

Equivalent circuit representation of arrays composed of Coulomb-coupled nanoscale devices: modelling, simulation and realizability

Árpád Csurgay^{1,‡} and Wolfgang Porod^{2,*,†}

¹*Department of Electromagnetic Theory, Budapest University of Technology and Economics, Egrý József utca
18, Budapest H-1111, Hungary*

²*Center for Nano Science and Technology, University of Notre Dame, 275 Fitzpatrick Hall, Notre Dame,
Indiana 46556-5637, U.S.A.*

SUMMARY

Technology and physics of discrete nanoscale electronic components are reasonably well understood, but there exists a gap between device physics and nanoelectronic circuit integration. In this paper, we propose a modelling and simulation technique for integrated circuits composed of Coulomb-coupled nanodevices and subcircuits of metal-contacted devices. We assume that the Coulomb-coupled devices are far enough apart from each other that the overlap between their wave functions can be ignored. The internal electronic dynamics of the devices are described by quantum Markovian master equations, describing the dynamics of the devices as irreversible evolution of an open quantum system coupled to reservoirs. The electronic state of the devices are characterized by a finite-dimensional time-varying real vector. The state of the nuclei is characterized by classical state variables such as position and momenta. The Coulomb field generated by the device is described by the expectation value of the charge density approximated as multipole moments. Device–device couplings are determined by multipole interactions. In this way, the integrated circuit dynamics can be described by a set of coupled nonlinear differential equations. This set of mixed quantum-classical state equations leads us to the introduction of equivalent circuits. We conclude that integrated circuits composed of Coulomb-coupled and metal-contacted nanodevices do have circuit representations, thus circuit theory can be applied to build device models, to simulate and to design nanoelectronic integrated circuits. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS: nanotechnology; nanoelectronics; molecular dynamics; device modelling; circuit simulation

*Correspondence to: Wolfgang Porod, Center for Nano Science and Technology, University of Notre Dame, 275 Fitzpatrick Hall, Notre Dame, Indiana 46556-5637, U.S.A.

†E-mail: Porod@nd.edu

‡Currently at University of Notre Dame, on leave from Budapest University of Technology and Economics.

Contract/grant sponsor: NSF (National Science Foundation); INT96-15497

Contract/grant sponsor: HAS (Hungarian Academy of Science)

Contract/grant sponsor: Office of Naval Research MURI program

Received 27 April 2000

Revised 10 July 2000

1. INTRODUCTION

Nanoelectronics faces three major challenges: (1) new device behaviour due to the emergence of quantum phenomena; (2) device interconnection on the nanoscale needs new approaches; (3) as device size shrinks the increasing power dissipation becomes intolerable. Nanoelectronic discrete devices and simple circuits, such as wires, switches and logic gates, based on quantum phenomena have been demonstrated [1–3]. However, there has been no viable large-scale integration technique proposed.

Three ways of device interconnection have been suggested so far. Metal-contacted devices in the meso-scale range (10–100 nm), such as nanotransistors, resonant tunnelling devices, RTDs and single-electron transistors, SETs, can be interconnected with wires. As long as each device has metal contacts, i.e. they are all embedded into ‘heat baths’, then conventional interconnection with wires is possible. Circuit models of devices together with their interconnections have been developed. In this case circuit dynamics following the conservation laws of charge and energy obeys Kirchhoff’s laws [4,5]. Devices not metal contacted, e.g. quantum-dot arrays and molecules can be coupled by inter-device electron transport. However, in case of wiring and inter-device electron transport the current flow generates unavoidable dissipation. An alternative approach of device integration is electromagnetic field interaction between the devices, such as coupling by Coulomb- or magnetic forces. This approach can bring devices closer to each other and significantly decrease dissipation [6–9].

In this paper, we investigate integrated circuits composed of nanodevices coupled to each other by electrostatic forces. We shall assume that these Coulomb-coupled devices are far enough apart from each other that the overlap between their quantum-wave functions can be ignored. Relatively weak forces govern the interactions between devices thus their effects will be described using perturbation theory. In the unperturbed system there are no interactions between the devices, and the state functions are simple products of single-device state functions. The perturbation consists of the electrostatic interaction between the devices and that of the external electromagnetic forces.

The internal electronic dynamics of the devices is described by quantum Markovian master equations of finite-state systems [10–12]. This model describes the dynamics of a device as irreversible evolution of an open quantum system coupled to a reservoir (heat bath). The electronic state is characterized by a finite-dimensional time-varying vector: the coherence vector. The state of the nuclei is characterized by classical state variables such as position and momentum. The Coulomb-field generated by a device is described by the expectation value of the charge density approximated as multipole (monopole, dipole and quadrupole) moments. Device–device couplings are determined by multipole interactions, which result in perturbations of the isolated device dynamics. The coherence vector describes the electronic dynamics, the classical mechanical variables describe the vibrations of nuclei. We show that the integrated circuit dynamics can be described by a set of mixed quantum-classical state equations forming a set of coupled non-linear differential equations. This set of equations leads us to the introduction of ‘charges’ and ‘voltages’ obeying Kirchhoff’s equations, thus standard simulation methods of electronic circuits, such as e.g. SPICE, can be applied to simulate circuits composed of Coulomb-coupled nanodevices.

If both Coulomb-coupled and metal-contacted nanodevices are applied in the same circuit, the physical interface between a Coulomb-coupled and a metal-contacted nanodevice can be represented as a classical electromagnetic circuit. The boundary conditions on the side of the

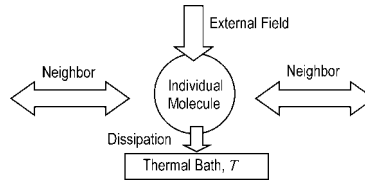


Figure 1. A nanodevice (molecule) coupled to its neighbours and excited by external field.

metal-contacted device are defined by the metal contacts, on the side of the Coulomb-coupled device by the electric field of its dipoles and quadrupoles. A classical circuit model of the interfaces can be designed using classical electromagnetic techniques [13,14].

In this paper we conclude that integrated circuits composed of Coulomb-coupled and metal-contacted nanodevices do have equivalent circuit representation, thus circuit theory can be applied to build device models, to simulate and to aid the design of nanoelectronic integrated circuits.

2. PHYSICAL APPROXIMATIONS IN DEVICE AND CIRCUIT MODELLING

Coulomb coupling between device structures has been found to be significant for both natural and artificial molecules (quantum dots). Stable molecules are formed by the mutual interaction of point-like nuclei and electrons. Artificial molecules are composed of solid-state quantum dots close to each other thus electrons can tunnel from one dot into the other. There is a third class of nanodevices composed of nanoscale metal dots separated by insulators such that electrons can tunnel between the metal. Wave-like behaviour of the electrons together with the fact that an electron's charge cannot be divided play dominant role in the internal dynamics of nanodevices.

In Appendix A, a concise characterization of molecules is presented [11,12,15] as 'prototypes' of nanodevices having electronic and mechanic (nuclear or phonic) degrees of freedom. Exact modelling of the quantum-dynamics of an array of coupled molecules is a formidable task. However, reasonable assumptions can lead us to models good enough for circuit design. In this paper (1) we approximate the model of an individual isolated molecule; (2) we develop models for structures with weak coupling between nanodevice neighbours; (3) we approximate the behaviour of the thermal bath and damping channels, and (4) we introduce models for the external forces as well (Figure 1).

1. We assume that an individual isolated molecule (or nanodevice) can have only a finite number of stationary electronic quantum states, $|\Phi_1\rangle, |\Phi_2\rangle, \dots, |\Phi_N\rangle$, and the evolution of its state in time can be characterized by a wave function. A isolated device is always in a pure electronic quantum state

$$|\Psi\rangle = c_1 |\Phi_1\rangle + c_2 |\Phi_2\rangle + \dots + c_N |\Phi_N\rangle \quad (1)$$

The probability amplitudes c_1, c_2, \dots, c_N form a complete set. The probability of finding a device in state $|\Phi_1\rangle$ is $|c_1|^2$, in state $|\Phi_2\rangle$ is $|c_2|^2$, and finding in state $|\Phi_N\rangle$ is $|c_N|^2$. The stationary states are orthogonal to each other

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij} \quad (2)$$

We also assume that the nuclear co-ordinate dependence of the isolated molecule's electronic stationary states, eigenenergies and eigenfunctions, are known in accordance with the Born–Oppenheimer approximation. We rely on the studies and results of quantum chemistry [9–12,15,16].

2. We assume that the devices in the array 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 of devices. In the unperturbed system there are no interactions between the devices, and the state functions are simple products of single-device state functions. Relatively weak forces govern the interactions between devices and magnetic forces can be ignored, thus Coulombic interactions dominate.

3. We assume that the molecular array is interacting with damping channels. One of them is a thermal bath in equilibrium with temperature T , another is a macroscopic measuring device providing continuous monitoring of the array's output. Since the damping channels do not participate in an active manner in the nanocircuit dynamics we do not aim at their detailed description. We are interested only in the device dynamics and the results of measurement. Since the array and the damping channels are coupled, it is impossible to introduce a wave function of the array or the damping channels alone. The array is not a closed quantum system any more, but it is now an open quantum system. There only exists a total wave function $\Psi(s,z)$ depending not only on the array's co-ordinate s , but also on the huge number of environment coordinate, z , as well. By reducing our attention on the array only, we must face the fact that the array does not possess a wave function as its state description any more. Nevertheless, the expectation value of any observable described by operator $\mathbf{A}(s)$ acting in the s -space of the relevant array only reads as

$$\langle A \rangle = \int \Psi^*(s,z) \mathbf{A}(s) \Psi(s,z) dz ds \quad (3)$$

If we introduce the density operator as

$$\rho(s,s') = \int \Psi^*(s,z) \Psi(s',z) dz \quad (4)$$

we can rewrite Equation (3) as

$$\langle A \rangle = \int [\mathbf{A}(s') \rho(s,s')]_{s=s'} ds \quad (5)$$

Note that the averaging with respect to the large number of reservoir co-ordinates has been absorbed in $\rho(s,s')$, called reduced density operator. It offers a systematic way to describe the dynamics of the reduced open quantum system embedded in a thermal environment.

If there are no damping channels coupled to a quantum system, i.e. it possesses a wave function (pure state), the density operator reads as

$$\rho(s,s') = |\Psi(s)\rangle \langle \Psi(s')| \quad (6)$$

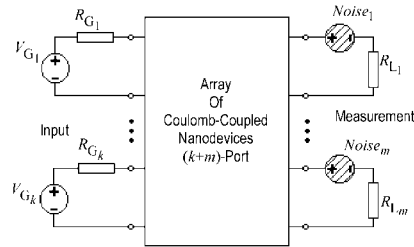


Figure 2. Boundary conditions of an array composed of Coulomb-coupled nanodevices are set by the input voltages and the ‘noisy’ measurement at the output.

In the representation (1) the density matrix is

$$\rho = |\Psi\rangle\langle\Psi| = \begin{bmatrix} c_1^* \\ c_2^* \\ \vdots \\ c_N^* \end{bmatrix} [c_1, c_2, \dots, c_N] = \begin{bmatrix} |c_1|^2 & c_1^* c_2 & \dots & c_1^* c_N \\ c_2^* c_1 & |c_2|^2 & \dots & c_2^* c_N \\ \vdots & \vdots & \ddots & \vdots \\ c_N^* c_1 & \dots & \dots & |c_N|^2 \end{bmatrix} \quad (7)$$

The density matrix is Hermitean, its trace is 1, it is equal to its square $\rho = \rho^2$, and its determinant is zero. The matrix of the density operator (4) of a mixed state is also Hermitean, its trace is also 1, but in mixed states its determinant is not zero and it is not equal to its square.

4. We make three assumptions in modelling the contributions of the applied external electric fields to the dynamics of the array of nanodevices. First we assume that the external fields act only on the devices and their effect on the thermal reservoir can be neglected. Second we assume that the external field is unaffected by the nanodevice and it may be treated classically. Third we assume that each nanodevice feels a spatially homogeneous external field, i.e. a molecule is not effected by the spatial variations of the field. Note that this is not true for the fields generated by the neighbours, because it is inherently inhomogeneous for its next neighbour.

Indeed, in most magnetic and optical resonance experiments the wavelength of the external field is two orders of magnitude longer than the size of a nanodevice, and the external fields act only on the relevant system but their effect on the reservoir can be neglected. Thus only the Hamilton operator of the nanodevice is perturbed by the external field.

