

# Electron Transfer Dynamics as Regulator of Biological Activity in Biomolecular Systems Coordinated by Trimer Nanoclusters

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**Abstract** — In the given paper the minimal theoretical model for the description of kinetic processes in the organic nanocomposite material is offered. The subject of simulation is a three-center nanocluster embedded in an organic matrix. It is assumed that this three-center nanocluster has two equivalent centers tunnel-coupled with the intermediate center. Here, it is taken into account the influence on the electron and vibrational dynamics of such nanocluster the following external factors: the periodic electric field and the surrounding matrix. It is supposed that the organic matrix contains in a basis the biopolymer or a supra-molecular protein system, and also it is considered as a weak ordered and nondissipative. Applying the extended Holstein's Hamiltonian, choosing the wave function in the form electron-vibrational coherent package and using the canonical Hamilton's equations the differential equation system relatively the chosen variational parameters was obtained. Hereafter, this differential equation system was solved numerically and some of the results, which represent the most interesting regimes of the electron density distribution, were depicted graphically. Finally, these regimes are analyzed with regard to their possible application in the optoelectronics and regard to their ability to affect the biological activity of investigated system.

**Index Terms** — electric field, electron localization, protein and biopolymer matrix, trimer nanocluster, vibrational modes

## I. INTRODUCTION

The supra-molecular protein systems and synthetic biopolymers coordinated by the various nanoclusters have been widely used as the components of organic electronics and pharmaceuticals [1, 2]. Whereby, there is the continued interest in characterizing of the properties of such biocomposite materials connected with the electron transfer dynamics [1, 2]. The most interesting problems for the supra-molecular protein systems and biopolymers, as the systems with a weak ordering and expressed inhomogeneity, are related to a nature of localized states in such systems and possibility of structural changes connected with a trapping of the charge or excitation on these states [2, 3]. The structural complexity of organic composite systems leads naturally to many questions: concerning to a correct description of the localized and delocalized states in such weak ordered systems; regarding to a relation of the protein conformation and electron excitations; relating to a connection of the structural relaxation dynamics and electron localization; about how can explicitly to observe and effectively to control a conformational rearrangement in such biocomposites and what are those parameters or processes that for this purpose are the most suitable. The theoretical approach proposed here gives an enough complete description with the account of main factors that can to influence on a biological activity of the synthetic biopolymers and supra-molecular protein systems coordinated by the trimer nanoclusters (NCs). The specific properties of the trimer NC as well as an organic weak ordered matrix take into account by an appropriate choice of model parameters.

## II. THEORETICAL APPROACH

Further, in this paper it is offered the minimal microscopic model for the organic nanocomposite material. This is the model for the three-center NC with one "excess" tunneling electron, which is embedded in an organic matrix and is under the action of an external periodic electric field. In the given model the matrix is taken into account as a nondissipative and the NC is the trimer of bridge type in which the trimer's centers are considered together with their nearest ligands environment. Such consideration of the embedded NCs can be applied as for the simplest small NCs in which the centers are the ions 3d-metals and their oxides with the various oxidation degrees and for a simulation of the large supra-molecular protein complexes, such as the Fenna-Matthews-Olson (FMO) protein complex. The FMO protein complex, which is the base functional unit coordinated in the vicinity of active site of the photosynthetic light-harvesting system, is also a trimer because it consists from the three pigment-protein complex [4, 5]. One of the main features proved experimentally for the supra-molecular protein systems is the existence of the long-lived coherences [4, 5]. In our model consideration this fact takes into account by a use of Davydov's ansatz for the wave function: it is expressed through variational parameters which are convenient for the simulation.

