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INFLUENCE OF THE ELECTROMAGNETIC FIELD ON THE NONLINEAR ELECTRON LOCALIZATION DYNAMICS IN THE NANOCLUSTER WITH TWO REDOX CENTERS

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Introduction

Phenomenon of electron localization-delocalization in the molecular cluster systems for the device applications in the molecular electronics and optoelectronics has the key aspects such as the control ways of the localization degree and its duration [1]. Many perspective multifunctional nanomaterials contain the metal-organic nanoclusters, which elementary representative is the nanocluster with two redox centers or dimer nanocluster [2–4]. The degree of the localization of the electron strongly depends basically on the ratio of constant of the electron-vibrational interaction to the tunneling constant between the electron states on the centers and in a less degree other parameters of the system. In the absence of an external field owing to the 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 through the electron-vibrational interaction creates the potential well for this electron and so eventually leads to less its transition probability on other centre. The metal-organic complexes with redox centers in which metal ions are build in the polymeric matrix, characterized by the π-electron conjugation and the high degree of the delocalization of the electron gained from the ion of the metal have the good transport properties and find the various application in the molecular electronics and optoelectronics [2, 3]. 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, 6]. The dynamics of the nonstationary electron state in the nanocluster with two redox centers is studied in [7].

The aim of the given investigation is the theoretical study of the influence of the electromagnetic field on the electron transport in the nanocluster with two redox centers. The analysis is based on the calculation of the difference of the probabilities of electron detection on the first and second centers of the nanodimer, respectively.

Theoretical model

Let's view the nanocluster consisting of two redox 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 nanodimer. We propouse that electron, being on each of nanodimer 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 (for detail, see also [6]).

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. From the made assumptions, the kinetic properties of the dimer nanocluster can be described by means of the model Hamiltonian of the two-level electron system, which includes the external electromagnetic field [6].

The presented approach is semi-classical as the vibrational mode is quantized, and the electromagnetic field is considered classically. Thus, the Hamiltonian of the considered system is:

$$H(t) = \frac{1}{2}\left(p^2 + \omega^2 q^2\right) + v\sigma_x + gq\sigma_z + (d_0 E_0)\cos(\Omega t)\sigma_z \tag{2}$$

Here p, q – the momentum and coordinate of the vibrational mode q with frequency ω; σ_x, σ_z, σ_y – Pauli's matrixes; v, g – the tunneling constant and constant of the electron-vibrational in

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teraction; E_0, Ω – the amplitude and frequency of the monochromatic electric field, d_0 – the electron dipole moment of the dimer. All parameters are taken in $\hbar\omega$ units.

For the description of model in the quasi-classical approximation Hamilton's canonical equations were applied. The time evolution of studied system describes with using Davydov's time-dependent wave function:

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

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

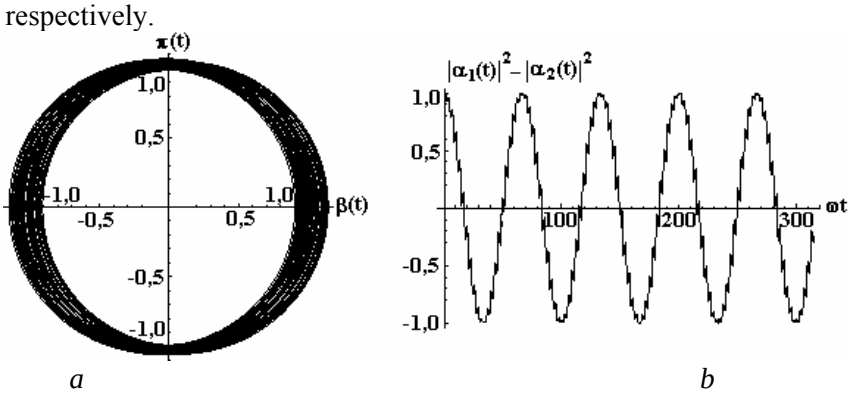
Solving the variation problem, it is obtain the system of the differential equations concerning the functions $\alpha_j(t)$ and $\beta(t)$, $\pi(t)$. Thus, the system of the linkage nonlinear differential equations for the values $\alpha_j(t)$ and $\beta(t)$, $\pi(t)$ is:

