PHYSICAL REVIEW E **109**, 024401 (2024)

Influence of donor or acceptor presence on excitation states in molecular chains: Nonadiabatic polaron approach

V. Matic, Z. Ivic, Z. Przulj, and D. Chevizovich*

Vinca Institute of Nuclear Sciences–National Institute of the Republic of Serbia,
University of Belgrade, P.O. BOX 522, 11001 Belgrade, Serbia

(Received 28 August 2023; accepted 4 January 2024; published 2 February 2024)

In this paper, we considered a molecular structure that consists of a molecular chain and an additional molecule (donor or acceptor) that can inject (or remove) single excitation (vibron, electron, etc.) onto the molecular chain. We assumed that the excitation forms a self-trapped state due to the interaction with mechanical oscillations of the chain structure elements. We analyzed the energy spectra of the excitation and showed that its state (when it migrates to the molecular chain) has the properties of the nonadiabatic polaron state. The conditions under which the excitation can migrate from one subsystem to another one were considered. It was shown that the presence of a "donor" molecule cannot significantly change the properties of the excitation located on the molecular chain. At the same time, the molecular chain can affect the position of the energy level of the excitation localized on the donor subsystem. Indirectly, this can influence the process of excitation migration from one subsystem to another one. The influence of the basic energy parameters of the system and the environment temperature on this process are discussed. The entire system was assumed to be in thermal equilibrium with the environment.

DOI: 10.1103/PhysRevE.109.024401

I. INTRODUCTION

Highly efficient, long-range transfer of charged particles (electron, hole, ...) and excitation energy (exciton) between two largely separated subunits, "donor" and "acceptor" molecules, is at the core of numerous phenomena taking place in complex molecular structures [1–23]. For example, they are elementary processes through which the energy captured in photosynthesis [1,3,4] or released in the hydrolysis of adenosine triphosphate (ATP) to ammonium dihydrogen phosphate (ADP) [2,17,18] is made available for further exploitation in biochemical processes within living cells. Also, donor-acceptor electron transfer in organic conductors and semiconductors is the basis of recent microelectronic devices such as light-emitting diodes or field-effect transistors [9,12,13]. The elucidation of the mechanisms of the electronic excitation energy transfer (EET) is crucial for the comprehensive understanding of the more complex processes in realistic conditions and future applications.

It is now widely accepted that the long-haul electron transfer is mediated through a molecular bridge (MB) connecting the donor with acceptor molecules. The structures composed of a large number of periodically arranged dipole-dipole coupled molecular groups (MGs) such as polypeptide chains [1–7,21], conjugated polymers [12,13], or DNA molecules [22,23] play the role of the MB. Accordingly, a particular structure is modeled as a long quasi-one-dimensional (quasi-1D) molecular chain (MC) in which excitation transfer takes place via successive tunneling between adjacent molecular units. The translational invariance of the system provides its theoretical consideration within *electronic band theory*. However, for the understanding of the EET in realistic conditions simple band model had to be revisited accounting for coupling with the environment (lattice vibrations phonons to be more specific). Considerations based on perturbation calculations [1] imply that due to the interaction with phonons a lifetime of the band states is far below that needed for long-distance transfer, comparable to the size of the MB. Nevertheless, lattice modes do not necessarily play a destructive role. In particular, in deformable quasi-1D materials, such as soft biological macromolecules and conjugated polymers [2,5,11,12,24–28], back-action of excitation on lattice may provide conditions for stable EET via *self-trapping* (ST) mechanism and formation of the complex quasiparticle polaron [29–31]. In this way, phonons, the main source of dissipation, are incorporated into this complex structure and no longer represent an obstacle to stable transfer. This is the basic idea behind the theory of long-haul EET in biological macromolecules proposed by Davydov, who, in the formation of large radius solitonlike polaron (*Davydov soliton*), saw the resolution of the crisis in bioenergetics [1,2,14,15,32,33]. Nevertheless, examinations [17,20] based on the general theory of ST phenomena [29] have shown that this idea is not generally acceptable. Namely, the excitations of soliton type may appear in quasi-1D systems with short-ranged electron-(exciton-) phonon interaction in the adiabatic strong-coupling limit [24–31]. Unfortunately, as discussed in [17,20], system parameters of most of the substances for which Davydov solitons have been proposed as EET mechanism in biological substances fall into a nonadiabatic regime where ST state, if any arise, would be Holstein's nonadiabatic (small) polaron, rather than soliton. For example, according to [17,18,34] such states would arise due to ST intramolecular vibration

---

[*] cevizd@vin.bg.ac.rs

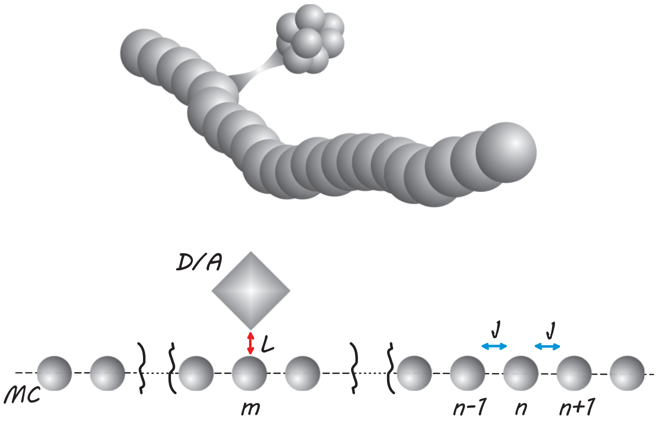

FIG. 1. Upper panel: a schematic presentation of the D/A-MC structure. Lower panel: simplified D/A-MC structure.

energy (amid-I quanta) in acetanilide (ACN) and α-helix. Their transport features are determined by the interaction strength and their transfer may occur coherently via band mechanism (small-polaron band), or in an incoherent way through random jumps between neighboring lattice sites [28].

On the other hand, the relevance of solitons as transfer mechanisms can not be fully excluded. The best-known examples are large polarons in conjugated polymers (polyacetylene, for example) studied extensively within the Su-Schrieffer-Heeger (SSH) model [12,13].

In this paper, we reconsider polaron-mediated EET processes accounting for the induced renormalization of energy parameters of attached donor or acceptor (D/A) molecule(s) and molecular chain. Particular attention is paid to examining how this effect may impede or enhance transfer reactions. So far, this problem has been considered within the framework of soliton theory [1,7], while here we focus on the nonadiabatic limit. The case of ST of a single excess excitation will be considered.

The paper is organized as follows: In Sec. II, we introduce the model and briefly discuss the character of ST states in dependence on system parameters. In Sec. III we sketch a mean-field model for nonadiabatic polaron and discuss its validity. The energy spectrum of ST states modified to account for D/A influence, is presented in Sec. IV. Extended discussion and comparison of present results with those where this influence was not considered, is presented in Sec. V. In the last section, we give a summary of the obtained results emphasizing their possible relevance.

II. MODEL

The system under consideration is sketched in Fig. 1. It consists of a long molecular chain to which a donor or acceptor molecule is attached. The MC consists of $N \gg 1$ equally spaced structure elements at distance R_0, while the D/A molecule is attached an aside particular structure element of the MC.

