

Role of the Dissipative Organic Matrix in the Two-electron Transfer in the Dimer Nanocluster

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Abstract — The influence of dissipative environment, such as a weak structured organic matrix, on the electron transfer kinetics in the dimer nanocluster with two electrons is theoretically investigated. The theoretical model within a stochastic approach is formulated as minimal. For this aim, Redfield's theory for the reduced density matrix is used, and then Haken-Strobl approximation is performed. For the dimer nanocluster the model "two centers – two electrons" is considered with using Hubbard's Hamiltonian. Thereby, the electron correlation is taken into account. It was found that the difference in the electron populations on the dimer nanocluster centers has an oscillatory time dependence with a beats, which is damping due to the influence of a dissipative environment. This shows that a dissipative environment leads to the relaxation in the nano-system studied here, so that the periodical switching of nanodimer between the states with the opposite directions of its dipole moment is dumped. Eventually, the dimer nanocluster relaxes from an initial state with two electrons on one center to the final state with a uniform distribution of electrons on the centers. It is shown how the process of switching is modified for the different values of the nanodimer parameters at given value of the dissipation parameter. The presence of the different switching regimes in the considered nano-system is interesting for various device applications due to the ability to control the state of such nano-system by action of the external electric and magnetic fields.

Index Terms — dimer nanocluster, dissipation, electron correlation, electron transfer, stochastic processes.

I. INTRODUCTION

The number and variety of investigations on the kinetics processes in the different nanocluster systems, with account of its interaction with surrounding organic matter, is growing rapidly. For the organic matrices are characteristic, that its can be considered as the weakly structured systems on the macro-level and as the multimode systems (due to a large number of high-frequency and low-frequency degrees of freedom). It should be noted, that not only matrices of organic type can be considered as a weakly structured matrices on the macro-level, but also the different polymeric or amorphous one. Definitely, the organic materials with embedded nanocomplexes (nanoclusters, nanostructures) began to acquire the importance for applications in micro- and nanoelectronics [1], [2], and the purpose of this study to formulate theoretically a simple enough approach for taking into account the influence of an organic matrix on the time dynamics of the nanocluster embedded in it.

The given paper presents the minimal theoretical model, which describes the features of the electron transfer in a nanocluster embedded in a weakly structured multimode organic matrix. Here, it is considered an elementary nanocluster system – a dimer nanocluster with two electrons in the model "two centers – two electrons", in which the electronic subsystem of each center is represented by one molecular orbital (for details see [3], [4]). Note that, such model of the dimer nano-system is suitable for consideration not only the tunnel-coupled molecular complexes (such as dimers of TCNQ or TTF molecules), but and the tunnel-coupled quantum dots. The

proposed model describes a nanodimer as a quantum mechanical system, which is stochastically interacted with a dissipative environment. Thus, it is assumed that a coupling between the electronic states of a nanodimer and the degrees of freedom of an organic matrix is described by Gaussian random variables. The stochastic process is Gauss-Markov of the "white noise" type, i.e. the correlation functions are δ -correlated in time. It is quite sufficient to describe the time dynamics of processes within nanodimer embedded in an organic matrix. As is known, the dissipative reservoir can be described in different manner with using different spectral densities of noise (see more detail ref. [5]–[7]). Eventually, that gives the different regimes of a dissipation and relaxation. In our case, the noise spectral density of the dissipative reservoir is a linear that leads to the dissipation regime of ohmic type. In such way, a weak structured matrix plays the role of a dissipative environment (i.e. thermostat), and its influence on a dimer nanocluster is taken into account in frame of Redfield's theory for the reduced density matrix [8]. Further, the quantum-mechanical calculation is performed using the Haken-Strobl model. Note that, Haken-Strobl approximation has been used successfully to model the different nano-systems, which are contained in the organic materials. So, for example in [9], Haken-Strobl approximation was efficiently used to study the energy transfer kinetics in the light-harvesting systems. Actually, this approximation allows significantly simplifying of the calculation, taking into account the most characteristic features of the nano-system, while the condition of smallness for the coupling of the nano-system and thermostat is not imposed.