For the theoretical simulation of the intracuster vibrational dynamics and extent of electron localization (delocalization) the model Holstein's Hamiltonian [6, 7] supplemented by the terms responsible for the interactions of a NC with an external periodic electric field and with a vibrational system of a nondissipative matrix, is used:

$$\begin{aligned}
 H = & t_0 \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} + g_1 q_1 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} + g_2 q_2 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \\
 & + \Delta \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + dE_0 \cos(\Omega t) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} + \\
 & + \sum_m \gamma_{mi} Q_i q_m + \frac{1}{2} \sum_{m=1}^2 (p_m^2 + \omega_m^2 q_m^2) + \frac{1}{2} (P_i^2 + \omega_{0i}^2 Q_i^2)
 \end{aligned} \quad (1)$$

Here,  $t_0$ ,  $g_m$  and  $\Delta$ , respectively, the tunneling parameter of an electron between the trimer's centers, the constant of the electron-vibrational interaction for  $m$ -th ( $m = 1, 2$ ) intracluster vibrational mode  $q_m$  and the detuning energy, which characterizes the nonequivalence of the intermediate trimer's center. Two other centers are considered as equivalent with equal values of electron energy levels, which is taken as the origin of count. The given intracluster vibrational modes are obtained after what a set of local vibrational modes was transformed into a set of generalized vibrational modes and the full-symmetric vibrational mode was eliminated from a consideration.

A further reasoning is based on the use of the time-dependent wave function, which has been written down as a superposition of electron-vibrational states in the coherent package form:

$$|\psi(t)\rangle = \sum_{j=1}^3 \alpha_j(t) \alpha_j^+ \exp \left[ -\frac{i}{\hbar \omega_0} \sum_{m=1}^2 (\beta_m(t) p_m - \pi_m(t) q_m) \right] |0\rangle \quad (2)$$

Here,  $\alpha_j(t)$ ,  $\beta_m(t)$ ,  $\pi_m(t)$  are the time-dependent variational parameters. They have a physical sense, respectively:  $|\alpha_j(t)|^2$  – the electron population on  $j$ -th center ( $j = 1, 2, 3$ ),  $\beta_m(t)$  and  $\pi_m(t)$  – the quantum-mechanical average values for the coordinate and impulse amplitudes of  $m$ -th intracluster vibration. Further, for obtaining of the system of differential equations relatively the indicated variational parameters values the canonical Hamilton's equations are used.

Thus, the system of differential equations obtained in a result has the following form:

$$\begin{aligned}
 \frac{d\pi_1}{dt} &= -\omega_1^2 \beta_1 - g_1 (|\alpha_1|^2 - |\alpha_3|^2) - \gamma_1 Q_i, \\
 \frac{d\pi_2}{dt} &= -\omega_2^2 \beta_2 - g_2 (|\alpha_1|^2 + |\alpha_3|^2) - \gamma_2 Q_i, \\
 \frac{d\beta_1}{dt} &= \pi_1, \quad \frac{d\beta_2}{dt} = \pi_2 \\
 i \frac{d\alpha_1}{dt} &= t_0 \alpha_2 + g_1 \beta_1 \alpha_1 + g_2 \beta_2 \alpha_1 + dE_0 \cos(\Omega t) \alpha_1 \\
 i \frac{d\alpha_2}{dt} &= t_0 (\alpha_1 + \alpha_3) + \Delta \alpha_2 \\
 i \frac{d\alpha_3}{dt} &= t_0 \alpha_2 - g_1 \beta_1 \alpha_3 + g_2 \beta_2 \alpha_3 - dE_0 \cos(\Omega t) \alpha_3
 \end{aligned} \quad (3a)$$

Note that the equations (3a) for the intracluster vibrational subsystem include the quantities, which characterize the NC's electron subsystem and matrix's vibrational mode  $Q_i$ , and the equations (3b) for the NC's electron subsystem contains the parameters of its

vibrational subsystem. Here also, it is assumed that the equation of motion for the external mode of matrix has the form characteristic for the harmonic oscillator under the action of the driving force, whose role is performed by the vibrational subsystem of trimer NC:

$$\frac{d^2 Q_i}{dt^2} + \omega_{0i}^2 Q_i = -\gamma_1 \beta_1 - \gamma_2 \beta_2 \quad (4)$$

All frequencies contained in the expressions (1) – (4) are taken in the units of characteristic frequency  $\omega_0$  of the matrix's mode, i.e. it is taken that  $\omega_{0i} = \omega_0$ . Also, in the expression (1), all summands are given in the units  $\hbar \omega_0$ .