We recall that the transport reactions take place as successive reactions $\mathrm{D}^* + \mathrm{MC} \rightarrow \mathrm{D} + \mathrm{MC}^*$ and $\mathrm{MC}^* + \mathrm{A} \rightarrow \mathrm{MC} + \mathrm{A}^*$, where the superscript asterisks denote the excited molecule. Our study is performed within a simplified scheme in which we did not consider the initial stage of the reaction, the excitation of the attached molecule. As a theoretical framework, we applied the Holstein molecular crystal model [21,28,35,36], modified to account for the presence of the D/A molecule. The system Hamiltonian is

$$\hat{H} = \hat{H}_{\mathrm{MC}} + \hat{H}_C. \tag{1}$$

Here, the first term on the right side is the Hamiltonian of molecular bridge specified in a usual way [28]:

$$\hat{H}_{\mathrm{MC}} = \mathcal{E}_0 \sum_n \hat{B}_n^\dagger \hat{B}_n - J \sum_n \hat{B}_n^\dagger (\hat{B}_{n+1} + \hat{B}_{n-1}) + \sum_q \hbar\omega_q \hat{b}_q^\dagger \hat{b}_q + \frac{1}{\sqrt{N}} \sum_{n,q} F_q e^{iqnR_0} \hat{B}_n^\dagger \hat{B}_n (\hat{b}_q + \hat{b}_{-q}^\dagger), \tag{2}$$

where $\hat{B}_n^\dagger$ and $\hat{B}_n$ are creation and annihilation operators of the excitation on the nth structure element of the MC. The $\mathcal{E}_0$ is the energy required to excite the corresponding excitation mode on the particular structure element of the MC. In the case of an electron in a polypeptide MC, it is the excitation energy of the weakest bound electron in the peptide group (the extra electron injected on the nth peptide group is at the state determined by the energy level $\mathcal{E}_0$). The J is the transfer integral between neighboring structure elements of MC. In the vibron case, it is the energy of the resonant dipole-dipole interaction; in the case of the electron, it corresponds to the overlap of electronic orbitals between neighboring molecules. The last two terms in Eq. (2) correspond to lattice modes and their interaction with molecular groups, where $\hat{b}_q^\dagger$ ($\hat{b}_q$) are the creation (annihilation) operators of the phonon in qth phonon mode (q is the phonon wave number).

Within Holstein's molecular crystal model, where excitation interacts with dispersionless optical phonons, system parameters have simple forms: $\omega_q \equiv \omega_0 = 2\sqrt{\kappa/M}$ and $F_q \equiv F = \chi\sqrt{\hbar/(2M\omega_0)}$. Here, κ is the "coefficient of elasticity" of the chain, M is the mass of the molecular group of the chain, and χ is the excitation-phonon interaction constant.

The system parameter space of the model may be reduced to just two parameters: adiabatic parameter $B = 2J/\hbar\omega_0$, and coupling constant $S = E_b/\hbar\omega_0$. Here $E_b = \frac{1}{N}\sum_q \frac{|F_q|^2}{\hbar\omega_0}$ denotes so-called small-polaron binding energy which measures the depth of the (self-)trapping potential. The mutual ratio of S and B determines the character of ST states. Two limiting cases are well understood: adiabatic $B \gg 1$ and the nonadiabatic $B \ll 1$. In the adiabatic limit, provided that $B > S$, a large polaron (soliton) may arise. In the opposite case ($B \ll 1$), fast phonons instantaneously follow polaron whose size is of the order of lattice constant [28,29].

The last term in Eq. (1) corresponds to the excitation Hamiltonian and its interaction with the molecular chain and may be specified as follows:

$$\hat{H}_C = \mathcal{E}_C \hat{C}^\dagger \hat{C} + L(\hat{B}_m^\dagger \hat{C} + \hat{C}^\dagger \hat{B}_m). \tag{3}$$

The first term above describes the excitation of the attached molecule, which can be either a donor or an acceptor. Operators $\hat{C}^\dagger$ and $\hat{C}$ are creation and annihilation operators of the excitation on the attached molecule with energy $\mathcal{E}_C$. The second one describes the excitation transfer between the attached

TABLE I. Parameters

Parameter	α-helix	ACN
J	7.8 cm^{-1} (0.97 meV)	7.8 cm^{-1} (0.97 meV)
κ	(13–20) N/m	(39–58) N/m
$\chi_{C=O}$	(35–62) pN	56(62) pN
χ_{NH}	–	≈330 pN
M	$\approx 5.7 \times 10^{-25}$ kg	$\approx 2.25 \times 10^{-25}$ kg

molecule and the MC, where L is the energy of resonant dipole-dipole interaction between the attached molecule and the nearest molecular group of MC. Usually, it can be assumed that $L \leqslant J$.

III. MEAN-FIELD TREATMENT: NONADIABATIC POLARON

Let us briefly recall the values of the physical parameters of the system that are important for our model. Here, we used values of system parameters for α-helix and ACN which are among the most experimentally studied substances in the context of polaron-mediated intramolecular energy transfer. So far available data [17,18,37–41] are listed in Table I.

At this stage, we must recall that, despite intensive studies, there still exists certain uncertainty in the values of system parameters. It especially concerns the exciton-phonon interaction constant χ since there are no reliable experimental data, but it is usually determined indirectly by employing a preassumed model [17,42–44]. The coefficient of the elasticity κ presented here is for the hydrogen-bonded structure elements of the MC. With the label NH we denoted the value of the χ in the case of the intramolecular excitation of the NH group of the peptide bond, while the $C = O$ label denoted the intramolecular excitation of the amide-I ($C = O$) stretching mode.

According to the values from Table I, the typical phonon frequency is about $\omega_0 \approx 10^{13}\ \mathrm{s}^{-1}$. This implies that the coupling constant may vary from 0.01 to 5. At the same time, the adiabatic parameter ranges from 0.01 to 1. Under these conditions, nonadiabatic polaron may be accurately described employing various methods based on Lang-Firsov unitary transformation (LFUT) and its variational extension in combination with perturbation theory. The explicit form of the LFUT operator is $\hat{U} = e^{-\sum_n \hat{B}^\dagger_n \hat{B}_n \hat{S}_n}$ where $\hat{S}_n = \frac{1}{\sqrt{N}} \sum_q \frac{F_q}{\hbar\omega_q} e^{iqnR_0} (\hat{b}_q - \hat{b}^\dagger_{-q})$ [21,36,45–47].

The LFUT exactly diagonalizes H_{MC} in the transportless limit $J = 0$. The transformed Hamiltonian $\hat{\hat{H}} = \hat{U}\hat{H}\hat{U}^{-1}$ attains a simple form $\hat{\hat{H}} = (\mathcal{E}_0 - \mathcal{E}_b)\sum_n \hat{B}^\dagger_n \hat{B}_n + \sum_q \hbar\omega_q \hat{b}^\dagger_q \hat{b}_q$, corresponding to two noninteracting Bose fields: phonon-dressed excitations and new phonons in lattice with shifted equilibrium position of the molecular group. As we have a single excitation problem, here we have neglected the effective excitation-excitation interaction. Here, the operators $\hat{B}^\dagger_n$ ($\hat{B}_n$) and $\hat{b}^\dagger_q$ ($\hat{b}_q$) are the creation and annihilation operators of these new quasiparticles. For nonvanishing J, "dressed" excitation and new phonons remain coupled through $-J \sum_n \hat{B}^\dagger_n (\hat{B}_{n+1} e^{\hat{S}_{n+1} - \hat{S}_n} + \mathrm{H.c.}) \equiv -Je^{-S} \sum_n e^{-\sum_q \beta_q \hat{b}^+_q} e^{\sum_q \beta^*_q \hat{b}_q} \hat{B}^\dagger_n \hat{B}_{n+1} + \mathrm{H.c.}$ Here S is coupling constant and $\beta_q = \frac{F_q}{\hbar\omega_q} e^{iqmR_0}$.