$$\begin{aligned}
i\frac{d\alpha_1}{dt} &= v\alpha_2 + g\beta\alpha_1 - d_0E_0\alpha_1\cos(\Omega\ \ t)\\
i\frac{d\alpha_2}{dt} &= v\alpha_1 - g\beta\alpha_2 + d_0E_0\alpha_2\cos(\Omega\ \ t)\\
\frac{d\pi}{dt} &= \omega\beta + g\left[|\alpha_1|^2 - |\alpha_2|^2\right]\\
\frac{d\beta}{dt} &= -\pi
\end{aligned} \tag{4}$$

The system (4), which describes nonlinear dynamics both the electron and vibrational subsystems, 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 – v, g, Ω, ω and (d_0E_0). The evolution in the electron subsystem is presented by the time dependence of the difference of the average values of the electron populations on the dimer centers. In the given research it is shown 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.

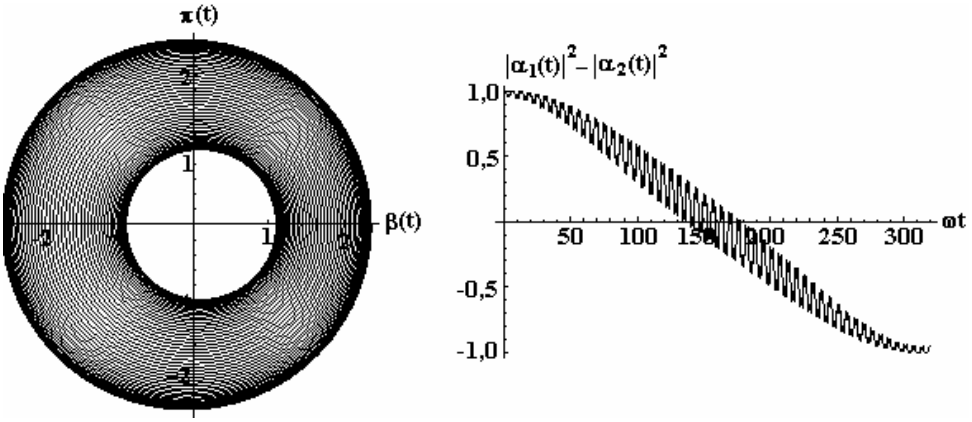
Results and discussions

The main results of given consideration, which follows from the numerical solution of (4) are presented on the fig. 1–5. On the each of figures 1-5 are displayed the time evolution for the electron and vibrational subsystems, respectively.



a *b*

Fig. 1. The phase portrait for cluster mode – a); The time dependence of the difference of the average values of the electron populations on the nanodimer centers – b). System parameters are $v = 0.2$; $g = 0.1$; $(d_0E_0) = 4.9$; $\Omega = \omega = 1$; $\pi(0) = 1$



a *b*

Fig. 2. The phase portrait for cluster mode – a); The time dependence of the difference of the average values of the electron populations on the nanodimer centers – b). System parameters are $v = 0.2;\ g = 0.1;\ (d_0 E_0) = 5.815;\ \ \Omega = \omega = 1;\ \pi(0) = 1$

