [11] are very promising.

We have applied the circuit models to explore potential architectures for signal processing.

III. SIGNAL PROCESSING IN MOLECULAR ARRAYS

We envisage a one-dimensional molecular chain composed of two-state molecules. The transition between states involves both electronic and mechanic transitions:

$$\text{State 1: } |\Phi_1\rangle, R_{10} \quad \text{State 2: } |\Phi_2\rangle, R_{20} \quad (7)$$

In a chain of molecules the switching frequencies at the end of the chain are different from those at the internal sites of the chain, because at the end there is only one neighbor. Molecules at the boundary have *four chirp frequencies* depending on the state of their neighbors and on their own state. A molecule at an internal site of the chain has two neighbors, thus it has *six chirp frequencies* depending on its own state and on the Coulomb-effect of its

neighbors. Let us refer to the state of the neighbors by an upper and to the state of the molecule by a lower index. The boundary molecule's four chirp-frequencies are ω_1^0 , ω_1^1 , ω_2^0 , and ω_2^1 . The six chirp frequencies of a molecule at an internal site of the chain are ω_1^{00} , ω_2^{00} , $\omega_1^{01} = \omega_1^{10}$, $\omega_2^{01} = \omega_2^{10}$, ω_1^{11} , ω_2^{11} .

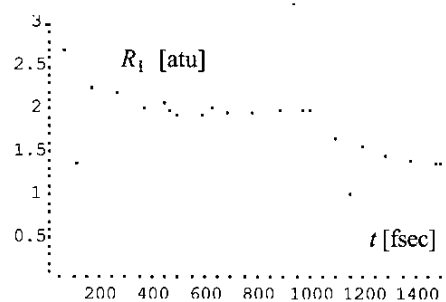
The molecular chain is programmed by a sequence of chirps of specific frequency. At the beginning of the signal processing the chain is always in its ground state (0,0,0, ...). First, the initial data are loaded by a sequence of chirps. The algorithm of the signal processing is performed by the next sequence of chirps. A simple example is the loading of a bit onto the second molecule of a chain. The loading is performed by a sequence of chirps with frequencies ω_1^0 , ω_1^{01} , ω_2^1 . Note, that this sequence transforms the initial ground state as (0,0,0, ...) \rightarrow (1,0,0,...) \rightarrow (1,1,0,...) \rightarrow (0,1,0,...). Figure 4 shows the distance between the nuclei of the first (R_1) and the second (R_2) molecule of a long chain when an ω_1^0 -chirp is flashed at $t=0$, ω_1^{01} -chirp at $t=500$ fsec, and ω_2^1 -chirp at $t=1000$ fsec on the molecular chain. Indeed, after the sequence of three pulses the state of the chain is (0,1,0,...).

It can be shown that by a sequence of chirps any given binary string can be loaded onto the chain.

A chain composed of a single type of molecule can not realize a universal machine. However, a chain formed from three different types of molecules, such as *ABC ABC ABC...*, can realize a universal 'replacement' computer, [12], if selective addressing of *A*, *B* and *C* can be insured [6].

It has been shown that two-dimensional cellular arrays have a unique computing potential [13], and in case of binary processing it has been explored using digital computers [14].

The dynamics in molecular chains and arrays is not binary. Fast switching between electronic eigenstates is combined with nuclear vibration and switching. In the arrays nonlinear waves are flowing, patterns are emerging. Cellular nonlinear networks (CNN) has been proposed and demonstrated as models of spatial-temporal dynamics [15].



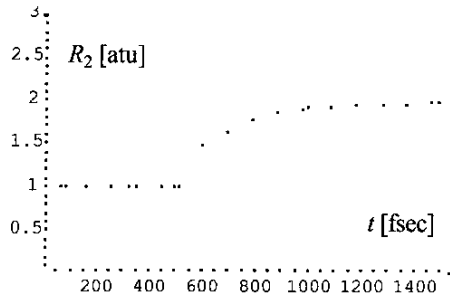


Figure 4 Nuclear switching of the first and second molecule in a chain programmed by a sequence of three chirps

Therefore, we are examining not only binary processing on polymer-like chains and arrays of molecules, but wave-like propagation and interference phenomena as well. Our preliminary simulations so far suggest that molecular arrays composed of molecules with two quantum states and a one-dimensional mechanical vibration and switching appear to be excellent candidates for digital-analog signal processors, i. e. for machines on flows [16].

