Modelling of influence of the electromagnetic field on processes of electron localization in the dimer nanocluster

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The quasi-classical model, which describes localized properties of the electron in the dimer's nanocluster was studied. In this consideration the dimer has been placed in an external electromagnetic field. It is shown, that the external electromagnetic field can operate by the localized properties of the system. The regimes of the electron localization and delocalization and conditions of the switching between them are revealed. The used model allows to describe the localized properties of the electron in the dimer's nanocluster for the different parameters of the system, and also specifies ways of parametrical management by these properties that have doubtless interest for the molecular optoelectronics.

(Received December 30, 2009; accepted January 19, 2010)

Keywords: Dimer, Nanocluster, Electron localization, Electromagnetic field

1. Introduction

The phenomenon of electron localization-delocalization in the molecular cluster systems and the expedients of guidance its degree and duration are the central problems for the molecular electronics and optoelectronics [1]. Most perspective multifunctional nanomaterials are metal-organic nanoclusters, whose elementary representative is dimer's nanocluster [2-4]. The degree of the localization-delocalization of the electron strongly depends on the relation between constant of the electron-vibrational interaction and tunneling constant between the electron states on the centers and other parameters of the nanodimer. In the absence of the external field that owes to electron-vibration interaction the electron in such molecular system is either fully localized on one of centers or partially delocalized. The conformation reorganization yielded by the additional electron on given centre and the deep potential well which itself creates this electron lead to less its transition probability on other centre. As known, the molecular system has good transport properties if it easily accepts and donates electrons. For this purpose the electron should be not localized on one centre, but must be delocalized on the most number of the centers, and so without lifting energy of the system. Metal-organic complexes in which metal ions are build in the polymeric matrix, characterized π-electron conjugation and high degree of the delocalization of the electron gained from the ion of the metal are good transport properties and are finding the application in the molecular electronics and optoelectronics [3, 4]. The external field essentially influences on the properties of the cluster systems, changing in particular their transport properties and changing the degree of the localization of the electron [5]. Dynamics of nonstationary state of the electron in the dimer's nanocluster, is studied in [6].

The aim of the given investigation is theoretically studying of the influence of the electromagnetic field on the electron transport in dimer's nanocluster. The analysis is based on the calculation of the difference of the probability of electron detection on the first and second centers of the dimer.

2. Theory (two-level model in the quasi-classical approach)

Let's view the dimer cluster consisting of two equivalent centers with one additional electron. The system is prepared so that the electron in the initial moment of time is localized on the first centre of the dimer. We propouse that electron, being on each of dimer centers, interacts only with full-symmetrical vibrations of the nearest environment $Q_i (i = 1,2)$ and can be tunneling from one centre to another centre.

Let's enter normal coordinates:

$$Q = (Q_1 + Q_2)/\sqrt{2}, \quad q = (Q_1 - Q_2)/\sqrt{2} \tag{1}$$

The first of two normal coordinates is excluded from viewing because this full-symmetrical coordinate is multiplied by unit electron matrix. Proceeding from the made assumptions, the kinetic properties of the dimer's nanocluster can be described by means of the model Hamiltonian of the two-level electron system, which is in the external electromagnetic field [7].

In the presented approach the vibrational mode quantized, and the electromagnetic field is considered classically. So, the Hamiltonian of the considered system is:

$$H(t) = \frac{1}{2}\left(p^2 + \omega^2 q^2\right) + v\sigma_x + gq\sigma_z + (\mathbf{d}_0\mathbf{E}_0)\cos(\Omega t)\sigma_z \tag{2}$$

Here p, q - the momentum and coordinate of the vibrational mode q with frequency ω; $\sigma_x, \sigma_z, \sigma_y$ - Pauli's matrixes; v, g - the tunneling constant and constant of the electron-vibrational interaction; $\mathbf{E}_0, \Omega$ - the amplitude and the frequency of the monochromatic electric field, $\mathbf{d}_0$ - the electron dipole moment of the dimer. All parameters are taken in $\hbar\omega$ units. In this work the quasi-classical approximation was used.

At the description of the time evolution the Davydov time-dependent wave function for the Hamilton canonical equations was applied:

$$\psi(t) = \exp(-i(\beta(t)p - \pi(t)q)\sum_{j=1}^{2}\alpha_j(t)\,a_j^+|0\rangle \qquad (3)$$

The wave function (3) depends from the variation parameters $\alpha_j(t)$ and $\beta(t), \pi(t)$, which are the time-dependent amplitude of the probability of the electron detection on the j-centre of the dimer and the average values of the coordinate and momentum of the vibrational mode, correspondently.