Hereafter, it is used that the processes in the vibrational system of the matrix can be considered as a much slower than in the NC. It allows to neglect the second derivative in (4), and the resultant expression for  $Q_i$  to substitute in (3a). Herein also, the constants  $\gamma_m$  are supposed equal, i.e.  $\gamma_m = \gamma$ . As a result, the vibrational degrees of freedom of the surrounding matrix are completely eliminated. Therefore, the equations for the intracluster modes will be explicitly linked. In addition to that the intracluster modes are implicitly connected due to electron-vibrational interaction. The existence of such cross-relations between the intracluster modes significantly affects on the character of energy exchange between them.

Note that, such consideration of the vibrational system of matrix corresponds to the simplest approximation – continuum, i.e. a matrix is considered as a quasi-homogeneous and is characterized by a single mode. In a more general case the model Hamiltonian (1) will contain the terms, which describe the contributions of additional matrix's modes with other frequencies and various  $\gamma_{mi}$  (i.e. will need to perform the summation on the index  $i$ ).

### III. RESULTS AND DISCUSSION

The numerical decision according to (3a) and (3b) for many different sets of model parameters were completed and some of the most interesting characteristic regimes leading to the stable electron density distributions represented graphically on Fig.1 as the cases a), b), c) for the values of electron populations on the NC's centers and on Fig.2 as the same cases a), b), c) for the values of vibrational energy of the intracluster modes.

The analysis of the numerical results obtained within the given theoretical model allows to make the conclusion about the extent of electron localization in the trimer's centers, and about the distribution of vibrational energy between the intracluster modes, and how they depend from the internal model parameters. Also, from the obtained data follows that such external model parameters, as a frequency of the external periodic electric field and intensity of the interaction of the NC's electron subsystem with the periodic electric field, are the convenient operating parameters for switching of the electron density distribution regimes in the trimer NC (as it follows from a comparison of Fig.1a and Fig.1b). Besides, the electron density distribution in the trimer NC is considerably determined by the account of the interaction of its intracluster modes with the external mode of surrounding matrix (this regime see Fig.1c).

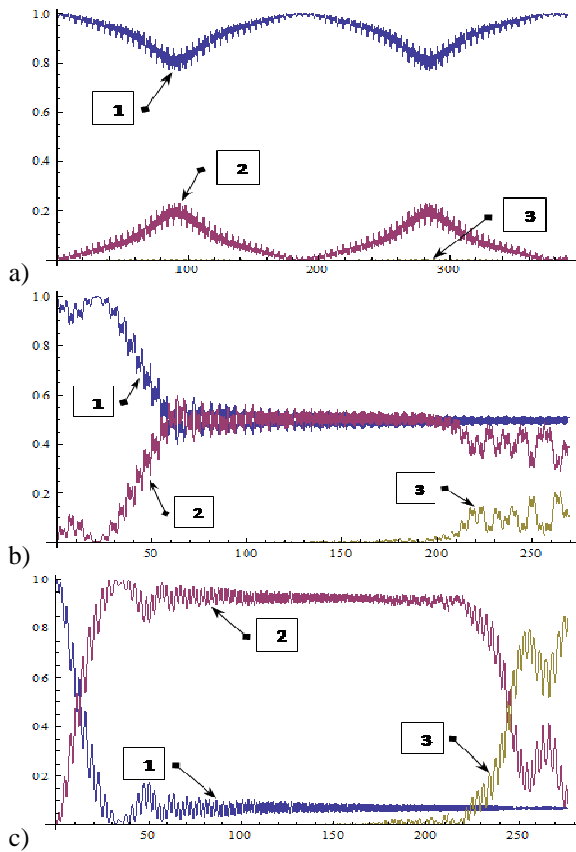


Fig.1. The time dependence of the electron population  $|\alpha_j(t)|^2$  on  $j$ -th center ( $j = 1, 2, 3$ ).