II. THEORETIAL APPROACH

An account of the electronic correlations in the nano-systems are most convenient when the calculation is performed using the Hubbard's Hamiltonian [3], [4], [10]. For the given dimer nanocluster Hubbard's Hamiltonian has the simplest view [4]. Due to the influence of environment on the nano-system the fluctuations of values of parameter U (Coulomb repulsion of electrons at the same center) and parameter F (the tunneling electron transfer between the dimer centers) occur. Namely, the change in the local potentials on centers leads mainly to a random variation of the parameter U , and the change in the potential inter-center barrier leads to a random variation of the parameter F . That is, the full Hamiltonian should contains the stochastic additives ($\delta U(t)$ and $\delta F(t)$, respectively) to parameters U and F , which are the functions of the electronic degrees of freedom of the dimer. Thus, the model Hamiltonian can be written as follows:

$$H = H_0 + V(t) \quad (1)$$

$$H_0 = U \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + F \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad (2)$$

$$V(t) = \delta U(t) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \delta F(t) \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \quad (3)$$

The analysis of the electron transfer kinetics in the dimer nanocluster is carried out from the time dependence of difference of the diagonal density matrix elements $\rho_{11}(t) - \rho_{33}(t)$. If the eigenvalues E_n and eigenfunctions $|\varphi_n\rangle$ of Hubbard's Hamiltonian are found, then is not difficult to execute the calculation of the wavefunction $|\varphi(t)\rangle$, representing it as a superposition of $|\varphi_n\rangle$ (see for example [3], [4]). Finally with account $V(t)$, the average value of the electron population difference on the dimer centers $\langle n(t) \rangle$ is found. This value is expressed through the difference of the density matrix elements $\rho_{11}(t) - \rho_{33}(t)$, which are found from Redfield's equation for the density matrix [8].

In common case, for the system described of Hamiltonian (1) the equation for the density matrix is written as a system of 9 differential equations in which the averaging over realizations of the random process is performed. Hereafter, for the simplicity and possibility to obtain for the solution in an analytical form was used Haken-Strobl model, which implies that the relaxation of excitation in a thermostat is much faster than in a small system (the limit of ultrashort correlation times in a dissipative reservoir), in fact the high-temperature approximation is assumed. So, the cross-fluctuations in this model are negligible, while the diagonal fluctuations are δ -correlated.

III. RESULTS AND DISCUSSION

Thus, in this approach the system of 9 differential equations is reduced up to 3 equations only for the

diagonal density matrix elements. Also it is taken into account that the sum of the diagonal density matrix elements equal to one. As a result, it is shown that in considered case the expression for the average value of the electron population difference on the centers of nanodimer, embedded in a weak structured matrix, has the following simple analytical appearance:

$$\langle n(t) \rangle = \frac{8F^2}{R} \left\{ \frac{\cos\left[\frac{(U+R)t}{2}\right]}{R+U} + \frac{\cos\left[\frac{(U-R)t}{2}\right]}{R-U} \right\} e^{-\gamma t};$$

$$R = \sqrt{U^2 + 8F^2} \quad (4)$$

In Haken-Strobl approximation used here it is obtained that the average value of the electron population difference on the dimer centers has a relaxation character in time with ohmic type damping due to the influence of the dissipative environment on the electron transfer kinetics.

In given paper the parameters U , F and γ are treated as phenomenological determined. Within the frames of the given consideration the weak structured matrix (in the role of a dissipative reservoir) is characterized by value of the single dissipation parameter γ , and the nanodimer is characterized by certain values of one-center Coulomb repulsion parameter U and tunneling parameter F . The values of parameters U and F are defined by chemical compound and structure of the molecular centers of dimer, distance between its centers, and generally depend also on internal vibrational dynamics of dimer nano-systems. As it is shown, for example in [4], the effect of the intra-molecular (on the molecular centers) and inter-center vibrations of nanodimer on its electronic subsystem is easy to take into account by performing the appropriate renormalization of parameters U and F . In general case, the parameter γ can be considered not only as phenomenological, such for example [11], for a particle in the two-well potential of the analytical expression for γ in the second-order perturbation theory is given.

Also, note that when for the studied process the detailed temporal dynamics is known from experiment, then on the basis of the fluctuating fluorescence analysis can be refined microscopic model and its base parameters. The theoretical calculation of the certain time characteristic for a nano-system embedded in a dissipative reservoir gives the value averaged over the fluctuating realizations in frame some model with certain type of the dissipation regime. With using the experimental methods, enabling the direct observation of fluctuations at the room temperature (that it is essential for the biological systems), such as the single-molecule spectroscopy [12], [13] is possible to get a lot of different experimental realizations for the fluctuating time characteristic of the studied nano-system. And then, on the optimum conformity of the theoretical time dependencies and experimental data (after averaging on experimental realizations) the values of model parameters U , F and γ (with the account of possible renormalization) can be appropriately identified. Also, in this way type of the dissipation regime can be specified.