The input–output operator of an electronic circuit relates the measurement of the output variables, i.e. the expectation values at the output, to the input variables which are set as boundary conditions to the array (Figure 2). The dynamics of the array’s density matrix uniquely determines the expectation values of the output. In this sense density matrices can characterize the internal electronic quantum state of molecules, or in general the electronic state of nanodevices. However, attention should be paid to the probabilistic nature of the density matrix, and also to the fact that its elements are complex numbers and they are not independent of each other (Hermitean matrix with trace 1).

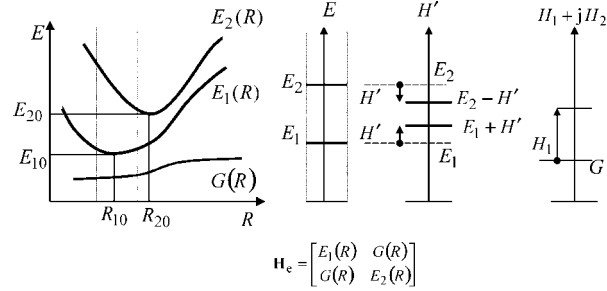


Figure 3. Potential energy surfaces (PES) of a molecule with two electronic states and one degree of freedom of nuclear vibration.

3. A CASE STUDY: NANODEVICE WITH TWO ELECTRONIC STATES AND ONE VIBRATIONAL DEGREE OF FREEDOM

3.1. Dynamics of an individual isolated molecule

In case of a two-state molecule, $|\Phi_1\rangle, |\Phi_2\rangle$, with one nuclear degree of freedom R , the pure state Hamiltonian matrix \mathbf{H} of an isolated molecule depends on R as shown in Figure 3.

$$\mathbf{H} = \begin{bmatrix} H_{11} & H_{12} \\ H_{12}^* & H_{22} \end{bmatrix} = \begin{bmatrix} E_1(R) & G(R) \\ G(R) & E_2(R) \end{bmatrix} \quad (8)$$

In this case the nanodevice is an isolated quantum system, its dynamics can be described by the time-dependent Schrödinger equation for the wave function

$$j\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \mathbf{H} |\Psi(t)\rangle \quad (9)$$

$$|\Psi\rangle = c_1(t) |\Phi_1\rangle + c_2(t) |\Phi_2\rangle \quad (10)$$

The density matrix is

$$\rho = |\Psi\rangle \langle \Psi| = \begin{bmatrix} c_1^* \\ c_2^* \end{bmatrix} [c_1, c_2] = \begin{bmatrix} |c_1|^2 & c_1^* c_2 \\ c_2^* c_1 & |c_2|^2 \end{bmatrix} \quad (11)$$

The time evolution of $\rho(t)$ can be derived from the definition (12)

$$\frac{\partial \rho}{\partial t} = \frac{\partial |\Psi\rangle}{\partial t} \langle \Psi| + |\Psi\rangle \frac{\partial \langle \Psi|}{\partial t} \quad (12)$$

Substituting Equation (10) into Equation (12) we get the Liouville–von Neumann equation

$$\frac{\partial}{\partial t} \rho(t) = -\frac{j}{\hbar} (\mathbf{H} \rho(t) - \rho(t) \mathbf{H}) \quad (13)$$

In a two-dimensional Hilbert space the number of independent real variables representing a Hermitean matrix is $n^2 = 4$, because between the $2n^2$ real numbers there are n^2 relations. If the trace of the matrix is 1, this is an additional relation, thus the number of independent

real variables is $s = n^2 - 1 = 3$. The density matrix depends on time, and its time dependence can be represented by $s = 3$ real-valued time functions $\lambda_1(t), \lambda_2(t), \lambda_3(t)$.

In Appendix B we introduce the two- and three-dimensional unitary groups SU(2) and SU(3) giving a technique to express any 2×2 Hermitean time-varying matrix, $\mathbf{A}(t)$, with three real time-varying functions as

$$\mathbf{A}(t) = \frac{1}{2} \text{Tr}\{\mathbf{A}(t)\} \mathbf{1} + \frac{1}{2} (\lambda_1(t) \mathbf{T}_1 + \lambda_2(t) \mathbf{T}_2 + \lambda_3(t) \mathbf{T}_3) \quad (14)$$

The trace of the density matrix is equal to $\mathbf{1}$, thus

$$\rho(t) = \frac{1}{2} \begin{bmatrix} 1 - \lambda_3(t) & \lambda_1(t) + j\lambda_2(t) \\ \lambda_1(t) - j\lambda_2(t) & 1 + \lambda_3(t) \end{bmatrix} \quad (15)$$

Substituting the density and Hamiltonian matrices into the Liouville–von Neumann equation, and expressing the time derivative of the coherence vector we get the Bloch equation describing the dynamics of the coherence vector

$$\hbar \frac{d\boldsymbol{\lambda}(t)}{dt} = \boldsymbol{\Omega} \cdot \boldsymbol{\lambda}(t) \quad (16)$$

where

$$\boldsymbol{\Omega} = \begin{bmatrix} 0 & -H_{22} + H_{11} & -j(H_{12}^* - H_{12}) \\ H_{22} - H_{11} & 0 & -H_{12} - H_{12}^* \\ j(H_{12}^* - H_{12}) & H_{12} + H_{12}^* & 0 \end{bmatrix} = \begin{bmatrix} 0 & -\omega_0 & -\omega_2 \\ \omega_0 & 0 & -\omega_1 \\ \omega_2 & \omega_1 & 0 \end{bmatrix} \quad (17)$$

Note that in a pure state the determinant of the density matrix is zero, thus $\lambda_1^2 + \lambda_2^2 + \lambda_3^2 = 1$, i.e. the coherence vector's length is one, and $(\boldsymbol{\Omega} \cdot \boldsymbol{\lambda}(t)) \cdot \boldsymbol{\lambda}(t) \equiv 0$, thus the length of the coherence vector does not change in time. This means that as long as the Hamilton matrix is Hermitean the dynamics remain in pure state and in a three-dimensional space the coherence vector points to the surface of a unit sphere.

The nuclear vibrations according to Equation (8) change the Hamiltonian in time, nevertheless, its Hermitean character remains untouched. If the nuclear vibration has only one degree of freedom (an example is a diatomic molecule) it can be characterized by two classical dynamic equations

$$\begin{aligned} \frac{d}{dt} R(t) &= \frac{1}{M} P(t) \\ \frac{d}{dt} P(t) &= \left\langle \Psi \left| -\frac{\partial}{\partial R} (\mathbf{V}_{\text{nn}} + \mathbf{V}_{\text{en}}) \right| \Psi \right\rangle = -\frac{\partial}{\partial R} \mathbf{V}_{\text{nn}} + \left\langle \Psi \left| -\frac{\partial}{\partial R} \mathbf{V}_{\text{en}} \right| \Psi \right\rangle \end{aligned} \quad (18)$$

where R and P are the position and momentum of the vibration, M is the vibrating mass, and $\mathbf{V}_{\text{nn}}, \mathbf{V}_{\text{en}}$ are the nucleus–nucleus and electron–nucleus potential energies, respectively. They are determined by the potential energy surfaces (PES) introduced in Appendix A. Figure 3 shows the PES for one mechanical degree of freedom. The expectation values in Equation (18) depend on the density operator, thus on the coherence vector. The Hamilton operator in Equation (18) depend on R . Thus the Bloch equation (16) together with the classical dynamical

equations (8) describe the pure-state dynamics of a stand-alone molecule. In case of a two state stand-alone molecule the coupled quantum-classical state equations are as follows:

$$\begin{aligned}\hbar \frac{d\lambda(t)}{dt} &= \Omega \cdot \lambda(t) \\ \frac{d}{dt}R(t) &= \frac{1}{M}P(t) \\ \frac{d}{dt}P(t) &= \frac{1}{2}(1 - \lambda_3)\frac{\partial E_1(R)}{\partial R} + \frac{1}{2}(1 + \lambda_3)\frac{\partial E_2(R)}{\partial R}\end{aligned}\tag{19}$$

Later on we shall show that the perturbations caused by the neighbours and the external electric field does not change the Hermitean character of the Hamilton operator, they just change the values of $\omega_0, \omega_1, \omega_2$ in Equation (17). The perturbation of the neighbouring molecules and that of the external electrical fields do not change the pure character of a molecule's state. The molecule's state changes in time, but at any instant it can be characterized by a wave function being a linear combination of the two stationary states according to Equation (10).

We have been relying upon the Born–Oppenheimer approximation separating the electronic and nuclear dynamics into a fast electronic transition between stationary states and an adiabatic vibration along the potential energy surfaces. Let us assume that initially the molecule is in its ground state, i.e. its electronic state is $|\Phi_1\rangle$, nuclear position is $R=R_{10}$ and no vibration takes place. An example of the electronic transition from the ground state of the molecule to a particular excited state is the absorption of light energy. Let the ground state and the excited state be characterized by their potential energy surfaces. In case of a simple diatomic molecule PES is a single-variable function having a single minimum. The minimum of an excited state belongs to a higher distance between the atoms, since electronic excitation results in a weakening of the molecular bond. The electronic transition can be considered to take place on a time scale fast compared to the relative motion of nuclei. Thus after a transition from $|\Phi_1\rangle$ to $|\Phi_2\rangle$ the nuclear position remains close to R_{10} thus the nuclear position is far from minimum on the potential energy surface of $|\Phi_2\rangle$, therefore vibration is generated.

3.2. Molecule in dissipative environment

Our model assumed so far that there is no environment around the molecule, thus this model describes a ‘lossless’ quantum-classical system without any relaxation or dissipation. Pure quantum-state dynamics of the electrons is coupled to lossless classical vibrations of the nuclei.

The isolated molecule represents a ‘closed’ quantum system, thus it can be described by a conservative reversible model described by Equation (19). The real nanodevice is always subject to the effect of its environment. It interacts locally with its own thermal bath, and the interaction of the molecular array with the macroscopic instruments setting the inputs and performing measurements should be taken into account as well. The state variables λ, R , and P cannot represent the wave function of the molecule any more, they describe the system only in the depth of the density matrix as an ‘open’ quantum system subject to the irreversible effect of the damping channels.

It has been shown [10–12] that the state at time t of any 2-level open quantum system can be described by a Hermitean (2×2) matrix $\rho(t)$. The time evolution from an initial state $\rho(0)$ is described by a completely positive semigroup preserving hermiticity, trace and positivity of $\rho(t)$ for $0 \leq t < \infty$. The master equation describing the evolution is a generalization of the reversible state equation (19). For quantum Markovian dynamics the general mathematical form of the Bloch equation has been given as

$$\begin{aligned} \hbar \frac{d\lambda(t)}{dt} &= \Omega\lambda(t) + \mathbf{R}\lambda(t) + \mathbf{k} \\ \frac{d}{dt}R(t) &= \frac{1}{M}P(t) \\ \frac{d}{dt}P(t) &= -\frac{1}{2}(1 - \lambda_3)\frac{\partial E_1(R)}{\partial R} - \frac{1}{2}(1 + \lambda_3)\frac{\partial E_2(R)}{\partial R} - \alpha \cdot P \end{aligned} \quad (20)$$

where Ω is the Bloch matrix of the conservative system, \mathbf{R} and \mathbf{k} are the damping matrix and damping vector, respectively, and α characterizes the nuclear relaxation. The value of α is zero or positive, the damping matrix and vector have been studied and determined for various damping channels [10,11]. Their general forms are

$$\mathbf{R} = \begin{pmatrix} -\gamma_1 & \alpha & \beta \\ \alpha & -\gamma_2 & \delta \\ \beta & \delta & -\gamma_3 \end{pmatrix}, \quad \mathbf{k} = \begin{pmatrix} k_1 \\ k_2 \\ k_3 \end{pmatrix} \quad (21)$$

with the constraint that the matrix \mathbf{A} composed of the elements of \mathbf{R} and \mathbf{k}

$$\mathbf{A} = \begin{pmatrix} \frac{1}{2}(\gamma_1 + \gamma_2 - \gamma_3) & \alpha + jk_3 & \beta + jk_2 \\ \alpha - jk_3 & \frac{1}{2}(\gamma_1 - \gamma_2 + \gamma_3) & \delta + jk_1 \\ \beta - jk_2 & \delta - jk_1 & \frac{1}{2}(-\gamma_1 + \gamma_2 + \gamma_3) \end{pmatrix} \quad (22)$$

should be positive semidefinite. This imposes a set of inequalities that the damping parameters should satisfy. In case of a two-level system with a single local damping channel between the two states $|\Phi_1\rangle \Leftrightarrow |\Phi_2\rangle$ with probabilities w_{12} from state 1 to 2 and w_{21} from 2 to 1 the damping matrix is diagonal with $\gamma_1 = \gamma_2 = \hbar/2(w_{12} + w_{21})$, $\gamma_3 = \hbar(w_{12} + w_{21})$ and $k_3 = \hbar(w_{21} - w_{12})$. The simplest model of the transition rates depend only on the temperature T of the environment, on the energy difference between the two states $\Delta E = E_2 - E_1$, and on a parameter τ_0 determining the time scale of the transitions

$$w_{12} = \frac{1}{2\tau_0} \left[1 + \tanh\left(\frac{E_2 - E_1}{k_B T}\right) \right], \quad w_{21} = \frac{1}{2\tau_0} \left[1 - \tanh\left(\frac{E_2 - E_1}{k_B T}\right) \right] \quad (23)$$