The interaction of dressed excitation with displaced phonons is highly nonlinear in phonon operators and corresponds to intersite tunneling of dressed excitation surrounded by many phonons. From its explicit form, one may see that in the case of high occupancy of phonon modes $\hat{b}^\dagger \hat{b}_q \gg 1$ and in the strong coupling limit $S \gg 1$, it rapidly tends to zero, implying further treatment employing perturbation theory. For that purpose, it is necessary to define the Hamiltonian of interaction which may be treated as a small perturbation. In practice, this involves a simple trick: the adding and subtracting $\langle \hat{\hat{H}} \rangle_{\mathrm{ph}}$ to $\hat{\hat{H}}$, which, after the appropriate rearrangement yields the model Hamiltonian consisting of the sum of polaron effective Hamiltonian and the residual interaction with new phonons: $\hat{\hat{H}} = \langle \hat{\hat{H}} \rangle + H_{\mathrm{int}}$ [46]. The last term here $H_{\mathrm{int}} = \hat{\hat{H}} - \langle \hat{\hat{H}} \rangle$ is usually treated as a perturbation. The validity of perturbation treatment is determined by values of coupling constant S and adiabatic parameter B. In particular, it holds in a nonadiabatic ($B \ll 1$) and strong coupling ($S \gg 1$) regimes, while it fails in the weak coupling case.

To overcome this difficulty, a variational extension of the LFUT method, sometimes called the partial dressing approach, is suggested [20,35,36]. It further involves mean-field approximation based on assumptions that the phonon ensemble is in the thermodynamic equilibrium with the surrounding thermal bath at the temperature T and that dressed quasiparticle represents a "good" eigenstate of a system whose features may be satisfactorily described within an effective Hamiltonian with a renormalized tunneling parameter. Technically, the partial dressing approach involves modified LFUT in which $F_q/\hbar\omega_q$ is replaced by a variational parameter (f_q) whose optimized form follows employing the Bogoliyubov theorem [20,47]. Such a treatment enables the extension of LFUT approaches toward adiabatic and weak coupling limits. It relies on the picture that dressed quasiparticle represents a good eigenstate of the system, and analysis of ST states has been usually performed within an effective Hamiltonian $\langle \hat{\hat{H}} \rangle \equiv \hat{\mathcal{H}}_{\mathrm{exc}}$. In the present case, for the weak coupling and nonadiabatic limits variational parameter is $\sim \frac{F_q}{\hbar\omega_q}$ [21,35,36], and effective Hamiltonian reads as

$$\begin{aligned}\hat{\mathcal{H}}_{\mathrm{exc}} = {} & \mathcal{E}_C \hat{C}^\dagger \hat{C} + (\mathcal{E}_0 - \mathcal{E}_b) \sum_n \hat{B}^\dagger_n \hat{B}_n \\ & - Je^{-W_J(T)} \sum_n \hat{B}^\dagger_n (\hat{B}_{n+1} + \hat{B}_{n-1}) \\ & + Le^{-W_L(T)} (\hat{B}^\dagger_m \hat{C} + \hat{C}^\dagger \hat{B}_m),\end{aligned} \tag{4}$$

where $W_J(T) = \frac{1}{N} \sum_q \frac{|F_q|^2}{(\hbar\omega_q)^2} [1 - \cos(qR_0)] \coth(\frac{\hbar\omega_q}{2k_BT})$ and $W_L(T) = \frac{1}{2N} \sum_q \frac{|F_q|^2}{(\hbar\omega_q)^2} \coth(\frac{\hbar\omega_q}{2k_BT})$ are the renormalization factors of J and L, respectively. Model Hamiltonian (4) is the basis for the examination of stationary properties of nonadiabatic polarons, while its dynamics, particularly kinetics, may be examined accounting for the residual interaction.

The analytic mean-field approaches based on LFUT are still widely used and further developed [48,49] even though there are several nonperturbative, numerically exact

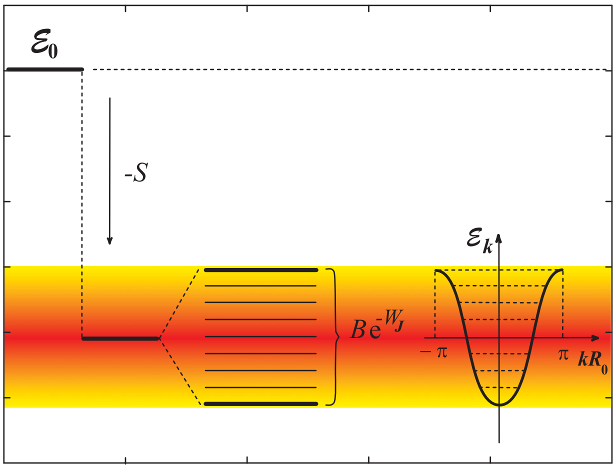

FIG. 2. The creation of a polaron energy band in 1D regular structure (ST excitation process).

methods (such as multiple Davydov ansatz [50] or hierarchical equations of motion [51]) that may exactly evaluate the exciton-phonon dynamics. Nevertheless, these methods are often numerically demanding and nontrivial to implement.

IV. ENERGY SPECTRA OF EXCITATION IN THE D/A-MC STRUCTURE

To examine the influence of the D/A molecule on the energy spectra of dressed excitation located on the molecular bridge, we pass to the k space using the transformation $\hat{B}_n = \frac{1}{\sqrt{N}}\sum_k e^{-iknR_0}\hat{B}_k$. Here, quasiparticle wave number k takes N different values from the interval $kR_0 \in [-\pi, \pi]$. We have

$$\hat{\mathcal{H}}_{\rm exc} = \mathcal{E}_C\hat{C}^\dagger\hat{C} + \sum_k \mathcal{E}_k\hat{B}_k^\dagger\hat{B}_k + \sum_k(\lambda_k^*\hat{B}_k^\dagger\hat{C} + \lambda_k\hat{C}^\dagger\hat{B}_k), \quad (5)$$

where

$$\mathcal{E}_k = \mathcal{E}_0 - \mathcal{E}_b - 2Je^{-W_J(T)}\cos(kR_0),$$
$$\lambda_k = \frac{1}{\sqrt{N}}Le^{-W_L(T)}e^{-ikmR_0}. \quad (6)$$

Here, $\mathcal{E}_k$ is the nonadiabatic polaron band energy at the MC. This expression is identical to the one obtained for the nonadiabatic polaron formed at the MC in the absence of the D/A molecule [21,35,36]. The energy diagram of the excitation ST process is schematically presented in Fig. 2.

To find the energy spectrum of dressed excitation in the D/A-MC system, it is necessary to diagonalize the Hamiltonian (5). If we consider Eq. (5) as a quadratic form

$$\hat{\mathcal{H}}_{\rm exc} = [\hat{C}^\dagger \quad \hat{B}_1^\dagger \quad \dots \quad \hat{B}_N^\dagger] \times \underbrace{\begin{bmatrix} \mathcal{E}_C & \lambda_1 & \lambda_2 & \dots & \lambda_N \\ \lambda_1^* & \mathcal{E}_1 & 0 & \dots & 0 \\ \lambda_2^* & 0 & \mathcal{E}_2 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ \lambda_N^* & 0 & 0 & \dots & \mathcal{E}_N \end{bmatrix}}_{\hat{\mathbb{E}}} \begin{bmatrix} \hat{C} \\ \hat{B}_1 \\ \dots \\ \hat{B}_N \end{bmatrix}$$

its complete diagonalization can be achieved by applying such unitary transformation that will diagonalize the matrix $\hat{\mathbb{E}}$ containing the coefficients from the Hamiltonian (5). Mathematically, this problem reduces to solving the eigenproblem of the coefficient matrix $\hat{\mathbb{E}}$,

$$\hat{\mathbb{E}} \cdot \mathbb{X} = \mathcal{E} \cdot \mathbb{X}$$

which has nontrivial solutions provided that $\det(\mathbb{E} - \mathcal{E} \cdot \mathbb{I}) = 0$ is satisfied. Here, symbol $\mathcal{E}$ represents the set of eigenvalues of the matrix $\hat{\mathbb{E}}$, and $\hat{\mathbb{X}}$ are corresponding eigenvectors. At the same time, the set of values of the parameter $\mathcal{E}$ determines the energy spectrum of the quasiparticle belonging to the entire D/A-MC structure. By solving the above determinant, we obtain the secular equation that determines the quasiparticle energy spectrum:

$$\mathcal{E}_C - \mathcal{E} - \sum_k \frac{|\lambda_k|^2}{\mathcal{E}_k - \mathcal{E}} = 0, \quad (7)$$

where $|\lambda_k|^2 = |\lambda|^2 = \frac{1}{N}L^2e^{-2W_L(T)}$ (it does not depend on k!). Because we are interested in stable states of the excitation in the D/A-MC structure, we will limit ourselves to the analysis of the lowest energy states obtained by solving Eq. (7). In addition, we will look for those solutions of Eq. (7) that satisfy the condition $\mathcal{E}_0 - \mathcal{E} > 2J$. This condition is satisfied for quasiparticles that form the narrow energy band, and biomolecules, as a rule, belong to such a class of systems [1]. The sum over the k can be easily calculated if we replace it with the integral

$$\frac{1}{N}\sum_{k=-\pi/R_0}^{\pi/R_0} A_k \to \underbrace{\frac{R_0}{2\pi}\int_{-\pi/R_0}^{\pi/R_0} A(k)dk}_{x=R_0k} = \frac{1}{2\pi}\int_{-\pi}^{\pi} A(x)dx.$$

Besides, it is useful to present the obtained expressions using the set of dimensionless system parameters: the coupling constant S, adiabatic parameter B, normalized energy of the excitation in the D/A-MC structure $\bar{\mathcal{E}} = \mathcal{E}/\hbar\omega_0$, normalized energy level of the excitation on the D/A molecule $\bar{\mathcal{E}}_C = \mathcal{E}_C/\hbar\omega_0$, and transfer parameter $\gamma = L/J$. The parameter L provides information about the probability of excitation delocalization from the D/A molecule to the nearest structure element of the MC, while the parameter J provides information about excitation delocalization from one structure element to the neighboring one along the MC. Thus, the relative ratio of these two parameters tells us how much easier (or harder) the excitation can migrate along the MC, compared to its delocalization from one molecule to another one. After introducing the set of dimensionless parameters and performing the above-mentioned integration, we obtain

$$\bar{\mathcal{E}}_C - \bar{\mathcal{E}} - \frac{\gamma^2B^2e^{-S\coth(1/2\tau)}}{4\sqrt{(\bar{\mathcal{E}}_0 - S - \bar{\mathcal{E}})^2 - B^2e^{-2S\coth(1/2\tau)}}} = 0, \quad (8)$$

where $\tau = k_BT/\hbar\omega_0$ is the normalized temperature. The obtained equation determines the lowest energy of dressed excitation belonging to the D/A-MC structure. This equation is the main result of our analysis. It allows us to analyze how the properties of injected excitation depend on basic energy parameters of the structure and the environment temperature. Let us notice here that the solutions of Eq. (8) must

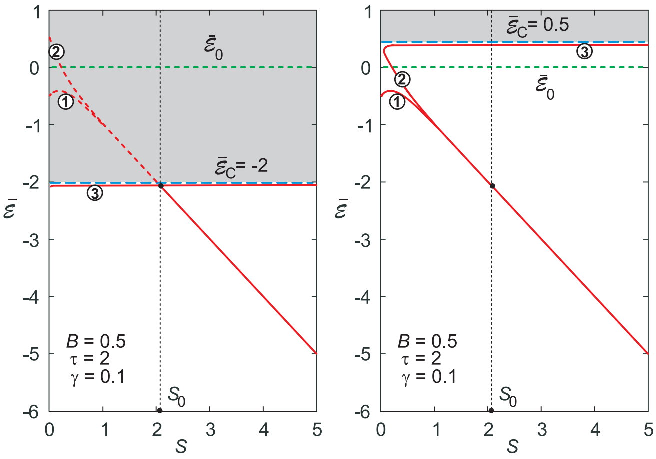

FIG. 3. Typical dependence $\bar{\mathcal{E}}(S)$ for the fixed values of $\bar{\mathcal{E}}_0$, τ, B, γ, and for two values of $\bar{\mathcal{E}}_C$. Short dashed line is the bare excitation energy $\mathcal{E}_0$ of the molecules in MC. The long dashed line is the excitation energy of the D/A molecule. In consistency with the second condition in Eq. (9), S_0 is the intersection point of the branches 1 and 3. The shaded area on the graph represents those values of the energy $\bar{\mathcal{E}}$ that do not satisfy the second condition in Eq. (9).

satisfy the conditions

$$(\bar{\mathcal{E}}_0 - S - \bar{\mathcal{E}})^2 - B^2 e^{-2S\coth(1/2\tau)} > 0, \quad \bar{\mathcal{E}}_C > \bar{\mathcal{E}}. \tag{9}$$

The conditions (9) exclude all values of the $\bar{\mathcal{E}}$ belonging to the interval $\mathcal{E}_{UP} < \bar{\mathcal{E}} < \mathcal{E}_{LO}$. Here, $\mathcal{E}_{LO} = \bar{\mathcal{E}}_0 - S - Be^{-S\coth(1/2\tau)}$ and $\mathcal{E}_{UP} = \bar{\mathcal{E}}_0 - S + Be^{-S\coth(1/2\tau)}$ correspond to the edges of the nonadiabatic polaron energy band, formed due to the excitation self-trapping at the MC, but in the absence of the D/A molecule. Let us note that the ambient temperature affects the excitation energy $\bar{\mathcal{E}}$ only through the exponential factor $e^{-S\coth(1/2\tau)}$, which reduces the adiabatic parameter B: $B(\tau) = Be^{-S\coth(1/2\tau)}$. In principle, the increasing of the ambient temperature τ leads to a rapid reduction of the value of the parameter B.

To compare the obtained results with the nonadiabatic polaron picture, it is most convenient to base further analysis on the study of the functional dependence $\bar{\mathcal{E}}(S)$, treating B, γ, and τ as parameters [20,35,36,45]. For that purpose, we solved Eq. (8) numerically: we transformed it into a polynomial of the fourth degree in the variable $\bar{\mathcal{E}}$ and obtained

$$(\bar{\mathcal{E}}_C - \bar{\mathcal{E}})\{(\bar{\mathcal{E}}_0 - S - \bar{\mathcal{E}})^2 e^{2S\coth(1/2\tau)} - B^2\} - \left(\frac{\gamma B}{2}\right)^4 = 0.$$

Its typical solutions in the nonadiabatic regime and values of coupling constant varying from a weak to strong coupling limit are presented in Fig. 3. The function $\bar{\mathcal{E}}(S)$ for each set of parameters B, γ, τ, $\bar{\mathcal{E}}_C$, and $\bar{\mathcal{E}}_0$ consists of three branches (full curves in Fig. 3), depicted as 1, 2, and 3. This means that, for a given set of parameters, Eq. (8) has three solutions for each value of S. The solutions that satisfy the second condition of in Eq. (9) lie in the area of the $(S, \bar{\mathcal{E}})$ plane, which is below the dashed line ($\bar{\mathcal{E}} = \bar{\mathcal{E}}_C$). For $S < S_0$, physically meaningful solutions (these solutions correspond to the minimal value of the system energy) correspond to the points at the branch 3. At higher values of S, all three solutions exist. Nevertheless, the points from the branch 1 correspond to the minimal value of the excitation energy. As one can remark, in this region of S the branches 1 and 2 are practically inseparable.

