# ABOUT REGIMES OF BIPOLARON TRANSFER IN THE ORGANIC DIMER CLUSTER

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**abstract:** The model for the organic dimer cluster proposed in this paper takes into account the electron correlation (the organic charge transfer complexes are strongly correlated systems) through the dimer Hubbard's model. Moreover, in the offered model the internal structure of the dimer and each of its monomers is taken into account by introducing of the additional term into the Hamiltonian for describing of the interaction of electrons with vibrational subsystem. Thus, it provides the ample opportunities to describe in detail the polarizing and conduction properties of the organic dimerized systems. It is obtained the time dependence of difference in electron populations on the dimer's centers. From the analysis of electron subsystem's dynamics of the studied dimer cluster the different regimes for the bipolaron formation and charge transfer were revealed.

## Introduction

Recently in the physical chemistry the great attention is given to studying of that as the structural organization of a material on the nano-level manifests in its various properties. The toolkit of the atomic engineering gives a possibility to build the cluster molecular structures with essentially new properties [1÷3]. In other hand, that demands the ability to manage the atom-molecular interactions on the local level to within one atom. The materials formed from the molecular clusters tend to have the unique physical characteristics on the macro-level. Such materials began to be used actively in molecular electronics, nano- and optoelectronics [4,5]. In this regard, it is interesting the question about the microscopic nature of the nonlinearity or how a nonlinear medium is arranged at the molecular level. So, in the organic materials, whose molecular structural elements contain the conjugated bonds, the reasons of the nonlinear optical properties are connected with a big polarizability of the π-electron cloud. In general, the macroscopic properties of materials are defined both the intrinsic properties their structural elements and the properties of linkage between these structural elements. As example, each molecule can be considered as a separate source of the nonlinear polarization, and if the distance between molecules is much less than length of a wave of an incident light, the collective nonlinear

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factor can be considered as the sum of the molecular factors with some correction [6]. Thereby, the elaboration of the theoretical models, which describe the different properties of the molecular structural units constituting the material, is in demand.

Among the immense family of the organic materials it is necessary to allocate especially the organic compounds TTF (tetrathiafulvalene) and TCNQ (tetracyanoquinodimethane). From the viewpoint of the device applications they are promising because possess both the nonlinear optical properties [7] and high conductivity [5,8]. When molecules of TCNQ and TTF (see on Fig. 1) give or accept an electron, they become the stable cation- and anion-radicals, accordingly. The given radicals in combination both among themselves and with other molecular radicals or the ions of metals form various complexes with charge transfer. The molecules of TTF and TCNQ have the planar structure and form a crystal with layered packing. The crystals of these compounds possess a strong anisotropy due to formation of the quasi-one-dimensional structures in type of the stacks and have the pronounced polarizing properties. It is essential, that in the quasi-one-dimensional structures due to the Peierls's effect the dimerization occurs [5]. That is, the formation of the dimerized charge-transfer complexes based on the radicals $TTF^+$ or $TCNQ^-$ [5,8] is a characteristic feature of the considered compounds. Thereby, the dimer complexes can be regarded as the basic structural and functional elements of such quasi-one-dimensional organic compounds.
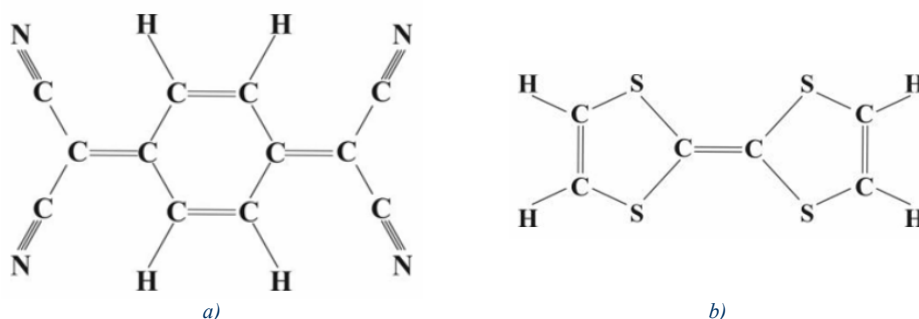


a)                                                              b)

**Fig. 1** a). The scheme of structure for the molecule $(NC)_2CC_6H_4C(CN)_2$ – TCNQ; б). The scheme of structure for the molecule $(H_2C_2S_2C)_2$ – TTF.