Thus

$$\gamma_1 = \gamma_2 = \frac{\hbar}{2\tau_0}, \quad \gamma_3 = \frac{\hbar}{\tau_0}, \quad k_3 = \frac{\hbar}{\tau_0} \tanh\left(\frac{E_2 - E_1}{k_B T}\right) \quad (24)$$

If we assume that the potential energy surfaces in Figure 3 can be approximated by parabolic functions as

$$E_1 = E_{10} + E_{11}(R - R_{10})^2 \quad \text{and} \quad E_2 = E_{20} + E_{11}(R - R_{20})^2 \quad (25)$$

then the dynamics of a molecule in its environment can be described by a set of ordinary non-linear differential equations

$$\begin{pmatrix} \frac{d\lambda_1}{dt} \\ \frac{d\lambda_2}{dt} \\ \frac{d\lambda_3}{dt} \end{pmatrix} = \left[\frac{1}{\hbar} \begin{pmatrix} 0 & -\omega_0 & -\omega_2 \\ \omega_0 & 0 & -\omega_1 \\ \omega_2 & \omega_1 & 0 \end{pmatrix} - \frac{1}{2\tau_0} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \right] \begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \end{pmatrix} + \frac{1}{\hbar} \begin{pmatrix} 0 \\ 0 \\ \frac{\hbar}{\tau_0} \tanh \frac{E_2 - E_1}{k_B T} \end{pmatrix} \quad (26)$$

$$\frac{dR}{dt} = \frac{1}{M} P$$

$$\frac{dP}{dt} = -2E_{11}R + E_{11}(R_{20} + R_{10}) + \lambda_3 E_{11}(R_{20} - R_{10}) - \alpha \cdot P$$

This set of mixed quantum-classical equations describes the time evolution of the molecule. The coherence vector determines the electronic evolution in the depth of the density matrix, thus the expectation values of measurements are determined by it. The nuclear vibration and relaxation are coupled to the electronic dynamics through λ_3 . Notice that the molecular state equations resemble circuit dynamics. Equation (28) could be the state equation of a non-linear circuit with state variables $\lambda_1, \lambda_2, \lambda_3, R$ and P . We are going to explore this analogy.

3.3. Equivalent circuit of a two-state nanodevice

Let us assign to $e\lambda_1, e\lambda_2, e\lambda_3$ (where e is the electron's charge) charges on three capacitors of equal value $c_0 = c_1 = c_2 = c_3 = 1As/V$, and let us introduce as state variables the voltages of these three capacitors, $x_1(t) = e\lambda_1/c_1, x_2(t) = e\lambda_2/c_2, x_3(t) = e\lambda_3/c_3$. The state variables of the nuclear vibration are proportional to the position and momentum co-ordinates. The coefficients will be chosen such that the state variable proportional to the position, $x_4(t) = c_4 \cdot R(t)$, has current dimension, and the state variable related to the momentum, $x_5(t) = c_5 \cdot P(t)$, has voltage dimension. The numerical value of the constants can be arbitrary, e.g. 1, but their physical dimension is chosen to be $[c_4] = A/m$, and $[c_5] = m/A \cdot s^2$. Dynamic equations (26) can be expressed with these newly introduced state variables

$$\begin{pmatrix} c_0 \frac{dx_1}{dt} \\ c_0 \frac{dx_2}{dt} \\ c_0 \frac{dx_3}{dt} \end{pmatrix} = \left[\frac{c_0}{\hbar} \begin{pmatrix} 0 & -\omega_0 & -\omega_2 \\ \omega_0 & 0 & -\omega_1 \\ \omega_2 & \omega_1 & 0 \end{pmatrix} - \frac{c_0}{2\tau_0} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \right] \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix} + \frac{e}{\hbar} \begin{pmatrix} 0 \\ 0 \\ \frac{\hbar}{\tau_0} \tanh \frac{E_2 - E_1}{k_B T} \end{pmatrix} \quad (27)$$

$$L \frac{dx_4}{dt} = x_5$$

$$C \frac{dx_5}{dt} = -x_4 + c_4(R_{20} + R_{10}) + c_4 \frac{c_0}{2e} (R_{20} - R_{10}) x_3 - \alpha C x_5$$

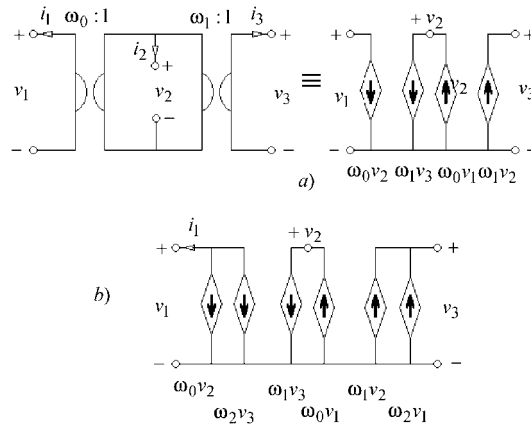


Figure 4. Equivalent circuit of non-energetic three ports representing an isolated molecule.

The elements with memory of the equivalent circuit will be the capacitors $c_0 = c_1 = c_2 = c_3 = 1As/V$, an inductor with $L = M \cdot c_5/c_4$, and a capacitor with $C = c_4/2c_5E_{11}$. State equations (27) can be represented as an equivalent circuit shown in Figure 5. Four state variables are voltages of capacitors and one of them is current flowing through an inductor. Equations (27) satisfy Kirchhoff's laws.

Note that matrix $c_0/\hbar\Omega$ is an admittance matrix of physical dimension A/V , and for any voltage vector \mathbf{x} it satisfies $(\mathbf{x})^T(c_0/\hbar\Omega) \cdot \mathbf{x} \equiv 0$. This implies that in the equivalent circuit of this admittance matrix can be represented as a 'non-energetic' three port. Its equivalent circuit can be built from three gyrators or from six controlled-sources. Figure 4(a) shows a two-gyrator circuit and a circuit composed of voltage-controlled current sources realizing a three-port admittance

$$\begin{pmatrix} i_1 \\ i_2 \\ i_3 \end{pmatrix} = \begin{pmatrix} 0 & -\omega_0 & 0 \\ \omega_0 & 0 & -\omega_1 \\ 0 & \omega_1 & 0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$$

and Figure 4(b) represents a

$$\begin{pmatrix} i_1 \\ i_2 \\ i_3 \end{pmatrix} = \begin{pmatrix} 0 & -\omega_0 & -\omega_2 \\ \omega_0 & 0 & -\omega_1 \\ \omega_2 & \omega_1 & 0 \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}$$

three-port admittance.

Figure 5 shows the equivalent circuit of a molecule with two electronic states and one vibrational degree of freedom, characterized by state equations (27). The nuclear vibration is represented by an equivalent resonant circuit coupled to the electronic dynamics by voltage $x_3(t)$. The capacitors can be chosen to be $c_0 = c_1 = c_2 = c_3 = 1$, and the resonant circuits capacitor C and inductor L take the values as above. The resistors are $r_1 = r_2 = 2\tau_0/c_0$; $r_3 = \tau_0/c_0$; $G = \alpha \cdot C$.

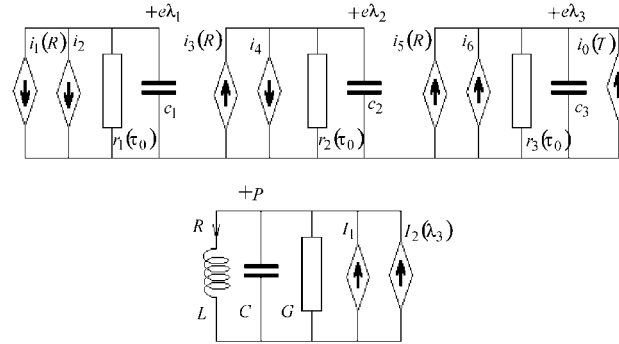


Figure 5. Equivalent circuit model of a molecule with two electronic states and one degree of freedom of nuclear vibration.

The source currents of the of the voltage-controlled current generators are

$$i_1 = (c_0/\hbar)\omega_0x_2; \quad i_2 = (c_0/\hbar)\omega_2x_3; \quad i_3 = (c_0/\hbar)\omega_0x_1; \quad i_4 = (c_0/\hbar)\omega_1x_3$$

$$i_5 = (c_0/\hbar)\omega_2x_1; \quad i_6 = (c_0/\hbar)\omega_1x_2; \quad i_0 = \frac{e}{\tau_0} \tanh \frac{E_2 - E_1}{k_B T}$$

$$I_1 = c_4(R_{20} + R_{10}); \quad I_2 = \frac{c_4 C (R_{20} - R_{10})}{2e} x_3$$

The equivalent circuit represents a mixed quantum-classical dynamics. A very fast electronic sub-circuit shown on the upper part of the figure is coupled to a slow nuclear vibration through the current I_2 , which is generated by the voltage x_3 . A feedback from the nuclear dynamics is expressed in the R -dependence of the controlled-source currents. In Section 7 we shall continue to explore the analogy between molecular and nonlinear circuit dynamics.

4. ELECTRONIC DYNAMICS OF A NANODEVICE WITH N EIGENSTATES

If a nanodevice has by N orthogonal electronic stationary eigenstates, $|\Phi_1\rangle, |\Phi_2\rangle, \dots, |\Phi_N\rangle$, its pure states can be characterized by

$$|\Psi\rangle = c_1(t)|\Phi_1\rangle + c_2(t)|\Phi_2\rangle + \dots + c_N(t)|\Phi_N\rangle \quad (28)$$

If there is no reservoir coupled to the relevant system the density operator reads

$$\rho(s, s') = |\Psi(s)\rangle\langle\Psi(s')| \quad (29)$$

and the density matrix is

$$\rho = |\Psi\rangle\langle\Psi| = \begin{bmatrix} c_1^* \\ c_2^* \\ \vdots \\ c_N^* \end{bmatrix} [c_1, c_2, \dots, c_N] = \begin{bmatrix} |c_1|^2 & c_1^* c_2 & \dots & c_1^* c_N \\ c_2^* c_1 & |c_2|^2 & \dots & c_2^* c_N \\ \vdots & \vdots & \ddots & \vdots \\ c_N^* c_1 & \dots & \dots & |c_N|^2 \end{bmatrix} \quad (30)$$

The density matrix is Hermitean, its trace is 1, its determinant is zero and it is equal to its square $\rho = \rho^2$.

The time evolution of $\rho(t)$ can be derived from its definition

$$\frac{\partial \rho(t)}{\partial t} = \frac{\partial}{\partial t} \langle \Psi | + | \Psi \rangle \frac{\partial \langle \Psi |}{\partial t} = -\frac{j}{\hbar} (\mathbf{H} \rho(t) - \rho(t) \mathbf{H}) \quad (31)$$

If a nanodevice is coupled to a heat bath, still the density matrix can be defined, it is still Hermitean, its trace remains one, but its determinant is not any more zero and it is not any more equal to its square.