To obtain a deeper insight into the nature of these branches, let us consider the energy spectrum of $\hat{\mathcal{H}}_{\text{exc}}$ when $\gamma \ll 1$. In that case, the last term of the Hamiltonian (5) can be treated as a perturbation

$$\hat{H}_{\text{pert}} = \sum_k (\lambda_k^* \hat{B}_k^\dagger \hat{C} + \lambda_k \hat{B}_k \hat{C}^\dagger).$$

The energy spectrum of the unperturbed part of the Hamiltonian (5) is determined by the energy level $\bar{\mathcal{E}}_C$ (corresponding to the quantum state of the single excitation localized on the D/A molecule $|1_C\rangle = \hat{C}^\dagger|0\rangle$) and the energy spectra $\bar{\mathcal{E}}_k$ (corresponding to the states $|1_k\rangle = \hat{B}_k^\dagger|0\rangle$ of self-trapped excitation localized on MC, in the absence of the attached molecule), which forms an energy band due to the assumed translation invariance of the molecule. Due to the presence of the perturbation, the energies of these states in the second order of the perturbation theory become

$$\bar{\mathcal{E}}_C^{(\text{pert})} = \bar{\mathcal{E}}_C - \frac{\gamma^2 B^2}{4} \frac{e^{-S\coth(1/2\tau)}}{\sqrt{(\bar{\mathcal{E}}_0 - \bar{\mathcal{E}}_C - S)^2 - B^2 e^{-2S\coth(1/2\tau)}}},$$
$$\bar{\mathcal{E}}_k^{(\text{pert})} = \bar{\mathcal{E}}_k = \bar{\mathcal{E}}_0 - S - Be^{-S\coth(1/2\tau)}\cos(kR_0). \tag{10}$$

At the same time, the vectors corresponding to these (perturbed) energies differ slightly from the initial (unperturbed) ones. This means that the perturbed state originating from the state $|1_C\rangle$ (for example) is still very close to the initial one. The quasiparticle whose distribution of the probability of finding has a dominant value in the vicinity of the D/A molecule remains centered on the D/A molecule even after the appearance of the perturbation (that is, after the appearance of the interaction with MC). Therefore, we can consider that the excitation that was initially located on the D/A molecule, after the D/A molecule comes into contact with the MC, slightly changes excitation energy, but it remains centered on the D/A molecule. The same conclusion is valid in the case of states corresponding to excitation initially localized on the MC. Of course, when the interaction of the D/A subsystem with the MC becomes large enough, this picture ceases to be applicable. Then the entire structure represents a unique quantum system, and the excitation belongs to the structure as a whole. But, even in this case, we will call the states of the quasiparticle whose energy is close to $\bar{\mathcal{E}}_C$ as states of a particle "centered" on D/A molecule, and those states close to energies $\bar{\mathcal{E}}_k$ as states of dressed excitation "localized" on MC.

As it can be noticed from Eq. (10), for $\gamma \ll 1$ the energy level of the excitation centered on the D/A molecule is slightly reduced. The magnitude of this reduction depends on system parameters and ambient temperature. To see the impact of this correction, let us plot the $\bar{\mathcal{E}}_C^{(\text{pert})}(S)$ and compare it with branch 3, predicted by Eq. (8). From Fig. 4 we can see that $\bar{\mathcal{E}}(S)$ obtained by perturbation calculation (dashed line) approximates the branch 3 (full line) well, for large values of the parameter S. The difference becomes larger when S attains small values. With increasing γ, the difference between the curve obtained by perturbation theory and our model becomes larger (right panel). As we can remark, the energies presented by the branch 3 are close to the energy of the excitation,

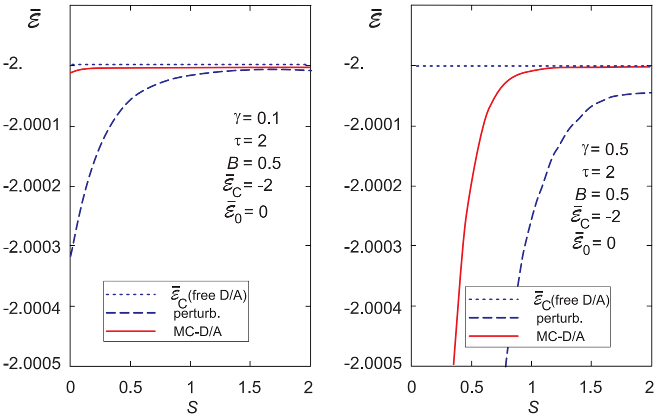

FIG. 4. The dependence $\bar{\mathcal{E}}(S)$ obtained by solving Eq. (8) and that predicted by the perturbation theory.

localized on the D/A molecule in the absence of the MC (free D/A). Therefore, in the case when $\gamma \sim 1$ the states corresponding to the points from the branch 3 can be identified as states originating from an excitation state, centered on the D/A molecule.

On the other hand, the band states $\bar{\mathcal{E}}_k^{(\text{pert})}$ of the self–trapped excitation on the MC are practically unaffected by the presence of the attached molecule. Here, $\bar{\mathcal{E}}_{k=-\pi}^{(\text{pert})}$ coincides with $\mathcal{E}_{UP}$ and $\bar{\mathcal{E}}_{k=0}^{(\text{pert})}$ coincides with $\mathcal{E}_{LO}$. Even for significant values of the parameter γ, the difference between the solutions from branches 1 and 2 [obtained by solving Eq. (8)] differ slightly from those predicted by $\mathcal{E}_{LO}$ and $\mathcal{E}_{UP}$. This especially concerns to the region where $S > S_0$ (from the graph in Fig. 3).

As we can see from Fig. 3, both branches 1 and 2 show typical dependence $\mathcal{E}(S)$ like nonadiabatic polaron quasiparticle, including for large values of S, where the function $\mathcal{E}(S)$ has the form $\mathcal{E}_{SP} \sim -S$ [17,19,21,29]. Like "standard" nonadiabatic polaron, the dressed excitation centered on the MC has the properties of the fully dressed, hardly mobile quasiparticle. That is the reason why the branches 1 and 2 can be identified as the upper and lower edges of the nonadiabatic polaron energy band for polaron self-trapped on MC, even in the case when $\gamma \sim 1$. Since they represent the lowest values of the dressed excitation energy, the branches 1 and 3 play the most important role in the analysis of the polaron stability.

The result obtained here is consistent with our expectations since the MC is usually a significantly larger system than the D/A molecule and the interaction between these two subsystems is much weaker than that between the neighboring structural elements of the MC itself. In the case when the attached molecule is larger, it could interact with the MC not only locally. Such interaction can influence on the mechanical oscillations of the MC, which could significantly change the properties of the nonadiabatic polaron formed on the MC.

Now we can make the basic interpretation of the graphics in Fig. 3. According to the obtained results presented in the left panel on Fig. 3, there are two basic regimes. The first one, where the excitation is centered on the D/A molecule, and the second one, where it migrates to the MC and forms the dressed quasiparticle. These two regimes are separated by the intersection point S_0. In the parameter space, for all $S < S_0$ energy values represented by the curve 3 are the most energetically stable solutions, i.e., the excitation remains located in the vicinity of the attached molecule. For the values $S > S_0$, we find that the energetically most favorable state corresponds to the branch 1. Therefore, we expect that for these values of the system parameters, the excitation initially located on the D/A molecule will pass to the MC and (due to the interaction with the phonons of the MC) forms a hardly mobile but quite stable nonadiabatic polaron state. In the case when the system parameters take such values that all obtained solutions satisfy conditions (9), the polaron states corresponding to the points from the branch 1 represent the most favorable energetic excitation states, for each value of the parameter S. In this case, the intersection point S_0 does not exist, and such D/A molecule represents typical donor structure, even without lowering the excitation energy on the MC due to the polaron effect. This situation is presented in the right panel of Fig. 3.