As a tool for the theoretical research of such dimer complexes will be formulated the minimum model, which performs the adequate description of dynamics of system and reveals the regimes of behaviour of system according to its internal and external parameters. Such model should have a minimum quantity of possible parameters which correspond to the most typical properties of studied system.

For the problem investigated in given work, it is necessary to consider two most prominent aspects. First, the considered dimer complexes are systems with strong electron correlation. In this connection, as the basis in the theoretical model, it is used the dimer Hubbard's model, which is quite approaching for the description of features of kinetics of such systems [9]. However, the dimer Hubbard's model does not allow to consider the feature of internal vibration structure of dimer and its monomers. With this purpose here the dimer Hubbard's Hamiltonian is supplemented by the term, which is responsible for the second prominent aspect – the electron-vibrational interaction. The diagonal part of the linear electron-vibrational interactions, i.e. the term of the polaron type in the Holstein's Hamiltonian [7], is considered. It allows to take into account the polaron effect leading to

that an electron localized on the one of the dimer's centers, will be polarize its environment and create a polarization well on the given center, i.e. the electron transfer on to other dimer's center will be more difficult.

Thus, the one-center Coulomb repulsion, as well as the resonant electron transfer, promotes leaving of electron on other center of dimer, but the polarization of environment prevents it.

## Theoretical Aspects

The theoretical model considered here allows revealing such ratios between values of modeling parameters of system at which one of possible variants for the transfer of two electrons (initially localized on one of the centers of organic dimer) is realized:

1). $C_1^{2e} + C_2^0 \rightarrow C_1^{1e} + C_2^{1e}$ is interpreted as the transition in Heitler-London state;

2). $C_1^{2e} + C_2^0 \rightarrow C_1^0 + C_2^{2e}$ is interpreted as the synchronous two-electron transfer;

3). $C_1^{2e} + C_2^0 \rightarrow C_1^{1e} + C_2^{1e} \rightarrow C_1^0 + C_2^{2e}$ is interpreted as the two electron transfer through intermediate Heitler-London state.

In the given approach the organic dimer cluster which can be formed from the cation-radicals TTF$^+$ or anion-radicals TCNQ$^-$ is considered as the system of «two centers – two electrons». The model stated here for the electron subsystem of dimer is taken into account only those electron states which are most essential in the charge transfer process. Namely, if to neglect the polarization of lower orbitals and influence of π-π* transitions on the charge transfer, then a many-electron wave function each of radical can be replaced by a molecular orbital with one unpaired electron [7]. Thus, within the limits of considered model each radical monomer in the dimer is presented by one molecular orbital: for cation-radical it is a half-filled HOMO orbital, and for anion-radical it is a half-empty LUMO orbital.

So, to a starting point in our consideration is accepted the dimer Hubbard's Hamiltonian, in which the electron-vibrational interaction as term of the polaron type [7] is added:

$$\hat{H} = \hat{H}_e + \hat{H}_{e-v} + \hat{H}_v ; \qquad (1)$$

$$\hat{H}_e = t_0 \sum_{\sigma} (a_{1\sigma}^+ a_{2\sigma} + a_{2\sigma}^+ a_{1\sigma}) + U_0 \sum_{i,\sigma} \hat{n}_{i\sigma} \hat{n}_{i-\sigma} ;$$

$$\hat{H}_v = \sum_k \hbar \omega_k (b_k^+ b_k + \frac{1}{2}) ;$$

$$\hat{H}_{e-v} = \sum_{i,k} g_{ik} \hat{n}_i (b_k^+ + b_k) ;$$

$$\hat{n}_i = \hat{n}_{i\sigma} + \hat{n}_{i-\sigma} ; \ \hat{n}_{i\sigma} = a_{i\sigma}^+ a_{i\sigma} ; \ i = 1,2$$