The number of real variables representing a Hermitean matrix of complex elements is not $2N^2$ but only N^2 , because between the $2N^2$ real numbers there are N^2 relations. If the trace of the matrix is 1, this is an additional relation, thus the number of independent real variables is $s = N^2 - 1$. Thus a time-dependent Hermitean density matrix can be represented by s real-valued time functions $\lambda_1(t), \lambda_2(t), \dots, \lambda_s(t)$.

It can be shown that any $N \times N$ Hermitean time-varying matrix, $\mathbf{A}(t)$, can be expressed as (Appendix B)

$$\mathbf{A}(t) = \frac{1}{N} \text{Tr}\{\mathbf{A}(t)\} \mathbf{1} + \frac{1}{2} \sum_{i=1}^s \lambda_i(t) \cdot \mathbf{T}_i \quad (32)$$

In case of ρ the trace is equal to 1, thus it reads

$$\rho(t) = \frac{1}{N} \mathbf{1} + \frac{1}{2} \sum_{i=1}^s \lambda_i(t) \cdot \mathbf{T}_i \quad (33)$$

The matrix of the Hamilton operator is also Hermitean, thus it can be expressed as

$$\mathbf{H}(t) = \frac{1}{N} \text{Tr}\{\mathbf{H}(t)\} \mathbf{1} + \frac{1}{2} \sum_{j=1}^s H_j(t) \cdot \mathbf{T}_j \quad (34)$$

The s -dimensional vector composed of the scalar time functions $\lambda_1(t), \lambda_2(t), \dots, \lambda_s(t)$ is called coherence vector, which defines the quantum mechanical state in the same depth as the density matrix $\rho(t)$. The trace of the Hamiltonian and the s -dimensional vector composed of $H_1(t), H_2(t), \dots, H_s(t)$, being scalar time functions describes a system in the depth of its Hamilton operator.

The time evolution of the coherence vector can be derived if we substitute Equations (33) and (34) into Equation (31) and express the time derivatives from the Equation

$$\sum_{i=1}^s \frac{\partial \lambda_i}{\partial t} \mathbf{T}_i = \frac{1}{2} \sum_{j=1}^s \sum_{i=1}^s H_j (\mathbf{T}_j \mathbf{T}_i - \mathbf{T}_i \mathbf{T}_j) \lambda_i \quad (35)$$

The solution of Equation (35) can be expressed using the f_{ijk} structure constants of the special unitary algebra $SU(n)$, forming an anti-symmetric matrix (see Appendix B)

$$\Omega_{ik} = - \sum_j f_{ikj} H_j = \sum_j f_{ijk} H_j = - \Omega_{ki} \quad (36)$$

The time evolution of the coherence vector is described by a set of coupled ordinary differential equations, called Bloch equation

$$\hbar \frac{\partial \boldsymbol{\lambda}(t)}{\partial t} = \boldsymbol{\Omega} \cdot \boldsymbol{\lambda}(t) \quad (37)$$

where

$$\hbar \frac{\partial \lambda_i(t)}{\partial t} = \sum_{k=1}^s \omega_{ik} \lambda_k, \quad \omega_{ik} = \sum_{n=1}^s H_n f_{nik} \quad (38)$$

In Appendix B we give the generators and structure constants of $SU(n)$ for $n=2$ and 3 . For any n f_{nik} is anti-symmetric, thus $\omega_{ik} = -\omega_{ki}$, and we have

$$\boldsymbol{\Omega} = -\boldsymbol{\Omega}^T \quad (39)$$

From Equation (39) it follows that

$$|\boldsymbol{\lambda}(t)| = \text{constant for any } t \quad \text{because } \frac{\partial}{\partial t} |\boldsymbol{\lambda}(t)|^2 = (\boldsymbol{\lambda}(t) \cdot (\boldsymbol{\Omega} + \boldsymbol{\Omega}^T) \boldsymbol{\lambda}(t)) = 0 \quad (40)$$

thus $|\boldsymbol{\lambda}(t)|$ is a constant of motion.

It has been shown (see e.g. References [10–12]) that the state of any N -level open quantum system can be described by a Hermitean ($N \times N$) matrix $\rho(t)$. The time evolution from an initial state $\rho(0)$ can be described by a completely positive semigroup preserving hermiticity, trace and positivity of $\rho(t)$ for $0 \leq t < \infty$. In terms of the infinitesimal generator \mathbf{L} of the semigroup a quantum master equation can be derived

$$\frac{\partial}{\partial t} \rho(t) = \mathbf{L}[\rho(t)] \quad (41)$$

The density matrix $\rho(t)$ can be replaced by a $s = (N^2 - 1)$ -dimensional real vector $\boldsymbol{\lambda}(t)$, and the original master Equation (41) can be transformed into an inhomogeneous vector equation in a real vector space

$$\frac{\partial}{\partial t} \boldsymbol{\lambda}(t) = \mathbf{G}[\boldsymbol{\lambda}(t)] + \mathbf{k} \quad (42)$$

State equation (42) is a generalization of Bloch equation (34). For quantum Markovian evolution the general mathematical form of Equations (41) and (42) has been given in References [10–12] as generalized Bloch equations

$$\hbar \frac{\partial}{\partial t} \boldsymbol{\lambda}(t) = \boldsymbol{\Omega} \boldsymbol{\lambda}(t) + \mathbf{R} \boldsymbol{\lambda}(t) + \mathbf{k} \quad (43)$$

where $\boldsymbol{\Omega}$ is the Bloch matrix of the conservative (lossless) system, \mathbf{R} and \mathbf{k} are the damping matrix and damping vector respectively. The $\boldsymbol{\lambda}(t)$ vector evolves in the s -dimensional real space, it undergoes some kind of rotation and its length changes. Whereas rotation is due to the Hamiltonian as well as the non-Hamiltonian terms the change of length is exclusively caused by non-Hamiltonian contributions.

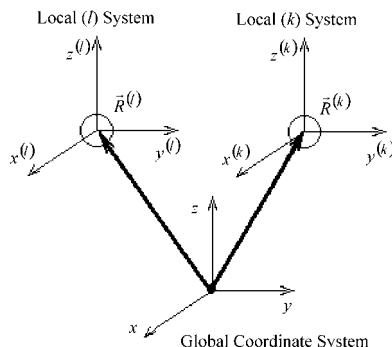


Figure 6. Local and global co-ordinate system for two interacting molecules.

5. INTERMOLECULAR COULOMB FORCES REPRESENTED BY MULTIPOLE MOMENTS

We assume that the position of each molecule is fixed in space, thus the nuclei of a molecule can vibrate, the electron-cloud density around a molecule can change in time, but no molecule can have translatory motion, i.e. it cannot move away from its local co-ordinate system (Figure 6). We also assume that the molecules are far enough apart from each other that the overlap between their wave functions can be ignored. We can identify sets of private electrons and Hamilton operators as belonging to each molecule, intermolecular forces are relatively weak and their effects can be considered as perturbations.

A molecule is a dynamic system composed of its N_{nuc} nuclei and its n electrons (in case of an artificial molecule, the role of the nuclei is replaced by the geometry of the dots). If molecules were very far apart from each other such that Coulomb interactions were negligible, the integrated system wouldn't be perturbed. In the unperturbed system the molecular Hamilton operators just add up, and the state functions of the system are simple products of the molecular state functions. As molecules are getting closer to each other interaction energy emerges. We assume that all the contributions to the interaction energy between molecules, except for the negligible magnetic terms, derive ultimately from the Coulomb interactions between their particles. In order to model the interaction, we need to be able to describe the way in which charge is distributed in a molecule. It is known that Coulomb interactions between charges localized inside spheres around the charges can be specified by the interactions between multipoles (point charges, dipoles, quadrupoles, octopoles, etc.) representing the charge distribution inside the isolated sphere surrounding a molecule. The time-varying Coulomb field of a molecule can be represented by multipoles of fixed positions with time-varying multipole moments. If the dynamics of the nuclei and the time-varying electronic charge of a molecule were known, then the potential outside the sphere could be determined.

The charge density operator at some spatial point \mathbf{r} can be given as the quantized classical charge density expression

$$\rho(\mathbf{r}) = -e \sum_{i=1}^n \delta(\mathbf{r}_i - \mathbf{r}) + e \sum_{j=1}^N z_n \delta(\mathbf{R}_j - \mathbf{r}) \quad (44)$$

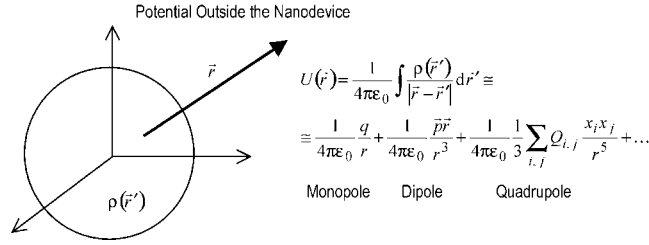


Figure 7. Coulomb-field of a nanodevice.

from which the expectation value can be calculated by

$$\rho_\lambda(\mathbf{r}) = -en \sum_{\sigma} \int |\Psi_\lambda(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_n, \sigma, \mathbf{R})|^2 d\mathbf{r}_2 \dots d\mathbf{r}_n + \sum_{j=1}^N \sum_{\sigma} eZ_j \int \delta(\mathbf{R}_j - \mathbf{r}) \Psi_\lambda(\mathbf{x}, \sigma, \mathbf{R})^2 d\mathbf{x} d\mathbf{R} \quad (45)$$

The time-varying Coulomb field of a molecule can be represented by multipoles of fixed positions with time-varying multipole moments. If the dynamics of the nuclei described by Q_a , ($a=1, 2, \dots, N$) point charges in points $\mathbf{R}_A(t)$, and the time-varying electronic charge of a molecule $\rho_e(\mathbf{r}, t)$ are known, then the potential outside the sphere (in a co-ordinate system whose origin is fixed to the center of the sphere) is

$$U(\mathbf{r}, t) = \frac{1}{4\pi\epsilon_0} \left[\sum_a \frac{Q_a}{|\mathbf{r} - \mathbf{R}_A(t)|} + \int \frac{\rho_e(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}|} d^3r \right] = \frac{1}{4\pi\epsilon_0} \int \frac{\rho(\mathbf{r}, t)}{|\mathbf{r} - \mathbf{r}|} d^3r \quad (46)$$

where $\rho(\mathbf{r}, t)$ is the total charge distribution including nuclei and electrons. Note that $\rho(\mathbf{r}, t)$ is changing in time, thus it generates an electromagnetic field. However, the wavelength of the generated field is much longer than the size of the molecules, thus quasi-static approximation is justifiable.

The $U(\mathbf{r}, t)$ potential can be expanded in terms of multipole potentials (Figure 7)

$$U(\mathbf{r}, t) = \frac{1}{4\pi\epsilon_0} \left(\frac{q}{r} + \frac{\mathbf{p} \cdot \mathbf{r}}{r^3} + \frac{1}{3} \sum_{i,j} Q_{i,j} \frac{x_i x_j}{r^5} + \dots \right) \quad (47)$$

where q is the total charge (or ‘monopole’ moment), \mathbf{p} is the electric dipole moment

$$\mathbf{p}(t) = \int \mathbf{r}' \rho(\mathbf{r}', t) d^3r' \quad (48)$$

and $Q_{i,j}$ are the ij element of the traceless quadrupole moment tensor

$$Q_{i,j}(t) = \int (3x'_i x'_j - r'^2 \delta_{i,j}) \rho(\mathbf{r}', t) d^3r' \quad (49)$$

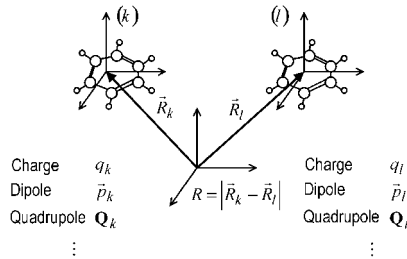


Figure 8. Interaction energy of molecules (k) and (l) representing by the interactions of their charges, dipole and quadrupole moments.

The multipole moment of rank n is called '2ⁿ-pole' moment. A monopole (rank 0) requires a single point charge, a dipole (rank 1) two charges along a line, a quadrupole (rank 2) four charges arranged in a two-dimensional array. An octopole (rank 3) can be constructed from eight charges arranged in a three-dimensional array, the hexadecapole (rank 4) moment needs 16 charges, etc.