V. THE IMPACT OF THE D/A PRESENCE ON THE NONADIABATIC POLARON STATE

Let us now examine the impact of D/A presence on the excitation state in the D/A-MC structure. Here, we are primarily interested in what conditions must be satisfied, so that the attached molecule behaves as a donor or as an acceptor system. In general, for the D/A molecule to be a donor, the condition $\mathcal{E}_C > \mathcal{E}_0$ must be fulfilled. Due to the polaronic effect on the MC, this condition takes the form $\mathcal{E}_C > \mathcal{E}_0 - \mathcal{E}_b$, or in terms of the normalized parameters, we need $\bar{\mathcal{E}}_C > \bar{\mathcal{E}}_0 - S$. However, due to the interaction between the D/A molecule and the MC, the condition becomes much more complex and comes down to examining the mutual position of the bottom of the polaron energy band and the energy level of the excitation centered on the D/A molecule. In other words, it comes down to examining the relative position of branches 1 and 3, obtained by solving Eq. 8. This can be done by checking the influence of the parameters that appear within the framework of our model as a direct consequence of the existence of the D/A molecule, such as γ and $\mathcal{E}_C$. Indirectly, the presence of the D/A molecule can affect the properties of the dressed excitation by changing the properties of the MC, that is, by changing the values of those system parameters that are the primary characteristic of the MC. Such parameters are S and B.

A. The influence of γ

Here, we assumed that the transfer parameter γ can take the values from $\gamma \ll 1$ to $\gamma \sim 1$, that is, we supposed that L and J can be of the same order of magnitude. Numerical analysis of Eq. (8) shows that the increasing of γ slightly increases the distance between the branches 1 and 2 (spreads the polaron energy band). With the increase of γ, numerical values of the $\bar{\mathcal{E}}$ corresponding to the bottom of the polaron energy band (the branch 1) attain smaller values. At the same time, numerical values that correspond to the top of the polaron energy band (the branch 2) attain slightly larger values. As a consequence, the width of the polaron energy band increases slightly with increasing γ. Despite that, for $S > 1$ the width of the polaron energy band remains quite narrow, and the influence of the presence of the D/A molecule here is practically negligible.

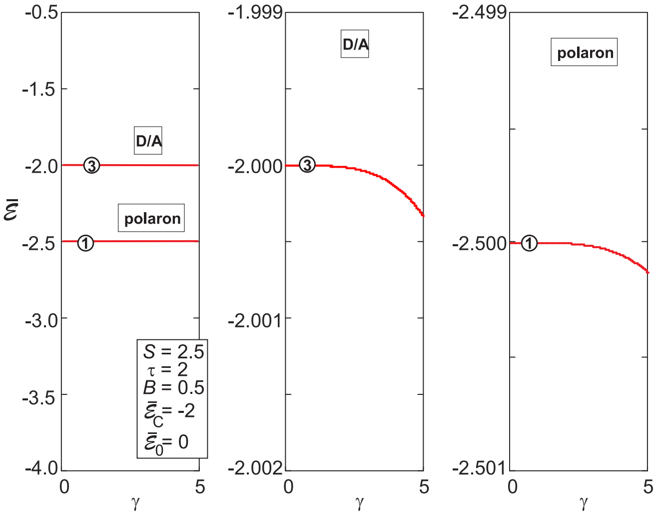

FIG. 5. The dependence $\bar{\mathcal{E}}(\gamma)$, obtained by solving Eq. (8), in strong coupling limit ($S > 1$). Left panel: the relative positions of the bottom of the polaron energy band (branch 1) and excitation energy level on the D/A molecule (branch 3) on γ. Their dependence on the γ can not be seen at the chosen scale. To show this, it is necessary to choose the suitable scale for each branch separately (the middle and the right panels). Middle panel: the dependence of the branch 3 on γ. Right panel: the dependence of the branch 1 on γ. The values of the fixed parameters were chosen so that the graphs show the area to the right of the point S_0.

The spreading of the branches 1 and 2 is very small, and at the scale like that in Fig. 3 is not visible, even for $S \ll 1$. A better insight into this can be gained from the right panel of Fig. 5, where the dependence of the branch 1 on γ is presented on a more convenient scale.

At the same time, the values of $\bar{\mathcal{E}}$ from the branch 3 decrease with increasing γ. For the large values of S, the displacement of the energies from the branch 3 is small, but it is more significant than the displacements of the branches 1 and 2, especially for the large values of γ (the middle and the right panels on Fig. 5).

As we can see, the change of γ practically does not affect polaron states on the MC, but it influences the excitation energy level on the D/A molecule. This influence is more significant in the weak coupling limit ($S \ll 1$), where all branches of the excitation energy spectrum are distorted. In the strong coupling limit, the change of γ practically does not affect either the excitation energy level on the D/A molecule or the energy of the polaron state on MC. As a consequence, the position of S_0 practically is not affected by γ.

B. The influence of $\mathcal{E}_C$

Here, we examine the influence of the difference $\mathcal{E}_C - \mathcal{E}_0$ on the properties of the single excitation in the D/A-MC structure (Fig. 6).

The first we notice is that the position of the polaron energy band (the branches 1 and 2) practically does not depend on the difference $\bar{\mathcal{E}}_C - \bar{\mathcal{E}}_0$. As can be seen, in the case $\bar{\mathcal{E}}_C - \bar{\mathcal{E}}_0 > 0$, the polaron state is energetically more favorable than the state of the excitation localized on the D/A molecule for all values

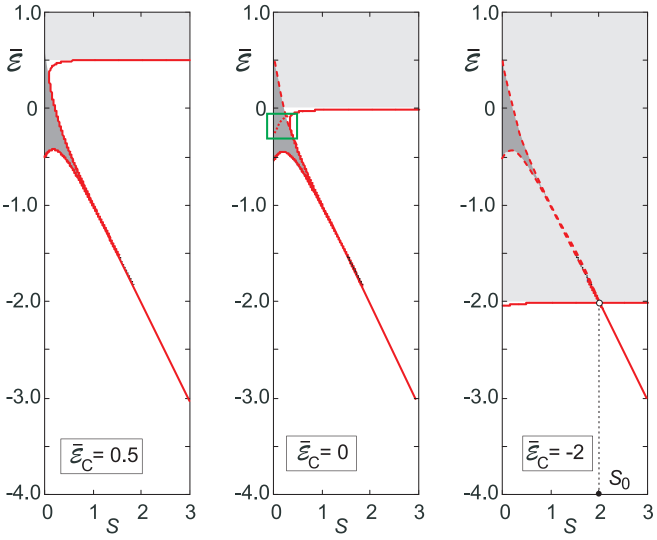

FIG. 6. The dependence $\bar{\mathcal{E}}(S)$, for $\bar{\mathcal{E}}_0 = 0$, $\gamma = 1$, $B = 0.5$, $\tau = 2$, for the three values of $\mathcal{E}_C$.

of the parameter S (left panel on Fig. 6). Physically, this means that the excitation can perform the transition from the attached molecule to MC, regardless of the coupling strength of the excitation with the phonon subsystem of the MC. The only condition that should be satisfied is that the excitation can form the nonadiabatic polaron state at MC (i.e., that S is large enough to form a quantum well where excitation can be "captured") [17,35,36]. The transfer parameter γ has no significant influence here, except for the extremely large values of γ and small values of S. In that case, the branch 3 can be so distorted that the exciton states localized on the D/A molecule become energetically more favorable than the polaron state on the MC. A similar situation is observed for the case $\bar{\mathcal{E}}_C = \bar{\mathcal{E}}_0$. Let us note that in this case the energy level of the excitation localized on the D/A molecule can be "nested" in the polaron energy band (rectangle area on the middle panel of Fig. 6). For these values of the system parameters, the excitation is in such a quantum state that it is delocalized to the entire D/A-MC structure, and it easily migrates from one subsystem to another one and vice versa [52].

The situation is quite different when $\bar{\mathcal{E}}_C - \bar{\mathcal{E}}_0 < 0$. In that case, there is a threshold value S_0 for the parameter S, below which the excitation remains on the D/A molecule, although the condition for the formation of the nonadiabatic polaron state on the MC is satisfied. But, for $S > S_0$ the D/A molecule can inject the excitation on the molecular chain. The effect is more pronounced for the strong coupling limit. At the same time, the larger difference $\bar{\mathcal{E}}_C - \bar{\mathcal{E}}_0$ implies the larger critical value S_0 (that is, the intersection point of the branches 1 and 3, moves toward larger values).