The time dependent electron-vibrational function (3) is presented in the factorized form, and the electronic part of the wave function is chosen in the form of superposition of electron states of system. The vibrational subsystem is presented in the form of the vibrational wave package. Solving the variation problem, it is obtain the system of the differential equations concerning the variation parameters $\alpha_j(t)$ and $\beta(t), \pi(t)$.

Thus, the system of the linkage differential equations for the amplitudes is $\alpha_j(t)$:

$$\begin{aligned}
i\frac{d\alpha_1}{dt} &= v\alpha_2 + g\beta\alpha_1 - \mathbf{d}_0\mathbf{E}_0\alpha_1\cos(\Omega t)\\
i\frac{d\alpha_2}{dt} &= v\alpha_1 - g\beta\alpha_2 + \mathbf{d}_0\mathbf{E}_0\alpha_2\cos(\Omega t)\\
\frac{d\pi}{dt} &= \omega\beta + g\left[|\alpha_1|^2 - |\alpha_2|^2\right]\\
\frac{d\beta}{dt} &= -\pi
\end{aligned} \qquad (4)$$

The system (4) is solved numerically. For the vibrational subsystem the numerical solution is presented by the phase portrait to planes "coordinate-momentum". On the phase portrait of the vibrational mode it is possible to observe dynamics of the vibrational wave package in depending from the examined parameters.

The evolution in the electron subsystem is presented by the time dependence of the difference of the average value of the electron population on the nanodimer centers. The objective of this research is to show what specific features of the behavior are realized in the electron and vibrational subsystems for the chosen values of the electron-vibrational interaction constant and the tunneling constant in depending from the intensity of the electromagnetic field.

3. Results and discussion

The main result obtained from the numerical solution of (4) is presented in the Figs. 1-5.

The case of the time evolution of the considered system for the value of the interaction energy with electromagnetic field $(\mathbf{d}_0\mathbf{E}_0)$=4.9 and for time corresponding to the value 100π (in dimensionless unities ωt) is presented on the Fig. 1. In this case the electron, which initially localized on the first nanodimer center, 9 times passes from centre to center, i.e. there are 9 switchings. Thus, the dynamics of vibrational wave package is characterized by the motion of the gravity center of the package on the classical trajectory. And at the each switching in the electron subsystem the wave package trajectory has only uniform displacement on the all its extent. Such behavior of the electron subsystem can be interpreted, as a regime of the periodically renewable full localization of the electron for time corresponding to the value of order 10π, and switching on other center with the subsequent localization on it.

The case $(\mathbf{d}_0\mathbf{E}_0)$=5.815, when for time corresponding to the value 100π only one switching of the electron from the center to the center was made, is presented on Fig. 2. Thus, the wave package moves so that its trajectory of the motion is between two concentric circles in a phase plane "coordinate-momentum". In this case switching of the electron localization on other center is carried out during of order 100π in unities ωt. The time dependence of the average value of the difference of the population of centers in the dimer has beats. These beats take place in all the subsequent cases below. Such features of the electron dynamics may be connected with the changing of the package form.

In Fig. 3 was presented the case $(\mathbf{d}_0\mathbf{E}_0)$=5.83, when for the observed time interval one can assume that the electron is completely delocalized between the centers of the nanodimer. The studied system relatively slowly goes to the delocalization state, whose duration is very sensitive to the field.

The cases presented on the Figs. 4 and 5 for $(\mathbf{d}_0\mathbf{E}_0)$=5.85 and 5.87 correspond to cases of the partial localization and almost full localization of the electron on the first center.

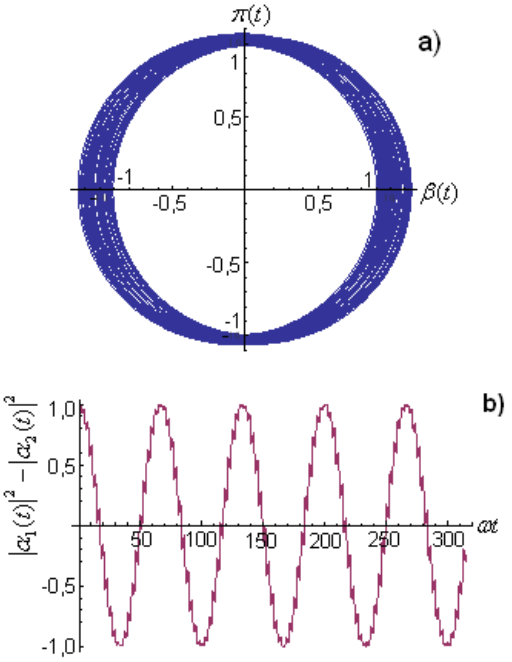

Fig.1. The phase diagram for cluster mode: (a) The time dependence of the difference of the average value of the electron population on the nanodimer centers; (b) System parameters are $v = 0.2;\ g = 0.1;\ (\mathbf{d}_0\mathbf{E}_0) = 4.9;$ $\Omega = \omega = 1;\ \pi(0) = 1.$