In a non-uniform electric field $V(\mathbf{r})$ the energy of a molecule can be expressed as

$$E = qV + \sum_{i=1}^3 p_{x_i} \frac{\partial V}{\partial x_i} + \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 Q_{i,j} \frac{\partial^2 V}{\partial x_i \partial x_j} + \dots \quad (50)$$

Let us have a look at a single molecule (k) in the Coulomb field of another molecule (l), and let us calculate the interaction energy. Figure 8 shows three co-ordinate systems, a 'global' one (\mathbf{r}) and two 'local' co-ordinate systems ($\mathbf{r}^{(k)}$ and $\mathbf{r}^{(l)}$) fixed to the molecules. Origins of the local systems are fixed to the centres of the spheres surrounding the molecules. The electric field of a molecule is represented by multipoles sitting in the origin of the local systems. The potentials of molecule (l) changes the potential energy operator of molecule (k) because $U^{(l)}(\mathbf{r})$ acts in the sphere of molecule (k) as a non-uniform electric field.

By introducing the vector $\mathbf{R} = \mathbf{R}^{(l)} - \mathbf{R}^{(k)}$ and gradients of $1/R$, ($R = |\mathbf{R}|$)

$$T = \frac{1}{R} \quad (51a)$$

$$T_{x_i} = \nabla_{x_i} \frac{1}{R} \quad (51b)$$

$$T_{x_i x_j} = \nabla_{x_i} \nabla_{x_j} \frac{1}{R} \quad (51c)$$

$$T_{x_i x_j x_m} = \nabla_{x_i} \nabla_{x_j} \nabla_{x_m} \frac{1}{R} \quad (51d)$$

$$T_{x_i x_j x_m x_n} = \nabla_{x_i} \nabla_{x_j} \nabla_{x_m} \nabla_{x_n} \frac{1}{R} \quad (51e)$$

interaction operator in terms of the multipoles of molecules (k) and (l) can be expressed as

$$\begin{aligned}
 H^{(kl)} = & \frac{1}{4\pi\epsilon_0} q^{(k)} \left[Tq^{(l)} - \sum_{i=1}^3 T_{x_i} p_{x_i}^{(l)} + \sum_{i=1}^3 \sum_{j=1}^3 T_{x_i x_j} Q_{x_i x_j}^{(l)} \right] \\
 & + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^3 p_{x_i}^{(k)} \left[T_{x_i} q^{(l)} - \sum_{j=1}^3 T_{x_i x_j} p_{x_j}^{(l)} + \frac{1}{3} \sum_{m=1}^3 \sum_{n=1}^3 T_{x_i x_m x_n} Q_{x_m x_n}^{(l)} \right] \\
 & + \frac{1}{3} \frac{1}{4\pi\epsilon_0} \sum_{i=1}^3 \sum_{j=1}^3 Q_{x_i x_j}^{(k)} \left[T_{x_i x_j} q^{(l)} - \sum_{m=1}^3 T_{x_i x_j x_m} p_{x_m}^{(l)} + \frac{1}{3} \sum_{m=1}^3 \sum_{n=1}^3 T_{x_i x_j x_m x_n} Q_{x_m x_n}^{(l)} \right] + \dots
 \end{aligned} \tag{52}$$

where $q^{(k)}$, $\mathbf{p}^{(k)}$ and $\mathbf{Q}^{(k)}$ are the charge, dipole and quadrupole moments of molecule (k) and $q^{(l)}$, $\mathbf{p}^{(l)}$ and $\mathbf{Q}^{(l)}$ are those of molecule (l). If both of them are just dipoles, or just quadrupoles, the interaction energy reduces to the dipole–dipole (H'_{dd}) or to the quadrupole–quadrupole interaction (H'_{qq}) terms, which can be expressed as

$$H'_{dd}{}^{(kl)} = \frac{1}{4\pi\epsilon_0} \sum_{i=1}^3 p_{x_i}^{(k)} \sum_{j=1}^3 T_{x_i x_j} p_{x_j}^{(l)} \tag{53}$$

or

$$H'_{qq}{}^{(kl)} = \frac{1}{4\pi\epsilon_0} \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 Q_{x_i x_j}^{(k)} \cdot \frac{1}{3} \sum_{m=1}^3 \sum_{n=1}^3 T_{x_i x_j x_m x_n} Q_{x_m x_n}^{(l)} \tag{54}$$

The interaction terms (52)–(54) have been derived for pairs of molecules, isolated from any others. However, they are based on the Coulomb interactions between nuclear and electronic charges, which are strictly additive, so the formulas can be generalized to an assembly of molecules by summing over the distinct pairs.

In the framework of our assumptions that the neighbours perturb the state of the relevant system, but their effect on the environment (thermal bath) can be neglected, the molecule's interactions with its neighbours are expressed as a perturbation on the isolated molecule's Hamiltonian

$$\mathbf{H} = \begin{bmatrix} E_1 & G \\ G & E_2 \end{bmatrix} + \begin{bmatrix} \sum_{j_{\text{neighbour}}} H'_j(t) & 0 \\ 0 & - \sum_{j_{\text{neighbour}}} H'_j(t) \end{bmatrix} \tag{55}$$

where E_1, E_2 , and G are representing the stand-alone molecule, $H'_j(t)$ is the perturbation of the neighbour j , and the sum should include all the neighbours, whose perturbation is not negligible.

In our two-dimensional arrangement of Coulomb-coupled molecules each molecule is fixed to the surface of a sheet. The interaction energy of the molecules, thus their interaction operator is determined by Equation (52). Note that the interaction energy depends on the dynamic state through the charge distribution.

Without loss of generality we can assume that the electron density of a molecule can be calculated as a sum of absolute squares of molecular orbital wave functions for all occupied

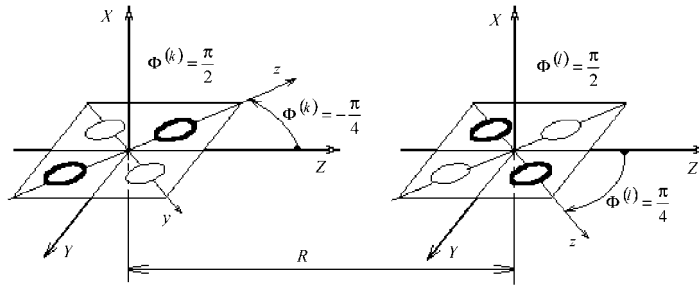


Figure 9. Interaction of two molecules characterized by their quadrupole moments.

orbital

$$\rho(\mathbf{r}) = \sum_{i=1}^m |\Psi_i(\mathbf{r})|^2 \quad (56)$$

If we express the molecular orbital $\Psi_i(\mathbf{r})$ as a linear combination of basis functions, then the electron density at a point \mathbf{r} can be given in terms of the density matrix elements as

$$\rho(\mathbf{r}) = \sum_{i=1}^m \left(\sum_{j=1}^n c_{ji} \cdot \varphi_j \right) \left(\sum_{l=1}^n c_{li}^* \cdot \varphi_l^* \right) = \sum_{j=1}^n \sum_{l=1}^n \rho_{jl} \varphi_j \varphi_l^* \quad (57)$$

Substituting Equation (54) into Equations (48) and (49) we get the contribution of the electrons to the dipole and quadrupole moments as

$$\mathbf{p} = e \sum_{j=1}^n \sum_{l=1}^n \rho_{jl} \int \mathbf{r}' \varphi_j(\mathbf{r}') \varphi_l^*(\mathbf{r}') d^3 r' \quad (58)$$

and

$$Q_{ij} = e \sum_{j=1}^n \sum_{l=1}^n \rho_{jl} \int (3x'_i x'_j - r'^2 \delta_{ij}) \cdot \varphi_j(\mathbf{r}') \varphi_l^*(\mathbf{r}') d^3 r' \quad (59)$$

Note that the integrals in Equations (58) and (59) depend only on the geometry of the molecule. The time-varying state depends on the density matrix elements, which are linear in the components of the coherence vector according to Equation (33). We conclude that the dipole and quadrupole moments of a molecule are linear in the coherence vector components.

We illustrate the multipole representation by a simple example. Figure 9 shows two interacting two-state molecules, (k) and (l). Both molecules have two orthogonal ground states, each can be represented by a quadrupole. In their local co-ordinate systems the quadrupoles lie either in the local z or in the y direction. The time-varying quadrupole tensor can be calculated from Equation (59). If the amplitude of the ground state in the z direction is denoted by subscript 1 and the ground state in the y direction by subscript 2 then the

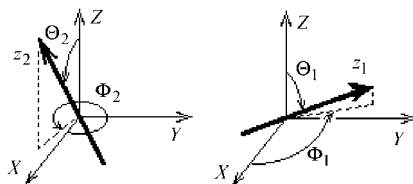


Figure 10. Transformations of quadrupole moments from local to global co-ordinate systems.

quadrupole moments in the local coordinate systems are given as

$$\begin{aligned}
 Q_{xy} &= Q_{yx} = Q_{xz} = Q_{zx} = Q_{yz} = Q_{zy} = 0 \\
 Q_{zz} &= e\rho_{11}2A - e\rho_{22}A \\
 Q_{yy} &= e\rho_{22}2A - e\rho_{11}A \\
 Q_{xx} &= -e\rho_{11}A - e\rho_{22}A \\
 A &= \int z^2 \varphi_1^2 d^3r = \int y^2 \varphi_2^2 d^3r
 \end{aligned} \tag{60}$$

If a line-like quadrupole's direction is the local z -axis, and \mathbf{n} is a unit vector (in the global co-ordinate system) in the direction of the molecular axis (Figure 10), then the quadrupole components in the global co-ordinate system can be expressed as

$$Q_{\alpha\beta} = Q \left(\frac{3}{2} n_\alpha n_\beta - \frac{1}{2} \delta_{\alpha\beta} \right) \tag{61}$$

where $n_x = \cos \Phi$, $n_y = \sin \Theta \cdot \sin \Phi$, $n_z = \cos \Theta \cdot \sin \Phi$. In our example $\Theta = \pi/2$, and $\Phi_1 = \pi/4$, $\Phi_2 = -\pi/4$.

The dynamical quadrupole tensor is

$$\mathbf{Q} = eA \begin{bmatrix} -\rho_{11} - \rho_{22} & 0 & 0 \\ 0 & \frac{1}{2}(\rho_{11} + \rho_{22}) & \frac{3}{2}(\rho_{11} - \rho_{22}) \\ 0 & \frac{3}{2}(\rho_{11} - \rho_{22}) & \frac{1}{2}(\rho_{11} + \rho_{22}) \end{bmatrix} \tag{62}$$

However, $\rho_{11} + \rho_{22} = 1$ and $\rho_{11} - \rho_{22} = -\lambda_3$, thus

$$\mathbf{Q} = eA \begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{3}{2}\lambda_3 \\ 0 & -\frac{3}{2}\lambda_3 & \frac{1}{2} \end{bmatrix} \tag{63}$$

The interaction term of molecule (k) and (l) can be determined by Equation (54)

$$H'_{qq}(kl) = \frac{3e^2 A^2}{2\pi\epsilon_0} \frac{1}{R^5} \lambda_3^{(k)} \lambda_3^{(l)} + \frac{3e^2 A^2}{2\pi\epsilon_0} \frac{1}{R^5} \tag{64}$$

6. NANODEVICES IN EXTERNAL ELECTRIC FIELDS

As long as our assumptions in Section 2 hold, the energy perturbation caused by an external electric field can be estimated as

$$\delta E = -\mathbf{p}(t) \cdot \mathbf{E}(t) + \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 Q_{i,j}(t) \frac{\partial E_j(t)}{\partial x_i} \quad (65)$$

where $\mathbf{p}(t)$ is the dipole, $Q_{i,j}$ the quadrupole moment of the nanodevice, and $\mathbf{E}(t)$ is the external electric field. If the field changes slowly in space, the second term can be neglected, and the perturbation of the Hamiltonian can be calculated as

$$\delta H_{ij} = \langle \Phi_i | -\mathbf{p} \cdot \mathbf{E} | \Phi_j \rangle = \delta H_{ji}^* \text{ for } i \neq j \quad (66)$$

The diagonal terms are not perturbed. In case of a two-state system

$$\delta H = \frac{1}{2} \begin{bmatrix} 0 & H_1 + jH_2 \\ H_1 - jH_2 & 0 \end{bmatrix} \quad (67)$$

If a system is interacting with a field of carrier frequency ω close to $(E_2 - E_1)/\hbar$, it is modulated by a time-varying envelope $E_0(t)$, and its polarization unit vector is \mathbf{e} , i.e.

$$\mathbf{E}(t) = 2|E_0(t)|[\text{Re}(\mathbf{e}) \cos(\omega t - \varphi(t)) + \text{Im}(\mathbf{e}) \sin(\omega t - \varphi(t))] \quad (68)$$

where $E_0(t) = |E_0(t)|e^{j\varphi(t)}$ is a slowly varying complex amplitude, then

$$H_1 + jH_2 = \langle \Phi_1 | H_{\text{int}} | \Phi_2 \rangle = \hbar \Omega(t) e^{j\varphi(t)} \cos(\omega t + \varphi(t)) \quad (69)$$

where

$$\Omega(t) = \frac{2|\mathbf{p}(t)||E_0(t)|}{\hbar} \quad (70)$$

In Equation (70) $\Omega(t)$ is known as the Rabi frequency.