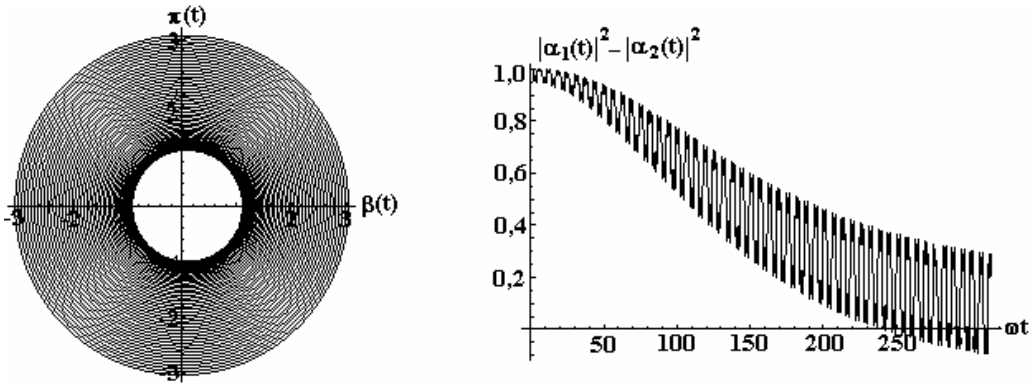


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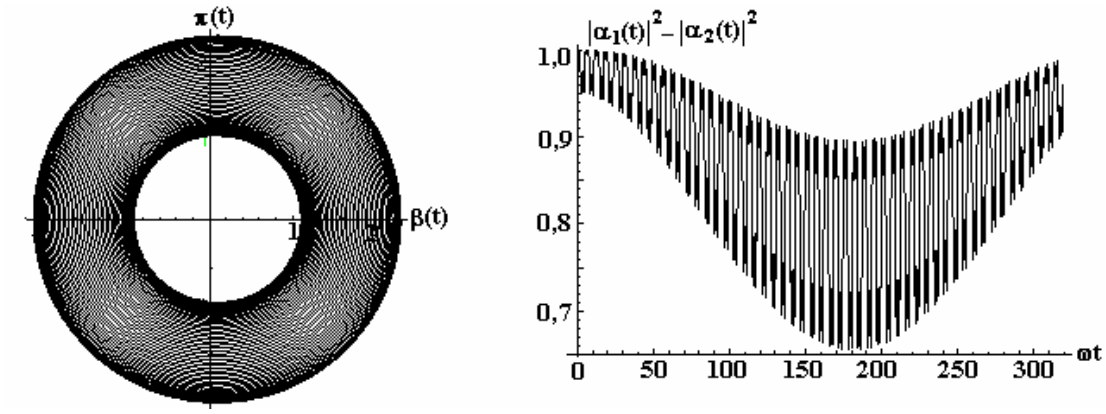
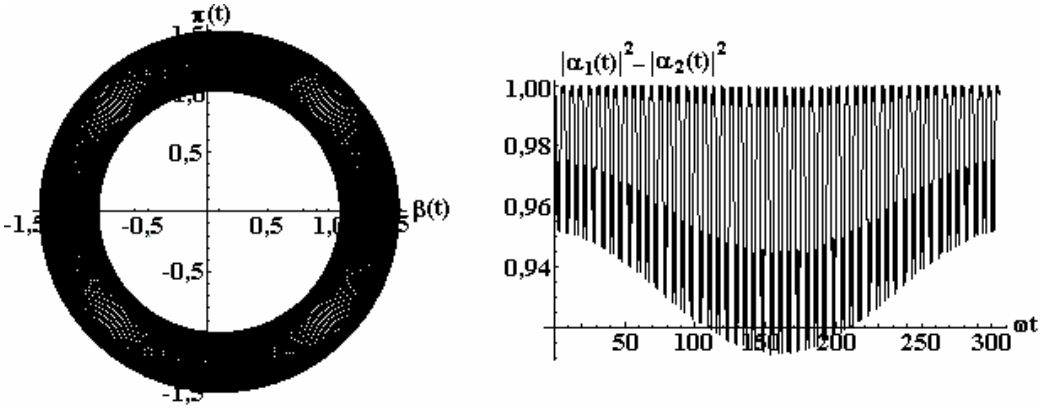
Fig. 3. The phase portrait for cluster mode – a); The time dependence of the difference of the average values of the electron populations on the nanodimer centers – b). System parameters are $v = 0.2;\ g = 0.1;\ (d_0 E_0) = 5.83;\ \ \Omega = \omega = 1;\ \pi(0) = 1$