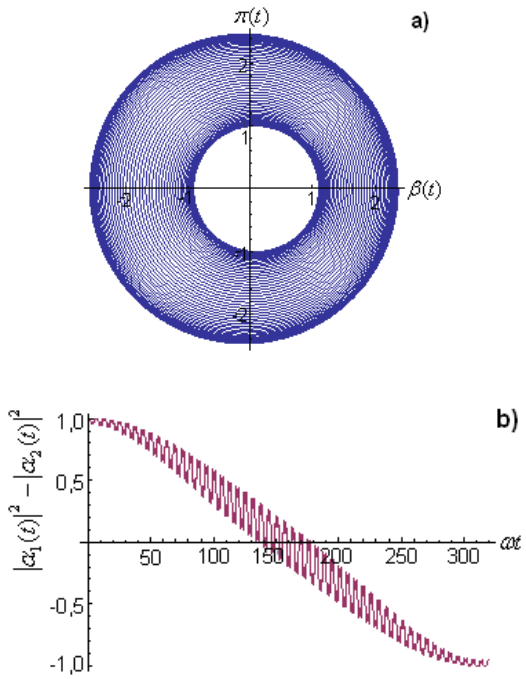

Fig. 2. The phase diagram for cluster mode – a); The time dependence of the difference of the average value of the electron population on the nanodimer centers – b). System parameters are $v = 0.2;\ g = 0.1;\ (\mathbf{d}_0\mathbf{E}_0) = 5.815;$ $\Omega = \omega = 1;\ \pi(0) = 1.$

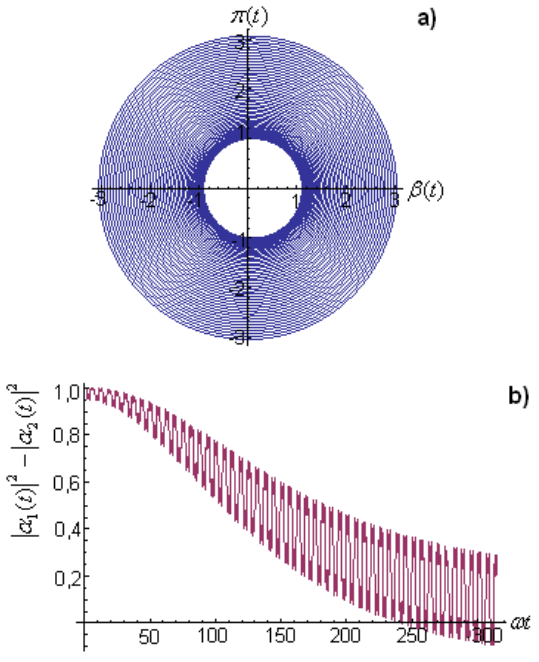

Fig. 3. The phase diagram for cluster mode – a); The time dependence of the difference of the average value of the electron population of the nanodimer centers – (b). System parameters are $v = 0.2;\ g = 0.1;\ (\mathbf{d}_0\mathbf{E}_0) = 5.83;\ \Omega = \omega = 1;\ \pi(0) = 1.$

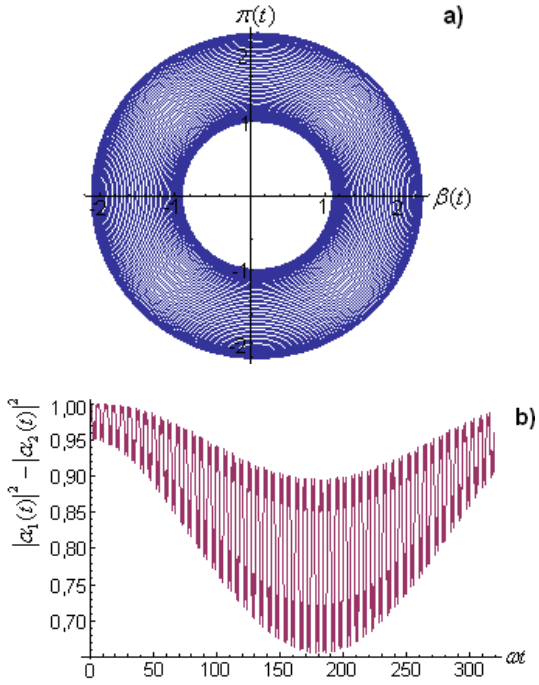

Fig.4. The phase diagram for cluster mode – a); The time dependence of the difference of the average value of the electron population on the nanodimer centers – b). System parameters are $v = 0.2;\ g = 0.1;\ (\mathbf{d}_0\mathbf{E}_0) = 5.85;$ $\Omega = \omega = 1;\ \pi(0) = 1.$