In this case the matrix $\mathbf{\Omega}$ in the generalized Bloch equation take the form

$$\mathbf{\Omega}(t) = \begin{pmatrix} 0 & -\omega_0 & -H_2(t) \\ \omega_0 & 0 & -H_1(t) \\ H_2(t) & H_1(t) & 0 \end{pmatrix} \quad (71)$$

7. EQUIVALENT CIRCUITS FOR COULOMB-COUPLED NANODEVICE ARRAYS

7.1. Modelling Coulomb-coupled molecules

In Section 3 we have illustrated the application of equivalent circuits for the simulation of Coulomb-coupled molecules. Later we have shown that the mixed quantum-classical state equations describing the dynamics of a molecular array are ordinary first-order non-linear differential equations. We presented a technique by which an equivalent circuit can be generated if the electronic state is built from a finite number, n , of eigenstates, and the mechanical degree of freedom of the nuclear vibrations is known. An approximate model of the thermal

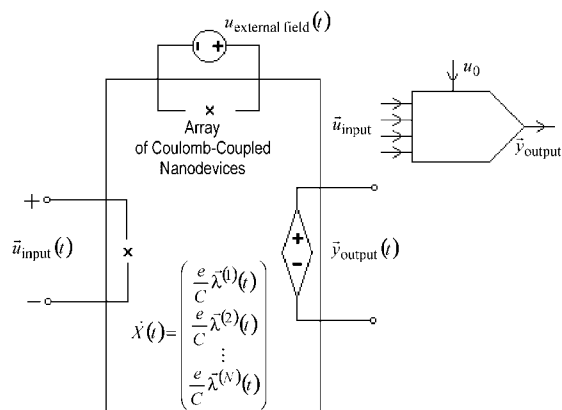


Figure 11. Equivalent circuit of a Coulomb-coupled array.

environment and that of the external electric fields have been built in into the equivalent circuit.

However, the experimental frame in which we run (or test) a nanocircuit has not been specified so far. In case of a Coulomb-coupled array of nanodevices or molecules the input and output of the circuit is a macroscopic system, for example a microelectronic circuit which sets the input and measure the output of a Coulomb-coupled array. The macroscopic embedding has to be designed to set the input boundary conditions as an electric field, and to sense the output electric field generated by the array. We assume that both the input and output macroscopic systems are interfaced to the array through metal contacted devices. At the input the voltages on metal contacts generate the electric field, and at the output the electric field of the nanodevices generate voltages on the metal contacts.

The physical interfaces between Coulomb-coupled devices and input–output units are modelled as equivalent circuits as well. The boundary conditions at the metal-contacted devices are defined by the geometry of the metal contacts driven by voltages of the embedding circuits. The Coulomb-field generated by the metal contacts interacts with the dipoles and quadrupoles of the Coulomb-coupled devices. The interaction is assumed to be classical, thus classical electromagnetic techniques can be used to develop the circuit model of the interface [14].

Figure 11 illustrates the model of the input and output of an array. In general the input is a time-varying electric field generated by a metal contacted input circuit. Looking back from the array, it can always be represented by a vector of λ_3 '-s (polarization) of virtual molecules (I_1, I_2, \dots denote the input ports)

$$\mathbf{u}_{\text{input}} = \left(\frac{e}{C} \lambda_3^{(I_1)}, \frac{e}{C} \lambda_3^{(I_2)}, \dots \right) \quad (72)$$

The external field will be represented by an independent time-varying voltage source $\mathbf{u}_{\text{external field}}(t)$. The measured output is also a vector of molecular λ_3 '-s (O_1, O_2, \dots denote the output ports)

$$\mathbf{y}_{\text{output}} = \left(\frac{e}{C} \lambda_3^{(O_1)}, \frac{e}{C} \lambda_3^{(O_2)}, \dots \right) \quad (73)$$

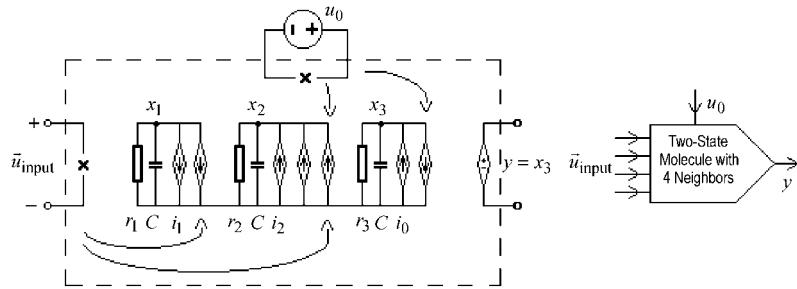


Figure 12. Equivalent circuit of a molecule in two-dimensional cluster. The Coulomb coupling is characterized by polarization voltages.

Note that e/C , i.e. the electron's charge divided by a capacitance has voltage dimension thus the inputs and outputs are virtual voltages indeed, which could be called polarization voltages. The internal electronic state variables are composed of the coherence vectors and the nuclear co-ordinates. If the nuclear vibration can be neglected and the number of molecules in an array is N_{mol} , then the number of state variables, i.e. the dimension of vector $\lambda(t)$ is $3N_{\text{mol}}$. A molecule's model in an array depends on the properties of the individual molecules and on the geometry of the two-dimensional cluster in which the molecules are located.

First, we envisage an empty cellular array, with specified raster geometry, and specified local co-ordinate systems at each cell. The distances between the origins of the local co-ordinate systems are given together with local orientations. We also specify the individual isolated molecules with their models located in their local co-ordinate system. The number of output ports of a molecule depends on the number of stationary eigenstates, and it is equal to the number of its polarization voltages. In case of a two-state molecule this number is 1, for a three-state molecule it is 2, etc. Next, we assign to each nanodevice as many input ports as the sum of the output ports of its neighbours. The cellular array defines the maximum number of neighbours a molecule can have. If every neighbouring cell is filled in by a molecule then all input ports are excited. However, if a neighbouring cell is empty, there will be zero polarization voltage at the corresponding input port. This way we can define a model for a nanodevice in such a way, that the model is invariant on the neighbours, i.e. the model itself does not depend on whether a neighbouring cell is filled by a molecule or it is empty. If the geometry of cluster, together with the local co-ordinate systems including the molecular orientations is fixed, a hierarchy of equivalent circuit models can be built.

We shall illustrate the procedure leading to a hierarchy of models. We start with a simple example shown in Figure 12. A two-electronic-state molecule is located in a two-dimensional cluster. We assume that no nuclear vibrations take place. The number of output polarization ports is one, the maximum number of neighbours is 8, thus the dimension of the input polarization-voltage-vector is 8.

The parameters C, r_1, r_2, r_3 is r_1, i_0, i_1, i_2 are determined by the geometry, potential energy surfaces and local damping channels of the individual molecule. Voltage-controlled current sources couple the input voltages and the external field to the internal dynamics. We can introduce a simplified notation to represent a molecule in a larger array. In a circuit a molecule is represented as a pentagon (Figure 7(b)). The input arrows on the sides of the pentagon

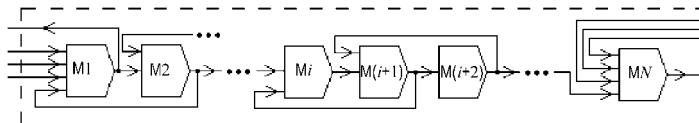


Figure 13. Equivalent circuit of a linear array of two-state molecules.

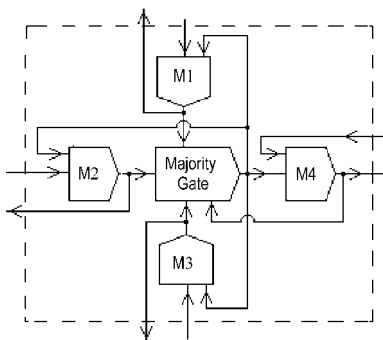


Figure 14. Equivalent circuit of a majority gate.

denote the input ports, the outgoing arrow on a corner stands for the output port. Three are input ports to which belong a cell filled with molecule, and there are those belonging to empty neighbouring cells. In order to simplify the notation the later ports are not shown as input arrows. If e.g. a two-state molecule has four neighbours, it has four input- and one output-port illustrated schematically in the figure.

Figure 13 shows the equivalent circuit of a molecular line composed of molecules presented on Figure 12. In case of a line a molecule in the midst of the line has only two neighbours, thus the input vector is two dimensional. However, the first molecule of a line can have more than one neighbour on its left, and the last one can have more than one neighbour on its right. To have an equivalent circuit model of a line we have to leave open the number of input ports at the first and at the last molecule of the line, because we do not know them. In our example we assumed that no more than four cells will be filled at the input and at the output of the line.

Figure 14 shows the equivalent circuit of a majority gate composed of four two state molecules. The signals flow in the direction of the thicker line, and there is a feedback to the neighbours shown by the thinner lines.

7.2. Interfacing Coulomb-coupled and metal-contacted nanodevices

We have seen that in a nanoelectronic integrated circuit the input electric field of a Coulomb-coupled molecular array is set by a metal-contacted microelectronic circuit, and the output electric field is measured similarly by voltages on metal contacts. The time-varying electric field $\mathbf{E}(\mathbf{r}, t)$ generated by the metal contacted input circuit (in general a microelectronic integrated circuit) couples to the dipoles and quadrupoles of the nearest molecules in the array. The time-varying voltage between the metal contacts and the molecular multipoles jointly generate the electrical field, which relates the voltages to the polarization-voltages. This relation

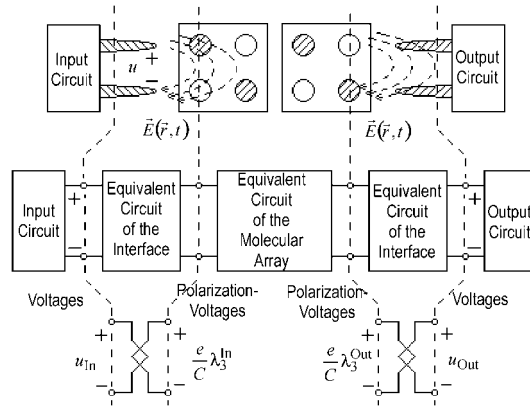


Figure 15. Equivalent circuit of the interfaces between Coulomb-coupled and metal-contacted nanodevices.

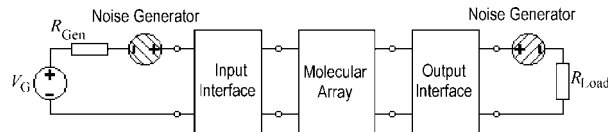


Figure 16. Modelling the damping channels of the input/output environment.

is represented as an equivalent circuit of the interface. To find this circuit we have to solve a classical electromagnetic problem. In the first approximation the problem is quasi-static, and the equivalent circuit can be composed of ideal transformers. In general, the equivalent circuit is a linear, reciprocal reactance circuit representing the coupling between the electric field generated by the metal-contacted microelectronic circuit and the polarization of the molecule [14].

At the output the electric field generated by the multipoles of the molecules is sensed and measured by the metal contacts of the output microelectronic circuit. The coupling of the polarization voltages to the voltages of the metal-contacted devices can be represented as a linear, reciprocal reactance circuit, similarly to the input. Figure 15 illustrates the equivalent circuits of both interfaces, both of them acting as linear filters.