Here, $\hat{n}_i$ is the operator of electron population on i-th center of dimer. The operators $a_{i\sigma}^+, a_{i\sigma}$ and $b_k^+, b_k$ are the electron's and phonon's operators of creation and annihilation, respectively. The electron part of Hamiltonian $\hat{H}_e$ is the dimer Hubbard's Hamiltonian, in which the Coulomb repulsion (only one-center) with parameter $U_0$ and resonant tunneling transfer of electron with parameter $t_0$ are considered. The inter-center Coulomb repulsion can be neglected, as it is much less one-center. $\hat{H}_{e-v}$ and $\hat{H}_v$ are the parts of full model Hamiltonian responsible for linear electron-vibrational interaction in system and a free vibrational subsystem, accordingly. The vibrational subsystem is presented, generally, by the various vibrational modes with different both the frequencies $\omega_k$, and constants of the electron-vibrational interaction $g_{ik}$.

The eigenfunctions of the dimer Hubbard's Hamiltonian are the linear combinations of following states:

$$|1\uparrow 2\downarrow\rangle, \ |1\downarrow 2\uparrow\rangle, \ |1\uparrow 2\uparrow\rangle, \ |1\downarrow 2\downarrow\rangle, \ |1\uparrow 1\downarrow\rangle, \ |2\uparrow 2\downarrow\rangle \qquad (2)$$

Finding of the matrix elements $\hat{H}_e$ on the basis of functions (2) and solving of problem on the eigenfunctions and eigenvalues, it is easy to show that the eigenvalues look like:

$$E_{1,3} = y \pm \sqrt{y^2 + 16}; \ E_2 = y; \ E_{4,5,6} = 0; \ y = U_0 / t_0 \qquad (3)$$

Thus, eigenvalues of the dimer Hubbard's Hamiltonian represent three singlet states and one triplet state.

The time dependence of difference in electron populations on the first and second dimer's centers is determined by the average value of the operator $\hat{n} = \hat{n}_1 - \hat{n}_2$ and looks like:

$$\langle n(t)\rangle = \langle \varphi(t)|\hat{n}|\varphi(t)\rangle \qquad (4)$$

Herewith, it is used the relation, which determines the time-dependent wave function through eigenvalues and eigenfunctions of the full Hamiltonian of system:

$$|\varphi(t)\rangle = \exp(-i\hat{H}t)|\varphi(0)\rangle = \sum_n \exp(-iE_n t)|\varphi_n\rangle\langle\varphi_n|\varphi(0)\rangle \qquad (5)$$

As a result the following analytical expression is received:

$$\langle n(t)\rangle = \frac{8}{(y^2+16)^{1/2}}\left\{\frac{1}{(16+y^2+y\sqrt{y^2+16})}\cos\left[\frac{\left(y+\sqrt{y^2+16}\right)t}{2}\right] + \right.$$
$$\left. + \frac{1}{(16+y^2-y\sqrt{y^2+16})}\cos\left[\frac{\left(y-\sqrt{y^2+16}\right)t}{2}\right]\right\} \qquad (6)$$

Let's write the Hamiltonian (1) on the basis of singlet states (2):

$$H = U_0 \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + t_0 \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} + \sum_k g_k (b_k^+ + b_k) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} + H_v \qquad (7)$$

For the further reasoning the transformation of polaron shift over Hamiltonian (7) is carried out:

$$\widetilde{H} = e^{-iT} \hat{H} e^{iT} ; \ \hat{T} = -i \sum_k \mu_k \hat{n} (b_k^+ - b_k) ; \ \mu_k = g_k /(\hbar \omega_k) \qquad (8)$$

Then, the Hamiltonian (8) can be expressed as:

$$\widetilde{H} = U \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \hat{H}_v + \hat{V} ; \ \hat{V} = F^+ S^+ + F^- S^- \qquad (9)$$

Here, the following designations are used:

$$U = U_0 - \sum_k \mu_k^2 \hbar \omega_k ; \ F^{\pm} = t_0 \exp(\pm \mu_k (b_k^+ - b_k)) ;$$

$$S^+ = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \end{pmatrix} ; \ S^- = \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad (10)$$

The average value of operator of difference in electron populations on the dimer's centers $\langle n(t) \rangle$ is calculated from the electron-vibrational Hamiltonian (9).