V. SUMMARY

In this paper, we reviewed our approach for the simulation of the interacting electronic and nuclear dynamics of Coulomb-coupled molecules subject to external electromagnetic pumping. The state of the nuclei has been characterized by classical state variables such as position and momentum, and the internal electronic dynamics of the molecules by quantum Markovian master equations of finite-state systems. Coherence is restricted to the internal dynamics of the molecules, which can result in internal electron and proton transfers.

The quantum-classical nanoelectronic and nanomechanical dynamics have been approximated as the dynamics of coupled nonlinear analog circuits.

Fast electronic switching, combined with slow mechanical nuclear vibrations, induced by pulses (chirps) have been analyzed, and strong selectivity with respect to switching on/off, and also with respect to the state of the neighbors (state 1 or 2) has been observed.

A 'Gedanken experiment' has been performed with a chain of polymer-like molecules. Simulations verified the realizability of a universal replacement computer.

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REFERENCES

[1] W. Porod, C. S. Lent, G. H. Bernstein, I. Amlani, G. I. Snider, J. L. Merz, Quantum-dot cellular

automata computing with coupled quantum dots, *Int. J. Electronics*, 1999, 86(5): 549 – 590.

[2] A. I. Csurgay, W. Porod, Equivalent circuit representation of arrays composed of Coulomb-coupled nanoscale devices, *Int. J. Circ. Theor. Appl.* 2001; 29: 3 – 35.

[3] G. Mahler, V. Weberuss, *Quantum Networks*, Springer, Berlin, 1995.

[4] H. Körner, G. Mahler, Optically driven quantum networks: Applications in molecular electronics, *Phys. Rev. B*: (1993) 48 (4) , 2335 – 2346

[5] A. I. Csurgay, W. Porod, Equivalent circuit representation of arrays composed of Coulomb-coupled nanoscale devices, *Int. J. Circ. Theor. Appl.* 2001; 29: 3 – 35.

[6] S. Lloyd, A Potentially Realizable Quantum Computer, *Science*, (1993) 261, 1569 – 1571

[7] S. Lloyd, Programming Pulse Driven Quantum Computers, *arXiv:quant-ph/9912086*, 17 Dec 1999

[8] Gy. Csaba, A. I. Csurgay, W. Porod, Computing architecture composed of next-neighbor-coupled optically pumped nanodevices, , *Int. J. Circ. Theor. Appl.* 2001; 29: 73 – 91

[9] J. Gordon, S. A. Rice, Active control of the dynamics of atoms and molecules, *Annual Review of Physical Chemistry*, 1997; 48: 601 – 641.

[10] R. Meyer, R.R. Ernst, Transitions induced in a double minimum system by interaction with a quantum mechanical heat bath, *J. Chem. Phys.* 1990, 93 (8), 5518 – 5532

[11] R. Meyer, R. R. Ernst, Hydrogen transfer in double minimum potential: Kinetic properties from quantum dynamics, *J. Chem. Phys.* (1987) 86 (2), 784 – 801

[12] R. P. Feynman, *Feynman Lectures on Computation*, Addison Wesley, Reading, 1996

[13] K. Zuse, *Rechnender Raum, Schriften zur Datenverarbeitung*, Vol.1, Freidr.Vieweg & Sohn, Braunschweig, 1969

[14] S. Wolfram, *A new kind of science*, Wolfram Media Inc., Champaign, 2002

[15] L. O. Chua, *CNN: A Paradigm for Complexity*, World Scientific, Singapore, 1998

[16] T. Roska, Computational and Computer Complexity of Analogic Cellular Wave Computers, *Proc. IEEE-CNNA-2002*, Frankfurt, July, 2002