a *b*

Fig. 4. The phase portrait for cluster mode – a); The time dependence of the difference of the average values of the electron populations on the nanodimer centers – b). System parameters are $v = 0.2;\ g = 0.1;\ (d_0 E_0) = 5.85;\ \ \Omega = \omega = 1;\ \pi(0) = 1$



a *b*

Fig. 5. The phase portrait for cluster mode – a); The time dependence of the difference of the average values of the electron populations on the nanodimer centers – b). System parameters are $\nu = 0.2;\ g = 0.1;\ (d_0E_0) = 5.87;\ \Omega = \omega = 1;\ \pi(0) = 1$

The further increase of the value (d_0E_0) up to the value 6.75 leads to the return of dynamics in the time behavior of the difference of the average values of the electron populations on the centers of the dimer nanocluster. For the value (d_0E_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 (d_0E_0) outside of the studied interval from 4.9 to 6.75 leads to the complete resumption of evolution in the considered system.

As known, in the quasi-classical approximation the dynamics of vibrational wave package is characterized by the motion of its gravity center on the classical trajectory. Note that in the studied case the vibrational subsystem and the electromagnetic field are interconnected through electronic subsystem, which interacts with each of them separately. Thus, the electromagnetic field and vibrational subsystem linked indirectly and between them the energy exchange occurs. Note also that the time dependence of the difference of the average values of the electron populations of centers in the nanodimer has beats. These beats take place in all the subsequent cases below (fig. 1–5). Such features of the nonlinear electron dynamics may be connected with the changing of the package form.

The case of the time evolution of the considered system for the value of the interaction energy with electromagnetic field (d_0E_0)=4.9 and for time interval 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 center of the nanodimer, 10 times passes from centre to center, i.e. there are 10 switchings. Herewith, at the each switching in the electron subsystem the phase trajectory center of the wave package has uniform shift along the axe of coordinates. 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 (d_0E_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. In this case switching of the electron localization on other center is carried out during of order 100π in unities ωt. While the wave package moves so that its phase trajectory lies between two non-concentric circles in the phase plane "coordinate-momentum", i.e. the phase trajectory center of the wave package still continues to shift.

On the fig. 3 was presented the case (d_0E_0)=5.83, when for the observed time interval can assume that the electron completely delocalized between the centers of the dimer. The studied system relatively slowly goes to the delocalization state, whose duration is very sensitive to the field intensity.

The results presented on the fig.4 and fig.5 for (d_0E_0)=5.85 and 5.87 correspond to cases of the partial localization and almost full localization of the electron on the first center, accordingly. In these cases the phase trajectory of the wave packet lies between two already concentric circles on the phase plane "coordinate-impulse".

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 dimer nanocluster.

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 $(d_0 E_0)$ (compare fig. 1 and fig. 2).

Secondly, it is the regime of the full delocalization of the electron in the dimer nanocluster (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 $(d_0 E_0)$. 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 $(d_0 E_0)$, the electron either switches to another center or remain or remains at the same center.

Thirdly, it is the regime of the partial or practically full localization of the electron on the first dimer center – the case of the locked electron (see fig. 4 and fig. 5).

Thus, the electromagnetic field plays the role of the external driving parameter. Herewith, the electron-vibrational dynamics in the studied system is so that at the fixed value $(d_0 E_0)$ one of the specified regimes of the localization of the electron is realized.

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Summary

The localized properties of electron in the nanocluster with two redox centers were studied using of the semi-classical approach. In this consideration nanocluster interacts with an external electromagnetic field. It is shown, that the external electromagnetic field can operate by the localized properties of the system. In resonance case the regimes of the electron localization and delocalization and also conditions of the switching between them are revealed. The used approach allows to describe the localized properties of the electron in the dimer nanocluster for the different parameters of the system, and also specifies ways of parametrical management by these properties.