Since:

$$\langle n(t) \rangle = \langle e^{i\widetilde{H}t} \hat{n} e^{-i\widetilde{H}t} \rangle \qquad (11)$$

Then, with using of the cumulant decomposition for T-exponent, the differential equation for $\langle n(t) \rangle$ is obtained:

$$\frac{d\langle n(t) \rangle}{dt} = \left\langle \exp_0 (i \int_0^t V(\tau) d\tau) \right\rangle \{ i \langle [V(t), n(t)] \rangle -$$

$$- \int_0^t d\tau \int_0^\tau d\tau_1 \langle [V(\tau), [V(\tau_1), n(\tau_1)]] \rangle + \frac{d\langle n_0(t) \rangle}{dt} \} \qquad (12)$$

The index '0' designates that the averaging procedure is performed with 'zero' Hamiltonian, i.e. without $\hat{V}$ in (9).

Let's notice that:

$$\langle V(t) \rangle = F \{ \langle S^+(t) \rangle + \langle S^-(t) \rangle \} ; \qquad (13)$$

$$F = \left\langle F^{\pm}(t) \right\rangle = t_0 \exp(-\sum_k g_k^2 \coth(\beta \hbar \omega_k / 2)); \; \beta^{-1} = kT$$

In the case of the enough low temperatures $kT < \hbar \omega_k$ since $\coth(\beta \hbar \omega_k / 2) \to 1$, it turns out that $F \approx t_0 \exp(-\sum_k g_k^2)$.

If to consider the electron-vibrational interaction in lowest order of cumulant decomposition, then the following system of four linked differential equations is obtained:

$$\frac{d\left\langle n(t) \right\rangle}{dt} = iF \{\left\langle k(t) \right\rangle - \left\langle m(t) \right\rangle\}$$

$$\frac{d\left\langle m(t) \right\rangle}{dt} = -iF \{\left\langle n(t) \right\rangle + \left\langle l(t) \right\rangle\} + iU \left\langle m(t) \right\rangle$$

$$\frac{d\left\langle k(t) \right\rangle}{dt} = iF \{\left\langle n(t) \right\rangle - \left\langle l(t) \right\rangle\} - iU \left\langle k(t) \right\rangle \tag{14}$$

$$\frac{d\left\langle l(t) \right\rangle}{dt} = -iF \{\left\langle k(t) \right\rangle + \left\langle m(t) \right\rangle\}$$

In system (14) following designations are entered:

$$n(t) = e^{i\tilde{H}t} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} e^{-i\tilde{H}t}; \qquad l(t) = e^{i\tilde{H}t} \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} e^{-i\tilde{H}t};$$

$$\tag{15}$$

$$m(t) = e^{i\tilde{H}t} \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 0 \\ 0 & -1 & 0 \end{pmatrix} e^{-i\tilde{H}t}; \qquad k(t) = e^{i\tilde{H}t} \begin{pmatrix} 0 & 0 & 0 \\ 1 & 0 & -1 \\ 0 & 0 & 0 \end{pmatrix} e^{-i\tilde{H}t}$$

The system of the differential equations (14) is considered with initial conditions:

$$\left\langle n(t) \right\rangle \Big|_{t=0} = 2 \, ; \; \frac{d\left\langle n(t) \right\rangle}{dt} \Big|_{t=0} = 0 \, ; \; \frac{d^2 \left\langle n(t) \right\rangle}{dt^2} \Big|_{t=0} = -4F^2 \tag{16}$$

Definitively, with account of the electron-vibrational interaction in the first order of cumulant decomposition, the analytical expression for the time dependence of difference in electron populations on the dimer's centers is obtained:

$$\langle n(t)\rangle = \frac{8F^2}{(U^2+8F^2)^{1/2}}\left\{\frac{1}{(U+\sqrt{(U^2+8F^2)})}\cos\left[\frac{\left(U+\sqrt{U^2+8F^2}\right)t}{2}\right]+\right.$$

$$\left.+\frac{1}{(U^2-\sqrt{(U^2+8F^2)})}\cos\left[\frac{\left(U-\sqrt{U^2+8F^2}\right)t}{2}\right]\right\} \qquad (17)$$

Here:

$$U = U_0 - \sum_k \mu_k^2 \hbar\omega_k \qquad (18)$$

## Results and discussions

As it is evident from (17), the general view of analytical expression for the time dependence of the value $\langle n(t)\rangle$ does not change actually on the form. The account of the electron-vibrational interaction in the first order of cumulant decomposition leads only to renormalizing of system's parameters.