C. The influence of B and τ

Finally, we analyzed the influence of the system temperature τ and the adiabatic parameter B on the excitation energy in the D/A-MC structure.

The dependence $\mathcal{E}(S)$ for different values of the normalized temperature τ is presented in Fig. 7. Similarly to previous

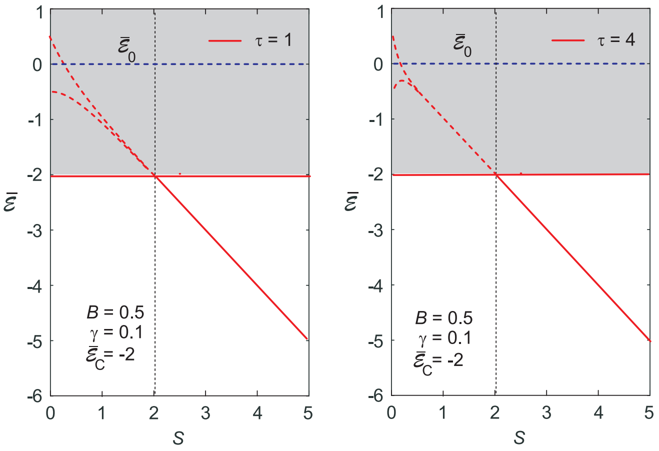

FIG. 7. The dependence $\bar{\mathcal{E}}(S)$ for different values of τ. The value $\tau = 4$ corresponds to the room temperature.

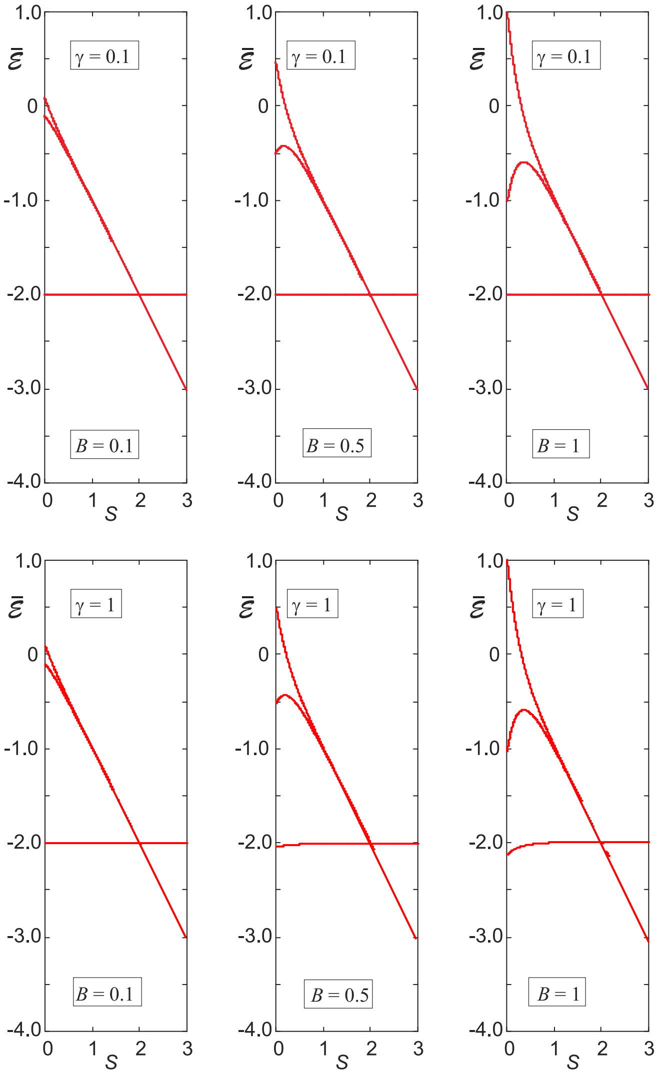

FIG. 8. The dependence $\bar{\mathcal{E}}(S)$, for $\tau = 2$, $\bar{\mathcal{E}}_0 = 0$, $\bar{\mathcal{E}}_D = -2$, for various values of B.

cases, the most remarkable changes in the excitation energy spectra occur in the area $S \ll 1$. According to the obtained results, the increasing of the system temperature τ brings curves 1 and 2 closer, that is, narrows the energy band of dressed excitation.

Let us now examine the influence of the adiabatic parameter B on the energy spectrum of the ST exciton state in the D/A-MC system. From Fig. 8 one can notice that the changing of B affects all branches of excitation spectra, especially for $S < 1$ and for large γ. Here, the increase of B leads to the spreading of the polaron band on the one hand, and the lowering of the excitation energy level on the D/A molecule on the other hand. But in the strong coupling limit, the energy spectrum of the excitation shows "strict" properties of the nonadiabatic polaron or the properties of the excitation localized on the D/A molecule (depending on whether the values of the system parameters correspond to the area below or above S_0).

In any case, the changing of B and τ does not affect the position of S_0, that is, the condition required for excitation transfer from the attached molecule on MC (and vice versa). It determines the width of the nonadiabatic polaron energy band and, consequently, its effective mass when excitation migrates on MC and forms the nonadiabatic polaron state.

VI. CONCLUSION

Let us now briefly summarize the main results of the presented paper. We have shown that excitation injected into the molecular chain by the "donor" molecule can form (due to the interaction with the phonons of the MC) a "dressed" quasiparticle, the properties of which correspond to the nonadiabatic polaron. At the same time, the presence of the attached molecule does not significantly change the conditions for the polaron formation on the molecular chain. On the other hand, the "acceptor" molecule can capture the excitation from the MC and destroy the polaron state. Whether the attached molecule behaves as a donor or an acceptor depends on the values of the basic energy parameters of the structure. First of all, on the values of $\mathcal{E}_C$, $\mathcal{E}_0$, and $\mathcal{E}$. Structures whose system parameters correspond to the area from the left of S_0 are typical acceptor systems, and those whose parameters are to the right of S_0 represent typical donor structures (of course, the condition $S \gg 1$ and $B \ll 1$ must be satisfied).

According to the proposed model, the presence of the D/A molecule does not affect the state of the nonadiabatic polaron localized on the MC. On the other hand, the MC can significantly change the excitation state of the D/A molecule. Its influence is most pronounced for large values of γ and in the weak interaction limit. The influence of the ambient temperature is reflected primarily in the reduction of the adiabatic parameter B. As the temperature increases, the system becomes more nonadiabatic, and the polaron energy band narrows. As a consequence, the inertness of the polaron increases.

Our conclusions are expected because the attached molecule is significantly smaller compared to the MC and interacts with it only locally. In the proposed model, this fact reflects in neglecting the influence of the attached molecule on the mechanical oscillations of the MC. When the attached molecule is large, its presence could change the exciton-phonon interaction constant F_q on the MC and indirectly affects the polaron properties. There is another interesting mechanism that can potentially change the phonon spectra of the MC and thus influence the properties of the energy spectra of the D/A-MC system, namely, the formed polaron can reversibly change the phonon spectrum of the medium in which the polaron forms. Such "feedback" effect of polaron has been studied in both adiabatic [53] and nonadiabatic limits [54]. According to the results of these studies, the feedback effect leads to the hardening of the phonon modes in the nonadiabatic limit. As a consequence, all the branches of the energy spectrum of the D/A-MC system can be changed.