For all cases a), b), c) shown on Fig.1 and on Fig.2:  $t_0 = 1/5$ ,  $g_1 = g_2 = 1$  and the time is expressed in the units  $\omega_0^{-1}$ . The Fig.1a and on Fig.2a shows the case without the influence of external factors. In this case the corresponding parameters for the electric field and the surrounding matrix are taken equal to zero, i.e.  $dE_0 = 0$  and  $\gamma = 0$ . For the cases b), c) on Fig.1 and Fig.2 the electric field parameters are  $dE_0 = 4$  and  $\Omega = 1/88$ . The other model parameters for the cases shown on Fig.1 and Fig.2 are: in a) –  $\Delta = 4.7$ ;  $\beta_1(0) = 0$ ;  $\pi_1(0) = 4$ ;  $\omega_{1,2} = \sqrt{2}$ , in b) –  $\Delta = 7$ ;  $\beta_1(0) = 0$ ;  $\pi_1(0) = 4$ ;  $\omega_{1,2} = \sqrt{2}$ , in c) –  $\Delta = 5.5$ ;  $\beta_1(0) = 0$ ;  $\pi_1(0) = 0.9$ ;  $\pi_2(0) = 0.9$ ;  $\omega_{1,2} = \sqrt{4}$ ;  $\gamma = 0.235$ .

It is revealed that depending on the ratio of the internal and external parameters of the presented model can occur or accumulation (localization) of the electron density on any of the centers of the trimer NC according to the share of its population, and in this case two other centers actively exchange an electron (delocalization), or on all three centers a some certain distribution of electron density is established. At that the vibrational and electron subsystems of the NC remain during a time evolution in a form of the coherent electron-vibrational package distributed on the NC's centers according to an extent of the electron localization on these centers.

An advantage of the offered model is that there are the different relations between its subsystems not only explicit according to the corresponding terms in (1), but also implicit as the cross-relations.

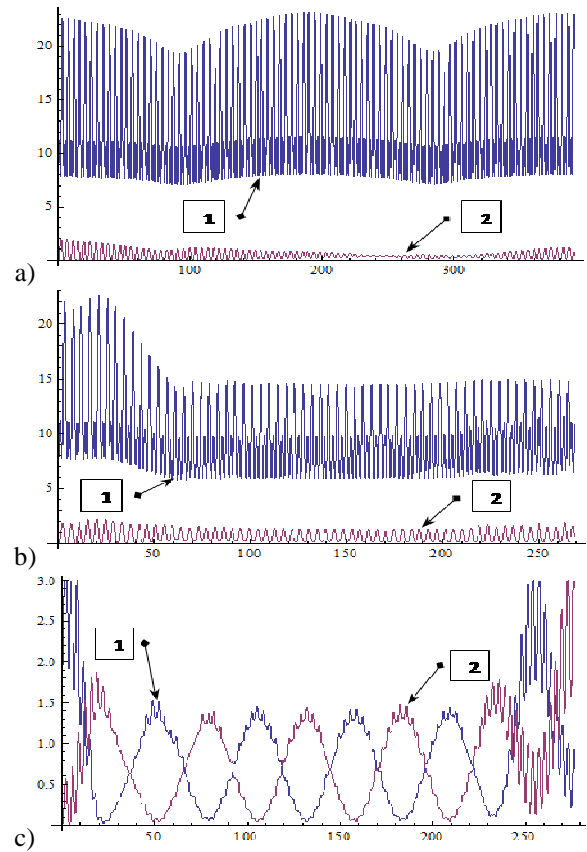


Fig.2. The time dependence of the vibrational energy  $\varepsilon_m(t)$  for  $m$ -th intracluster mode ( $m = 1, 2$ ),  $\varepsilon_m(t) = 1/2(\beta_m(t)^2 + \pi_m(t)^2)$ .

So, in our model the external periodic electric field affects not only on the electron dynamics in the NC (explicit), but also on the intracluster vibrational dynamics through the cross-relation between these modes due to the electron-vibrational interaction (implicit).

Note also that, a more complete model description suggests the account of dissipative effects in the matrix. So, as it was indicated in paper [4], in the supra-molecular protein systems the influence of dissipative effects in the matrix leads to the noise-assistant transport of excitation and at the certain conditions a noise in conjunction with a long-lived coherence can to play a constructive role supporting the transport of excitation.