Accordingly with (4), that is shown in Figs. 1–6, the

calculated time dependence $\langle n(t) \rangle$ has the damped oscillation structure with the beats. Since the average value of the electron population difference on the quantum dimer centers directly connected with the existence of dipole moment, then the curves on Figs. 1–6 actually show the changes of the dipole moment in time. It should be emphasized the fact that in the simulated system the switching regime takes place: the nanodimer relaxes to the state with the uniform distribution of electrons on the centers, at while periodically switching between the states with the opposite directions of the dipole moment.

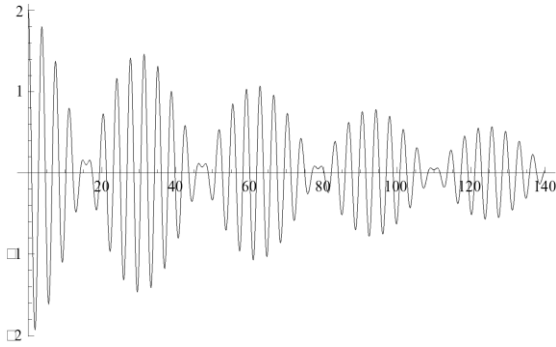


Fig. 1 The time dependence $\langle n(t) \rangle$ at $\gamma = 0,01$ and the values of parameters $U = 0,2$ and $F = 1,2$.

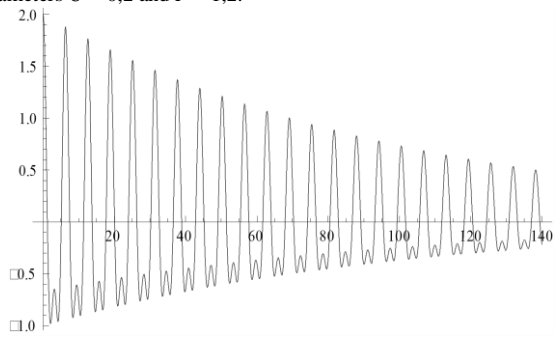


Fig. 2 The time dependence $\langle n(t) \rangle$ at $\gamma = 0,01$ and the values of parameters $U = 1,0$ and $F = 1,0$.

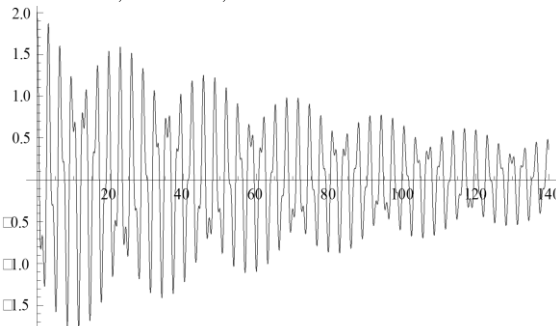


Fig. 3 The time dependence $\langle n(t) \rangle$ at $\gamma = 0,01$ and the values of parameters $U = 2,2$ and $F = 2,0$.

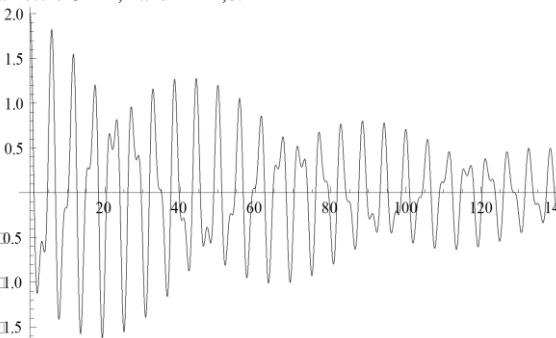


Fig. 4 The time dependence $\langle n(t) \rangle$ at $\gamma = 0,01$ and the values of parameters $U = 1,0$ and $F = 1,1$.

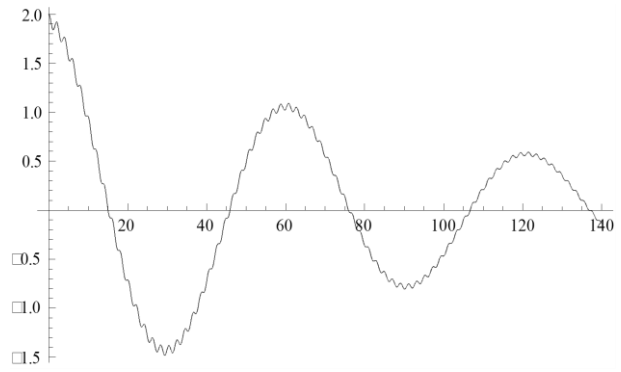


Fig. 5 The time dependence $\langle n(t) \rangle$ at $\gamma = 0,01$ and the values of parameters $U = 3,0$ and $F = 0,4$.