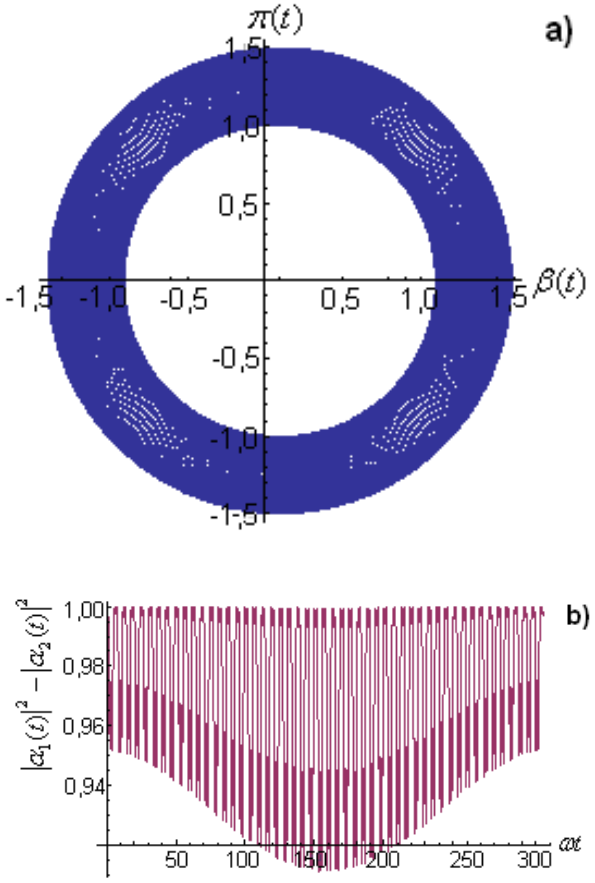

Fig.5. The phase diagram for cluster mode – a); The time dependence of the difference of the average value of the electron population on the nanodimer centers – b). System parameters are $\nu = 0.2$; $g = 0.1$; $(\mathbf{d}_0\mathbf{E}_0) = 5.87$; $\Omega = \omega = 1$; $\pi(0) = 1$.

The further increase of the value $(\mathbf{d}_0\mathbf{E}_0)$ up to the value 6.75 leads to the return of dynamics in the time behavior of the difference of the average value of the electron population on the nanodimer centers. For the value $(\mathbf{d}_0\mathbf{E}_0)$=6.75 the dynamics of electron subsystem almost completely coincides with the case given on the Fig. 1. Further change of the value of $(\mathbf{d}_0\mathbf{E}_0)$ outside of the studied interval from 4.9 to 6.75 leads to the complete renewal of evolution in the considered system.

4. Conclusions

Thus, the gradual change of the interaction energy of the electron subsystem with the electromagnetic field leads to the realization of the several regimes in the time evolution of the electron in the nanodimer.

Firstly, it is the regime with switching of full localization of the electron from one center to another. The time of the electron switching is strong depending from the interaction energy of the electron subsystem with the electromagnetic field $(\mathbf{d}_0\mathbf{E}_0)$ (see Figs. 1 and 2).

Secondly, it is the regime of the full delocalization of the electron in the nanodimer (see Fig. 3). The main feature of this regime is that the duration of the time period of the existence of delocalization is very sensitive to the value $(\mathbf{d}_0\mathbf{E}_0)$. The performed calculations show, that the gradual increase of the field at first increases the duration of the delocalization, and then to its decrease. And finally, in dependence of the value $(\mathbf{d}_0\mathbf{E}_0)$, the electron either switches to another center or remain or remains at the same center.

Thirdly, it is the regime of the full or the partial localization of the electron on the first nanodimer center - the case of the locked electron (see Figs. 4 and 5).

Thus, the electromagnetic field plays the role of the driving parameter. The electron-vibrational dynamics in the studied system is so that at the fixed value $(\mathbf{d}_0\mathbf{E}_0)$ one of the specified regimes of the localization of the electron is realized.

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