Despite this, the specificity of our model consist in that the vibrational energy is redistributed between the intracluster modes and besides there is the energetic exchange each of them with the external mode of matrix, therefore even in the presence of dissipative effects in the matrix they can be compensated due to the influence of electric field. Besides, the damping can be neglected according to a common reason, if the kinetic processes in the NC are a more fast in comparison with the relaxation rate in the dissipative matrix. As mentioned, our model already uses the assumption that the processes in the matrix are considered as the slowest. However, if there is a need to take into account the dissipative effects in the matrix then it can be done by the various methods, according to [4, 8, 9].

From the data represented on Fig.1 and Fig.2 it follows as the regimes in the electron and vibrational subsystems of trimer NC can to influence on the bioactivity of biocomposite system in whole. So, the cases a) and b) on

Fig.1 and Fig.2 correspond to the situation when the mutual influence of the protein matrix and trimer NC is absent because the interaction between them is equal to zero ( $\gamma = 0$ ). In our model, it is understood as a situation before the coordination of NC on the protein matrix, therefore the biological activity of the protein matrix does not change in these cases. Once NC is embedded in the matrix the situation changes substantially as can be seen on Fig.1c and Fig.2c ( $\gamma \neq 0$ ). As a rule, the embedded cluster is coordinated through its intermediate center in the vicinity to the active site of the supra-molecular protein system. The case c) corresponds to almost the maximum value of electron population on the intermediate center of trimer NC. Such changing of the charge distribution in the embedded NC will significantly affect on a biological activity of the protein system. Additionally, in this case the account of interaction between the intracluster modes and matrix's mode occurs and this promotes to the accumulation of energy in the degrees of freedom of the protein matrix. Thereby, the probability of conformational rearrangement of the protein system rises significantly and it can easily make the transition to the new conformation. But in the various conformations the protein system usually has the different level of biological activity. In this regard, we note that our model implies the possibility of realization of an interesting effect – let's call it the effect of the cascade changes of protein conformation. In general, for each new protein conformation is necessary to take into account other values for the parameters  $\gamma$  and  $\omega_0$ . With these updated values  $\gamma$  and  $\omega_0$  the regime of electron density distribution in the NC and the energy regime of the intracluster modes will vary, respectively, and they can become optimal again for the next conformational transition in a protein system, and so on. If necessary, in addition to this, it is possible to vary the parameters of periodic electric field to facilitate obtaining of the optimal regime in the NC capable to induce conformational changes in the supra-molecular protein system.

#### IV. CONCLUSIONS

Thus, the offered model is quite acceptable to describe the picture of the biological activity of supra-molecular protein and synthetic biopolymer systems coordinated by the different type of trimer NCs and the methods for a regulation of it. Indeed, the existence of the electron density distribution regimes in the trimer NC coordinated through its intermediate center in the vicinity of the protein's active site gives the possibilities to regulate the level of biological activity by adjusting the corresponding set of model parameters. So, if the parameters (amplitude and frequency) of electric field are changed, then in the NC a new charge and vibrational regimes are established and theirs cumulative effect on the protein's active site is modified, so that a biological activity is altered too.

Note that a switching of the electron density distribution regimes in the trimer NC is directly associated with the changes of dipole moment, i.e. the external periodic electric field is the effective controlling tool for a NC's

dipole moment. The given model, from this point of view can be interesting to possible a practical application of the simulation results in the opto- and microelectronics, when in the biopolymer matrix (for example, in the form of a film or a plate) a sufficiently large number of the similar trimer NCs is introduced, but herewith their concentration isn't so great and hence their coupling could be not considered. In this case, if to assume that the trimer NCs being chaotically distributed in a biopolymer matrix but yet to have the definite common orientation, then affecting on such biopolymer material by the external periodic electric field it is possible significantly to change its polarizing properties, as a conformation and biological activity. It will correspond to the agreed switchings of the dipolar moments in the separate trimer nanoclusters following to the electron density dynamics in them.

Thus, the theoretical approach developed here provides many opportunities for the effective theoretical investigations of different kinetic and optical processes in the complex biological nanocomposite systems.

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