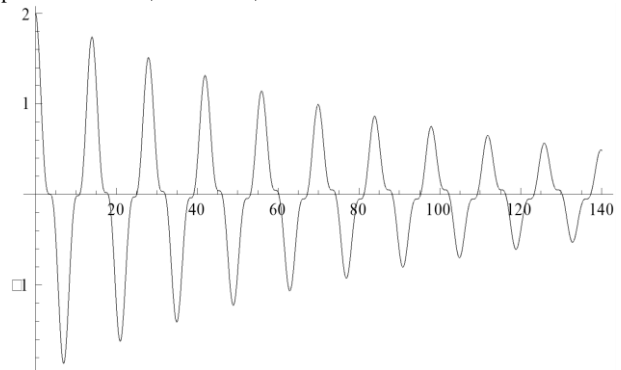


Fig. 6 The time dependence $\langle n(t) \rangle$ at $\gamma = 0,01$ and the values of parameters $U = 0,9$ and $F = 0,55$.

The time dependencies $\langle n(t) \rangle$ received at the various values of dimer nano-system parameters demonstrate as the switching regime is changed in depending on the ratio of parameters U and F . At ratio $U/F = 1$, takes place switching regime shown in Fig. 2, which is most asymmetric and it is very sensitive to the small variations of the values U and F . As shown in Fig. 3 and Fig. 4 a slight deviation of ratio U/F from 1 leads to a more symmetric regime of switching (as at $U > F$ and as at $U < F$). It is also essential, that at a given ratio U/F with rise U and F the number of these switching increases. Accordingly, by selecting of parameter values of U and F can be achieved a given number of switching with appreciable value of the dipole moment of the dimer. When U/F is much greater than 1 (Fig. 5) is most clearly manifested damped harmonic regime with small amplitude modulations.

It should be noted that the maximal symmetric regimes are obtained when U is in several times smaller than F (see Fig. 1), and as well as the $U/F = 1,62$ (see Fig. 6).

IV. CONCLUSION

As it follows from the analysis of the time dependence of $\langle n(t) \rangle$ the dissipative environment, in particular such as an organic matrix, significantly affects on the internal dynamics of electrons in the nanodimer with two extra electrons, so that the nanodimer in the switching regime eventually goes into the state in which it is sensitive to an action of magnetic field. So here, it is essential that at the initial time the two electrons in the dimer are on the same center, i.e. the dimer is a dipole-active. The stochastic influence of the environment on the dimer leads to the relaxation effect, so that the electrons are redistributed in finally one for each dimer center, i.e. the dimer is a

magnito-active. Thus, the dimer with two extra electrons relaxes from the initial dipole-active state to the final magnetic-active state. Herewith, the dipole moment direction of dimer is periodically switched on opposite during the relaxation process. Consequently, the dimer nano-system of the similar kind due to a presence of the switching regime in it can be used as an electronic switch, operating under the control of external magnetic and electric fields.

Thus, the minimal theoretical model for calculation of the time dependence of the average value of the electronic population difference on the dimer centers is as follows. The quantum-mechanical calculation is based on successive application of Redfield's approach (method of the reduced density matrix) and Haken-Strobl approximation, in accordance with which the noise spectral density of thermostat turns a linear. For the nanodimer the model "two centers – two electrons" is used. The Hamiltonian of problem corresponds to Hubbard's Hamiltonian, in which the stochastic terms $\delta U(t)$ and $\delta F(t)$ are included. These terms are describing the coupling between the nano-system and thermostat, which has a character of the stochastic Markov's process (type of "white noise"). The applied approach, in result, allows to simply carry out an analysis of the corresponding experimental data and to expedite modeling, to find the approximate quantitative estimations, and to use them for the qualitative description of behavior of such nano-systems.

Finally, as a consequence, for the dimer nano-system in the dissipative environment the possible response on the action of the external fields is determined both the electron transfer kinetics in the dimer nanocluster and parameters of the stochastic processes related with the influence of environment. The specified features of dynamics of such nano-systems make them attractive for use in the device applications, for example, as the switches of the various kinds.

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