However, the measurement at the output ports introduces an additional, non-local, damping channel, because the macroscopic system with its huge number of particles enforce similar effects on the molecular array as that of the thermal bath. In our model the damping channel of the measurement is represented by noise generators at the input and output ports. They represent a stochastic time dependence, their noise level and frequency spectrum can be adjusted to the specific microelectronic embedding. They are coupled to the molecules through polarization, however, their stochastic nature requires a time averaging, thereby they contribute to the damping matrix and vector [17,18]. Figure 16 illustrates a model in which the effect of the measurement's damping channel is indicated.

8. DISCUSSIONS ON REALIZABILITY

Having established a set of equivalent circuit models for Coulomb-coupled nanodevices, we are in a position to simulate the behaviour of integrated circuits composed of Coulomb-coupled and metal-contacted nanodevices.

Simulations are promising indeed. It has been shown that time-varying external fields can pump energy in the array realizing locally active cellular networks [17,19,20]. A molecular microprocessor architecture has been proposed with a four-phase adiabatic clock realized by a slowly time-varying external field [18]. The simulation techniques presented in this paper have been applied to design a new computational architecture composed of Coulomb-coupled optically pumped nanodevices (see Reference [21] in this special issue).

However, a fundamental question remains open: are the simulated architectures physically realizable?

Most of the theoretical approximations introduced in this paper had been experimentally verified, but our device and circuit models have not, because only discrete nanodevices and not integrated nanocircuits simulated by the methods of our paper have been built.

Nanoscale fabrication and testing are being explored. Nanotechnology is emerging. Recent results of the quantum chemist and solid-state physicist community are promising, indeed.

However, viable approaches to integrated nanoelectronics are missing. Realizability criteria have not been found for circuits that computing and communication need. Design methods for integrated nanoelectronic circuits would be needed to raise experiments from the device level to circuits.

Equivalent circuits presented in this paper invite circuit theorists to join physicists and chemists in their effort to explore the nanoscale. Development of integrated circuits composed of Coulomb-coupled and metal-contacted nanodevices is one of the challenges we face. We believe that further progress in nanoelectronics badly needs contributions from the circuit and system community.

APPENDIX A: MODELLING OF MOLECULAR DYNAMICS

The Hamilton operator of a molecule depends on the \mathbf{r}_i co-ordinates and \mathbf{p}_i momenta of the electrons, on the V_{en} potential energy of the electrons in the field of nuclei with coordinates \mathbf{R}_j , and on operator \mathbf{H}_{nn} representing the energy of the nuclear environment. The Hamilton operator has the general form

$$\mathbf{H} = (\mathbf{T}_e + \mathbf{V}_{ee} + \mathbf{V}_{\text{en}} + \mathbf{H}_{\text{nn}}) \quad (\text{A1})$$

Here the energy of the electrons is the sum of their \mathbf{T}_e kinetic, \mathbf{V}_{ee} repulsive Coulomb-pair interaction, and the attractive interaction between electrons and nuclei \mathbf{V}_{en} , given by

$$\mathbf{T}_e = \sum_i \frac{\mathbf{p}_i^2}{2m}, \quad \mathbf{V}_{ee} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad \mathbf{V}_{\text{en}} = \mathbf{V}_{\text{en}}(\mathbf{r}_i, \dots, \mathbf{R}_j) \quad (\text{A2})$$

m is the electron mass, e is the electron charge, and ε_0 is the vacuum permittivity. The electron–nuclear interaction term is

$$\mathbf{V}_{\text{en}} = -\frac{1}{4\pi\varepsilon_0} \sum_{i,k} \frac{Z_k e^2}{|\mathbf{r}_i - \mathbf{R}_k|} \quad (\text{A3})$$

and the nuclear kinetic energy plus their interaction terms read as

$$\mathbf{H}_{\text{nn}} = \mathbf{T}_{\text{n}} + \mathbf{V}_{\text{nn}} = \sum_k \frac{\mathbf{P}_k^2}{2M_k} + \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{k \neq l} \frac{Z_k Z_l e^2}{|\mathbf{R}_k - \mathbf{R}_l|} \quad (\text{A4})$$

where Z_k are the atomic numbers, \mathbf{R}_k and \mathbf{P}_k co-ordinates and momenta, M_k the masses of nuclei ($k = 1, 2, \dots, N$).

If the number of electrons is n_e the electronic dynamics has $3n_e$ spatial degrees of freedom. Each electron is assigned an additional quantum number σ_i to account for its spin. The device co-ordinates will be combined in vectors $\mathbf{x} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{n_e})$, $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$ and $\sigma = (\sigma_1, \sigma_2, \dots, \sigma_{n_e})$. An energy spectrum E_λ together with corresponding eigenfunctions $\Psi_\lambda(\mathbf{x}, \sigma, \mathbf{R})$ will be assigned to each molecule by solving the corresponding non-relativistic time-independent Schrödinger equation

$$\mathbf{H}\Psi_\lambda(\mathbf{x}, \sigma, \mathbf{R}) = E_\lambda \Psi_\lambda(\mathbf{x}, \sigma, \mathbf{R}) \quad (\text{A5})$$

Each solution of Equation (A5) describes a stationary state of the individual device. In this state the probability distribution $|\Psi_\lambda(\mathbf{x}, \sigma, \mathbf{R})|^2$ gives us information about the distribution of the electrons as well as the arrangement of the nuclei.

Since the individual molecule's Hamiltonian does not depend on spin, the solution of (A5) can be separated according to

$$\Psi_\lambda(\mathbf{x}, \sigma, \mathbf{R}) = \Psi(\mathbf{x}, \mathbf{R}) \cdot f(\sigma) \quad (\text{A6})$$

The individual spin states describe electrons whose spins are parallel (spin up) or anti-parallel (spin down) with respect to some direction in co-ordinate space.

Due to the large mass difference ($m/M < 10^{-3}$), electrons move much faster than nuclei. Thus assumption that the electronic degrees of freedom respond 'instantaneously' to any changes in the nuclear configuration is reasonable. According to the Born–Oppenheimer approximation the interaction between nuclei and electrons due to the motion of nuclei does not cause transition between different stationary electronic states, thus it is justified to define an electronic Hamiltonian of a individual molecule which carries a parametric dependence on the nuclear co-ordinates [19,22]:

$$\mathbf{H}_e(\mathbf{R}) = \mathbf{T}_e + \mathbf{V}_{ee} + \mathbf{V}_{en} \quad (\text{A7})$$

The electronic wave eigenfunctions are solutions of the electronic eigenvalue problem

$$\mathbf{H}_e(\mathbf{R})\Phi(\mathbf{x}, \mathbf{R}) = E(\mathbf{R})\Phi(\mathbf{x}, \mathbf{R}) \quad (\text{A8})$$

and they define a complete basis in the electronic Hilbert space, thus the molecular wave function can be expanded in this basis set as

$$\Phi(\mathbf{x}, \mathbf{R}) = \sum_k A_k(\mathbf{R})\Phi_k(\mathbf{x}, \mathbf{R}) \quad (\text{A9})$$

The expansion coefficients $A_k(\mathbf{R})$, satisfy an equation which can be derived by inserting Equation (A9) into Equation (A5)

$$(\mathbf{H}_{\text{nn}} + E_k(\mathbf{R}) + \Theta_{kk} - E)A_k(\mathbf{R}) = - \sum_{k \neq l} \Theta_{kl} A_l(\mathbf{R}) \quad (\text{A10})$$

where $E_k(\mathbf{R})$ is the energy belonging to the adiabatic electronic wave function Φ_k , $A_l(\mathbf{R})$ to Φ_l . The total energy is E , and Θ_{kl} is called non-adiabaticity operator

$$\Theta_{kl} = \langle \Phi_k | \mathbf{T}_{\text{nn}} | \Phi_l \rangle + \sum_j \frac{1}{M_j} \langle \Phi_k | \mathbf{P}_j | \Phi_l \rangle \mathbf{P}_j \quad (\text{A11})$$

where $\mathbf{P}_j = -j\hbar\nabla_j$ is the nuclear momentum operator of nucleus j .

Solution of Equation (A10) requires knowledge of the electronic spectrum for all configurations of the nuclei covered during their motion. Transitions between individual adiabatic electronic states become possible due to the electronic non-adiabatic coupling Θ_{kl} . If \mathbf{H}_{nn} has the form (A4), an effective potential function for the nuclear motion can be introduced, which assumes that the electronic system stays in its adiabatic state. The nuclear motion satisfies the eigenvalue problem

$$(\mathbf{T}_{\text{nn}} + U_k(\mathbf{R}))A_k(\mathbf{R}) = EA_k(\mathbf{R}) \quad (\text{A12})$$

where \mathbf{T}_{nn} is the nuclear kinetic energy operator, and the effective potential is given as

$$U_k(\mathbf{R}) = E_k(\mathbf{R}) + U_{\text{nn}}(\mathbf{R}) + \Theta_{kk} \quad (\text{A13})$$

The effective potential defines a hypersurface in the space of nuclear co-ordinates called potential energy surface (PES). According to Equation (A12) the nuclei can be considered to move in an effective potential generated by their mutual Coulomb interaction and the interaction with the electronic charge distribution corresponding to the configuration \mathbf{R} .

According to the Pauli principle the wave function of a system of electrons has to be anti-symmetric with respect to the interchange of any two electronic indices, thus Ψ will be anti-symmetric in electronic spatial and spin co-ordinates.

In *ab initio* quantum calculations the state is usually constructed from an anti-symmetrized product of one-electron molecular spin orbitals, which is a product of a one-electron spatial orbital and a one-electron spin function. The spin function can have two values: α or β , representing the spin-up or spin-down state of the electron. The one-electron spatial orbital is determined by solving the time-independent Schrödinger equation for a single electron in the electric field of the nuclei. The one-electron eigenvalue problem delivers a set of energy eigenvalues, $E_1, E_2, \dots, E_i, \dots$ and a set of spatial orthonormal orbital functions $\Phi_1(\mathbf{r}), \Phi_2(\mathbf{r}), \dots, \Phi_i(\mathbf{r}), \dots$. From every spatial orbital, $\Phi_i(\mathbf{r})$, two spin-orbital-functions can be constructed, $\Phi_i(\mathbf{r}_1)\alpha(1)$ and $\Phi_i(\mathbf{r}_1)\beta(1)$, where index i refers to the i th orbital, and (1) refers to electron #1.

The simplest anti-symmetrized wave function, called molecular configuration, is constructed in the form of a Slater determinant composed of the spin orbital $\Psi_1, \Psi_2, \dots, \Psi_i, \dots$, as follows:

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_2, \dots, \mathbf{r}_{n_e}) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \Psi_1(1) & \Psi_2(1) & \dots & \Psi_{n_e}(1) \\ \Psi_1(2) & \Psi_2(2) & \dots & \Psi_{n_e}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_1(n_e) & \Psi_2(n_e) & \dots & \Psi_{n_e}(n_e) \end{vmatrix} \quad (\text{A14})$$

where in $\Psi_i(k)$ i refers to the i th orbital, and k refers to the k th electron. A Slater determinant incorporates the exchange correlation between electrons, which means that the motion of two electrons with parallel spins is correlated. However, motion of electrons with opposite spins remains non-correlated, and wave function (A14) is not an exact solution of the Schrödinger equation, because the Coulomb forces between electrons were neglected.

The Hartree–Fock self-consistent field method (HF-SCF) significantly improves the accuracy of a configuration-type wave function. The method assumes that the field seen by the i th electron depends on the spin orbitals of the other electrons. Thus an iterative procedure based on the variation principle can improve the spin orbitals. According to the variation principle the best wave function is the one which gives the lowest possible energy calculated from

$$E = \langle \Psi | \mathbf{H}_e | \Psi \rangle \quad (\text{A15})$$

Applying the HF-SCF method the effect of the Coulomb forces between the private electrons can be taken into account. However, no Slater determinant can cope with the correlation of the motion of electrons with opposite spins.

Let us assume that the number of spatial basis functions determined by HF-SCF is K , therefore we have $2K$ spin orbital, and for electrons we have $\binom{2K}{n_e}$ different configurations (determinants) for n_e electrons. Note that the HF ground state is just one of these, the others are excited configurations.

It has been shown that an arbitrary anti-symmetric function can be written as a linear combination of all possible Slater determinants formed from a complete set of one-electron functions. Thus the set of n_e -electron determinants is a complete set for the expansion of any n_e -electron wave function [19,22].