In addition, we mentioned that the values of the basic parameters of biomolecules are not known exactly. The discussion about whether they belong to the adiabatic or nonadiabatic limit, as well as whether the interaction of the excitation with the mechanical oscillation of the MC belongs to the limits of the strong, medium, or even weak exciton-phonon interaction continues until now. To explain some effects that did not fit into the "standard" nonadiabatic polaron model, it is useful to apply the models based on the partial dressing approach. According to such models, two types of polarons can occur in MCs. The first one corresponds to a weakly dressed (almost free) excitation, while the second one corresponds to a heavily dressed (standard) nonadiabatic polaron. The transition between these two states in the parameter space occurs abruptly [35,36,55,56]. At the same time, the boundary in the parameter space that separates these two solutions depends on the environment temperature [35]. In that sense, it would be interesting to consider how the presence of the attached molecule affects these two solutions, especially the values of the system parameters that are characteristic of the boundary region separating the mentioned solutions. However, this goes beyond the scope of this paper and will be the subject of our further research.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia through the project Contract No. 451-03-47/2023-01/200017. The authors would like to acknowledge the contribution of the COST Action CA21169, supported by COST(European Cooperation in Science and Technology). We would like to thank Dr. S. Zdravkovic for the discussion and useful suggestions.

---

[1] A. S. Davydov, *Biology and Quantum Mechanics* (Naukova Dumka, Kiev, 1979).

[2] A. S. Davydov, *Solitons in Molecular Systems* (Reidel, Dordrecht, 1985).

[3] E. G. Petrov, *Physics of Charge Transfer in Biological Systems* (Naukova Dumka, Kiev, 1984).

[4] D. Voet and J. G. Voet, *Biochemistry*, 3rd ed. (Wiley, New York, 2004).

[5] T. Dauxois and M. Peyrard, *Physics of Solitons* (Cambridge University Press, Cambridge, 2006).

[6] V. N. Kharkyanen, E. G. Petrov, and I. I. Ukrainskii, J. Theor. Biol. **73**, 29 (1978).

[7] L. S. Brizhik, B. M. A. G. Piette, W. J. Zakrzewski, Phys. Rev. E **90**, 052915 (2014).

[8] X. Chen, X. Zhang, X. Xiao, Z. Wang, and J. Zhao, Angew. Chem. Int. Ed. **62**, e202216010 (2023).

[9] V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey, and J.-L. Bredas, Chem. Rev. **107**, 926 (2007).

[10] *Coherent Excitations in Biological Systems*, edited by H. Fröhlich and F. Kremer (Springer, Berlin, 1983).

[11] A. A. Gogolin, Phys. Rep. **157**, 347 (1988).

[12] D. K. Campbell, A. R. Bishop, and K. Fesser, Phys. Rev. B **26**, 6862 (1982).

[13] A. J. Heeger, S. Kivelson, J. R. Schrieffer, and W.-P. Su, Rev. Mod. Phys. **60**, 781 (1988).

[14] A. S. Davydov and N. I. Kislukha, Phys. Status Solidi B **59**, 465 (1973).

[15] A. S. Davydov and N. I. Kislukha, Zh. Eksp. Teor. Fiz. **71**, 1090 (1976) [JETP **44**, 571 (1976)].

[16] L. Cruzeiro, Low Temp. Phys. **48**, 973 (2022).

[17] D. M. Alexander and J. A. Krumhansl, Phys. Rev. B **33**, 7172 (1986).

[18] A. C. Scott, Phys. Rep. **217**, 1 (1992).

[19] D. Emin, Phys. Rev. B **33**, 3973 (1986).

[20] D. W. Brown and Z. Ivić, Phys. Rev. B **40**, 9876 (1989).

[21] D. Chevizovich, in *Nonlinear Dynamics of Nanobiophysics*, edited by S. Zdravkovic and D. Chevizovich (Springer, Singapore, 2022).

[22] E. M. Conwell and S. V. Rakhmanova, Proc. Natl. Acad. Sci. USA **97**, 4556 (2000).

[23] E. M. Conwell, Proc. Natl. Acad. Sci. USA **102**, 8795 (2005).

[24] H.-B Schüttler and T. Holstein, Ann. Phys. **166**, 93 (1986).

[25] E. W. Young, P. B. Shaw, and G. Whitfield, Phys. Rev. B **19**, 1225 (1979).

[26] P. B. Shaw and E. W. Young, Phys. Rev. B **24**, 714 (1981).

[27] A. H. Castro Neto, A. O. Caldeira, Phys. Rev. B **46**, 8858 (1992).

[28] T. Holstein, Ann. Phys. **8**, 325 (1959).

[29] E. I. Rashba, in *Excitons*, edited by E. I. Rashba and M. Struge (North-Holland, Amsterdam, 1982).

[30] S. I. Pekar, Zh. Eksp. Teor. Fiz. **16**, 335 (1946) [J. Phys. USSR **10**, 341 (1946)].

[31] L. D. Landau and S. I. Pekar, Zh. Eksp. Teor. Fiz. **18**, 419 (1948) [Ukr. J. Phys. **53**, 71 (2008)].

[32] D. Čevizović, Z. Ivic, D. Toprek, D. Kapor, Z. Przulj, Chaos, Solitons Fractals **73**, 71 (2015).

[33] D. Čevizović, Z. Ivic, Z. Przulj, J. Tekic, and D. Kapor, Chem. Phys. **426**, 9 (2013).

[34] J. Edler, R. Pfister, V. Pouthier, C. Falvo, and P. Hamm, Phys. Rev. Lett. **93**, 106405 (2004).

[35] D. Čevizović, S. Galovic, A. Reshetnyak, and Z. Ivic, Chin. Phys. B **22**, 060501 (2013).

[36] D. Čevizović, S. Galovic, and Z. Ivic, Phys. Rev. E **84**, 011920 (2011).

[37] A. C. Scott, Phys. Rev. A **26**, 578 (1982).

[38] C. Falvo and V. Pouthier, J. Chem. Phys. **123**, 184709 (2005).

[39] N. A. Nevskaya and Y. N. Chirgadze, Biopolymers **15**, 637 (1976).

[40] D. Hennig, Phys. Rev. B **65**, 174302 (2002).

[41] J. Edler, Femtosecond spectroscopy on vibrational self–trapping in molecular crystals and α-helices, Dissertation, Zurich, 2005.

[42] V. Pouthier, Phys. Rev. E **81**, 031913 (2010).

[43] V. Pouthier, Phys. Rev. E **78**, 061909 (2008).

[44] V. Pouthier, J. Chem. Phys. **132**, 035106 (2010).

[45] D. Čevizović, S. Galovic, S. Zekovic, and Z. Ivic, Phys. B: Condens. Matter **404**, 270 (2009).

[46] I. G. Lang, Y. A. Firsov, Z. Eksp. Teor. Fiz. **43**, 1843 (1962) [JETP **16**, 1301 (1963)].

[47] D. Yarkony and R. Silbey, J. Chem. Phys. **65**, 1042 (1976).

[48] Y. Zhang, C.-Y. Yam, Y.-H. Kwok and G.-H. Chen, J. Chem. Phys. **143**, 104112 (2015).

[49] N. Prodanović and N. Vukmirović, Phys. Rev. B **99**, 104304 (2019).

[50] Y. Zhao, K. Sun, L. Chen, and M. Gelin, WIREs Comput. Mol. Sci. **12**, e1589 (2021).

[51] Y. Tanimura, J. Phys. Soc. Jpn. **75**, 082001 (2006).

[52] G. D. Mahan, *Many-Particle Physics* (Plenum, New York, 1986).

[53] G. Kalosakas, S. Aubry, and G. P. Tsironis, Phys. Rev. B **58**, 3094 (1998).

[54] Z. Ivic, S. Zekovic, D. Cevizovic, and D. Kostic, Phys. B **355**, 417 (2005).

[55] A. Alvermann, H. Fehske, and S. A. Trugman, Phys. Rev. B **81**, 165113 (2010).

[56] P. Hamm and G. P. Tsironis, Phys. Rev. B **78**, 092301 (2008).