Herewith, as it follows from the expression (18), the account of the linear electron-vibrational interaction reduces the one-center Coulomb repulsion parameter. Thus, there is a possibility for the reduction of this parameter up to values close to zero. It actually means that at appreciable reduction of Coulomb repulsion of electrons on each center of dimer they have an opportunity of simultaneously tunneling from one dimer's center on another. It corresponds to the regime of synchronous two-electron transfer. Also note that the tunneling parameter is renormalized also towards reduction, as it shown in (18).

The time dependence of difference in electron populations on the dimer's centers shows, how the vibrational subsystem influences on the dynamics of electron subsystem. From the analysis of time dependence of the value $\langle n(t)\rangle$ follows that in the system at certain values of parameters the different variants of electron transfer are realized.

In the given model due to the account in Hamiltonian the polaron term, the electron transfer is considered as polaronic or bipolaronic. From the analysis of the value $\langle n(t)\rangle$ follows that in the dynamics of electron subsystem it is possible to allocate two typical regimes for the formation of bipolaron and charge transfer in the dimer: 1) when on each of the dimer's centers the electrons are distributed on one (delocalized pair of electrons), that within the limits of the given model it is possible to interpret as formation of two-center bipolaron; 2) when electrons are localized by pair on one center of dimer which is periodically transferred from center to center, i.e. in the dimer the one-center bipolaron is formed.

The performed analysis leads to one more important consequence that in the electron subsystem's dynamics of dimer is possible also the third regimes: 3) when the pair of electrons is periodically transferred on other center in two stages. Namely, the pair of electrons, initially localized on one center of dimer, is delocalized at first stage and the electrons are distributed on one on each of the centers, then at second stages the both electrons are localized on the another center. Such variant of the behaviour of electron

subsystem of dimer can be interpreted, as the regime with formation of bipolaron which periodically changes its localization from two-center to one-center. Realization of the able regime is possible and in the inorganic materials with difficult crystal lattice. As it is known [10], the local intra-molecular vibrations if to neglect the frequency dispersion of vibrational modes (that is characteristic for optical modes) lead to pairing of polaron on one center. But the vibrational modes of the crystal lattices (both optical and acoustic) besides the pairing of polarons on one center can lead to forming of two-center bipolaron [10]. Therefore, the realization of the third regime is promoted by the simultaneous account both the intra-molecular vibrations and inter-molecular vibrations. The considered model is not difficult to apply for the description of conduction properties of materials specified above, due to presence the dimerized stacks in them. In this case the inter-dimer transfer is easy considered, having added in Hamiltonian the term corresponding to tunneling of electron between dimers. It is obvious that for the transfer of bipolaron between dimers and inside dimer in such stacks there will correspond also one of the specified regimes. It should be noted that the regimes of bipolaron transfer between dimers and inside dimer do not necessarily coincide.

## Conclusions

Thus, the electron-vibrational model offered here for the organic dimer cluster describes the interaction of electrons with vibrational subsystem with account of the electron correlation through the Hubbard's model. It is important, that on the one hand the electron-vibrational interaction allows to consider the internal structure of dimer through its vibrational degrees of freedom. On the other hand it reduces the Coulomb repulsion of electrons that promotes to the synchronous electron transfer, i.e. the electron transfer can be realized by a pair of electrons. And since the considered dimers are the structural elements in the organic and metal-organic materials it is possible to assert that the conditions of bipolaron formation and dynamics of charge transfer in the dimer play an essential role at the study and defining the nonlinear optical and polarizing properties, and high conductivity in such materials.

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