Let us assume that we start from a set of open-shell Hartree–Fock unrestricted spin orbitals, K of them have spin α , and K have spin β

$$\{\Psi_j^\alpha | j = 1, 2, \dots, K\} \quad \text{and} \quad \{\Psi_i^\beta | i = 1, 2, \dots, K\} \quad (\text{A16})$$

The two sets are unrestricted in the sense that although the spatial orbitals in both sets form an orthonormal set, the two sets of spatial orbitals overlap with each other. Nevertheless, the set of $2K$ spin orbitals form an orthonormal set either from spatial orthonormality ($\alpha\alpha$ and $\beta\beta$ case) or spin orthogonality $\alpha\beta$ case).

The n_e -electron state will be represented by a linear combination of Slater determinants formed from the $2K > n_e$ spin orbitals. We assume that the n_e -electron state formed from the n_e lowest energy spin orbitals has been determined by the HF-SCF method, thus we have a HF determinant $|\Psi_0\rangle$ composed of the spin orbitals (A16). The set of possible determinants formed from the $2K$ orbitals includes $|\Psi_0\rangle$, but it also includes singly, doubly, etc. excited determinants differing from $|\Psi_0\rangle$ in having one, two or more orbital replaced by an orbital not present in $|\Psi_0\rangle$. The n_e -electron state can be represented by

$$|\Phi\rangle = \sum_i a_i |\Psi_i\rangle \quad (\text{A17})$$

where i runs from 0 to $\binom{2K}{n_e}$.

We assume that a nanodevice have n different stationary quantum states

$$|\Phi_1\rangle, |\Phi_2\rangle, \dots, |\Phi_n\rangle \quad (\text{A18})$$

and in

$$|\Psi\rangle = c_1|\Phi_1\rangle + c_2|\Phi_2\rangle + \dots + c_N|\Phi_n\rangle \quad (\text{A19})$$

the probability amplitudes c_1, c_2, \dots, c_n form a complete set. The probability of finding a device in state $|\Phi_1\rangle$ is $|c_1|^2$, in state $|\Phi_2\rangle$ is $|c_2|^2, \dots$, and finding in state $|\Phi_n\rangle$ is $|c_n|^2$. We also assume that

$$\langle\Phi_i|\Phi_j\rangle = \delta_{ij} \quad (\text{A20})$$

holds, i. e. the pure stationary states $|\Phi_i\rangle$ form an orthonormal set. The expectation value of an observable \mathbf{A} in a mixed state becomes

$$\langle A \rangle = \sum_{i=1}^n |c_i|^2 \langle\Phi_i|\mathbf{A}|\Phi_i\rangle \quad (\text{A21})$$

APPENDIX B: $SU(N)$ GENERATORS AND STRUCTURE CONSTANTS FOR $n=2$ AND 3 [10]

Let us denote by $|1\rangle, |2\rangle, \dots, |n\rangle$ the orthonormal eigenvectors spanning the n -dimensional Hilbert space. They define n^2 projection operators

$$\mathbf{P}_{kl} = |k\rangle\langle l|, \quad k, l = 1, 2, \dots, n \quad (\text{B1})$$

which define $s = n^2 - 1$ operators as follows:

$$\begin{aligned} \mathbf{U}_{ik} &= \mathbf{P}_{ik} + \mathbf{P}_{ki} \\ \mathbf{V}_{ik} &= \mathbf{j}(\mathbf{P}_{ik} - \mathbf{P}_{ki}) \\ \mathbf{W}_l &= -\sqrt{\frac{2}{l(l+1)}}(\mathbf{P}_{11} + \mathbf{P}_{22} + \dots + \mathbf{P}_{ll} - l\mathbf{P}_{l+1, l+1}), \end{aligned} \quad (\text{B2})$$

with $1 \leq i < k \leq n$, $1 \leq l \leq n - 1$. The generators of $SU(n)$ are determined by Equation (B2) as

$$(\mathbf{T}_1, \mathbf{T}_2, \dots, \mathbf{T}_i, \dots, \mathbf{T}_s) = (\mathbf{U}_{12}, \dots, \mathbf{U}_{n-1, n}, \mathbf{V}_{12}, \dots, \mathbf{V}_{n-1, n}, \mathbf{W}_1, \dots, \mathbf{W}_{n-1}) \quad (\text{B3})$$

It can be shown that any $n \times n$ Hermitean time-varying matrix, \mathbf{A} , can be expressed as a linear combination of the generators of $SU(n)$

$$\mathbf{A} = \frac{1}{n} \text{Tr}\{\mathbf{A}\} \mathbf{1} + \frac{1}{2} \sum_{i=1}^s \lambda_i \mathbf{T}_i \quad (\text{B4})$$

and the coefficients $\lambda_1, \lambda_2, \dots, \lambda_s$ are real numbers

SU(2) GENERATORS

$$\begin{aligned} \mathbf{T}_1 &= \mathbf{P}_{12} + \mathbf{P}_{21} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \\ \mathbf{T}_2 &= j(\mathbf{P}_{12} - \mathbf{P}_{21}) = \begin{bmatrix} 0 & j \\ -j & 0 \end{bmatrix} \\ \mathbf{T}_3 &= -\mathbf{P}_{11} + \mathbf{P}_{22} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \end{aligned} \quad (\text{B5})$$

SU(2) STRUCTURE CONSTANTS

$$f_{123} = f_{231} = f_{312} = 1, \quad f_{132} = f_{321} = f_{213} = -1, \quad \text{otherwise } 0 \quad (\text{B6})$$

SU(3) GENERATORS

$$\mathbf{T}_1 = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \mathbf{T}_2 = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \mathbf{T}_3 = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \mathbf{T}_4 = \begin{bmatrix} 0 & j & 0 \\ -j & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{T}_5 = \begin{bmatrix} 0 & 0 & j \\ -j & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \mathbf{T}_6 = \begin{bmatrix} 0 & 0 & j \\ 0 & -j & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \mathbf{T}_7 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{T}_8 = \begin{bmatrix} -\frac{1}{\sqrt{3}} & 0 & 0 \\ 0 & -\frac{1}{\sqrt{3}} & 0 \\ 0 & 0 & \frac{2}{\sqrt{3}} \end{bmatrix}$$

SU(3) STRUCTURE CONSTANTS

$f_{ijk} =$	+1	for	$(i, j, k) =$	(1, 4, 7)	(4, 7, 1)	(7, 1, 4)
	-1	for	$(i, j, k) =$	(4, 1, 7)	(1, 7, 4)	(7, 4, 1)
	$+\frac{1}{2}$	for	$(i, j, k) =$	(2, 1, 6)	(1, 6, 2)	(6, 2, 1)
				(3, 1, 5)	(1, 5, 3)	(5, 3, 1)
				(3, 2, 4)	(2, 4, 3)	(4, 3, 2)
				(2, 5, 7)	(5, 7, 2)	(7, 2, 5)
				(3, 7, 6)	(7, 6, 3)	(6, 3, 7)
				(5, 4, 6)	(4, 6, 5)	(6, 5, 4)
				$-\frac{1}{2}$	for	$(i, j, k) =$
	(1, 3, 5)	(3, 5, 1)	(5, 1, 3)			
	(2, 3, 4)	(3, 4, 2)	(4, 2, 3)			
	(5, 2, 7)	(2, 7, 5)	(7, 5, 2)			
	(7, 3, 6)	(3, 6, 7)	(6, 7, 3)			
	(4, 5, 6)	(5, 6, 4)	(6, 4, 5)			
	$+\frac{1}{2}\sqrt{3}$	for	$(i, j, k) =$			
				(2, 5, 8)	(5, 8, 2)	(8, 2, 5)
	$-\frac{1}{2}\sqrt{3}$	for	$(i, j, k) =$	(6, 3, 8)	(3, 8, 6)	(8, 6, 3)
				(5, 2, 8)	(2, 8, 5)	(8, 5, 2)
0	for	$(i, j, k) =$	0	otherwise		

ACKNOWLEDGEMENTS

The authors are grateful to L. O. Chua, G. I. Iafate, C. S. Lent, J. Nossek, T. Roska, and O. G. Wiest for stimulating discussions. This work was supported in part by a joint grant of NSF (National Science foundation INT96-15497) and HAS (Hungarian Academy of Sciences), and also by the Office of Naval Research MURI program.

REFERENCES

1. Ferry DK, Goodnick SM. *Transport in Nanostructures*. Cambridge University: Cambridge, 1997.
2. Jortner J, Ratner M. *Molecular Electronics, A 'Chemistry for the 21st Century' Monograph*. Blackwell Science: 1997; 1–117.
3. Iafate GJ, Scorsio MA. Application of quantum-based devices: trends and challenges. *IEEE Transactions on Electron Devices* 1996; **43**(10):1621–1625.
4. Seabaugh AC, Mazumder P (eds). *Proceedings of the IEEE Special Issue on Quantum Devices and Their Applications* 1999; **87**(4):535–687.
5. Grabert H, Devoret MH. *Single-Charge Tunnelling—Coulomb Blockade Phenomena in Nanostructures*. NATO ASI Series, vol. B-294, Plenum Press: New York, 1992.
6. Seminario JM, Tour JM. Ab Initio methods for the study of molecular systems for nanometer technology: toward the first-principles design of molecular computers. In *Molecular Electronics Science and Technology, Annals of the New York Academy of Sciences*, Aviram A, Ratner M (eds). New York Academy of Sciences: New York, 1998; 68–94.
7. Lent CS, Tougaw PD, Porod W, Bernstein GH. Quantum cellular automata. *Nanotechnology* 1993; **4**(1):49–57.
8. Porod W, Lent CS, Bernstein GH, Orlov AO, Amlani I, Snider GI, Merz JL. Quantum-dot cellular automata: computing with coupled quantum dots. *International Journal of Electronics* 1999; **86**(5):549–590.

9. Lent CS. Bypassing the transistor paradigm. *Science* 2000; **288**(5471): 1597–1599.
10. Mahler G, Weberruss VA. *Quantum Networks, Dynamics of Open Nanostructures*. Springer: Berlin, 1995.
11. May V, Kuhn O. *Charge and Energy Transfer Dynamics in Molecular Systems*. Wiley-VCH: Berlin, 1999.
12. Alicki R, Lendi K. *Quantum Dynamical Semigroups and Applications*. Lecture Notes in Physics, vol. 286. Springer: Berlin, 1987.
13. Chua LO. Device modelling via basic nonlinear circuit elements. *IEEE Transactions on Circuits and Systems* 1980; **27**(11):1014–1044.
14. Marcuvitz N, Schwinger J. On the representation of the electric and magnetic fields produced by currents and discontinuities in wave guides. *Journal of Applied Physics* 1951; **22**(6):806–819.
15. Szabo A, Ostlund NS. *Modern Quantum Chemistry, Introduction to Advanced Electronic Structure Theory*. Dover: Mineola, New York, 1996.
16. Stone AJ. *The Theory of Intermolecular Forces*. Clarendon Press: Oxford, 1996.
17. Lent CS, Timmler J. Private communication.
18. Niemier MT, Kogge, PM. Problems in designing with QCAs: layout-timing. *Special Issue on Nanoelectronic Circuits, International Journal of Circuit Theory and Applications*, 2001; **28**(6): in this issue.
19. Csurgay AI, Porod W, Lent CS. Signal processing with next-neighbour-coupled time-varying quantum-dot arrays. *IEEE Transactions on Circuits and Systems Part I* 2000; **47**(8).
20. Chua LO. *CNN: A Paradigm for Complexity*. World Scientific: Singapore, 1998.
21. Csaba Gy, Csurgay AI, Porod W. Computing architecture of next-neighbour-coupled optically pumped nanodevices. *Special Issue on Nanoelectronic Circuits, International Journal of Circuit Theory and Applications* 2001; **29**: in this issue.
22. Thorne KS (ed.). *Quantum Measurements*. (Braginsky VB, Khalili FY) Cambridge University Press: Cambridge, 1995.
23. Mandel L, Wolf E. *Optical Coherence and Quantum Optics*. Cambridge University Press: Cambridge, 1995.
24. Csurgay AI, Porod W. Network representation of molecular arrays. *Proceedings of ECCTD'99*: Streza, 1999; 815–818.
25. Chaudhuri JR, Banik SK, Deb B, Ray DS. Modified Bloch equations in the presence of non-stationary bath. *European Physics Journal* 1999; **D 6**:415–424.