Turkish Journal of Physics

Volume 31 | Number 5 Article 1

1-1-2007

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Turk J Phys
31 (2007) , 235 – 251.

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Received 27.02.2007

Abstract

In this paper a variational study of a tunnelling exciton (Frenkel exciton) coupled to an arbitrary number of phonon modes is presented. The results of our model are presented both for weak non-adiabatic cases and for strong cases; and we come to the conclusion that the tunnelling reduction factor, the ground state energy of the tunnelling exciton-phonons system, and the mean number of ground state phonons, as the functions of the exciton-phonons coupling strength, are continuous, a condition that does not apply in cases of the tunnelling exciton-phonons models presented in the previous studies. In comparison with the previous studies, the presented model leads to a significant decrease of the ground state energy both of the small polaron and of the tunnelling exciton-phonons system, mainly for weak non-adiabatic cases.

Key Words: Hamiltonian; Ground state approximation; Vacuum state.

PACS: 71.35.Aa

1. Introduction

In recent years much attention has been paid to two-state systems (tunnelling systems) linearly coupled to a boson field [1]. These systems are the fundamental models of the exciton motion, polaron motion, molecular polarons, defects in insulators, diffusion of impurities, charged particle motion in metals, tunnelling of atoms in glasses, spin–phonon relaxation, etc.

Up to now, the exact ground state wave functions of the two-state system linearly coupled to an arbitrary number of phonon modes have not been yet found. Therefore, there is continual interest to find these ground state wave functions, and of course, the analytical ground state wave functions; for, should these be found, the solutions could give us a better physical view on a studied problem than numerical methods. Of late, a combination of the unitary transformation and the variational principle has been used [2–6] to find out the approximations of these ground state wave functions. In this paper this method is also applied.

If the exact eigenfunctions and eigenvalues of an original Hamiltonian can not be found, then the shape of a unitary transformation of the original Hamiltonian can help us find a convenient form of the variational solution for a given problem. In our ground state model of the two-state system linearly coupled to an arbitrary number of phonon modes, the Lang-Firsov unitary transformation is applied to transform the studied problem into a small polaron system. After this unitary transformation a variational method using a trial ground state wave function is used. The construction of this trial ground state wave function follows

from a physical view of a studied problem so as to explain some ground state properties of the tunnelling exciton-phonons system.

In this paper, special attention is paid to the tunnelling reduction factor and the ground state energy values of the tunnelling exciton-phonons system the same as in the other works dealing with these quantities.

2. The Ground State Approximation

For further considerations, we introduce the concept a two-state exciton which will describe the exciton occupying two states represented by two orthonormal wave functions $|1\rangle$ and $|2\rangle$; these wave functions can be called orbits of the exciton.

The two-state exciton (or tunnelling exciton) linearly coupled ("adhered") to M phonon modes, and tunnelling between two sites 1 and 2, is described by the Hamiltonian

$$\begin{aligned} H = &-T\left[|1\rangle\langle 2| + |2\rangle\langle 1|\right] \otimes 1_B + \sum_{i=1}^{M} \hbar\omega_i \left[|1\rangle\langle 1| + |2\rangle\langle 2|\right] \otimes b_i^+ b_i \\ &+ \sum_{i=1}^{M} g_i \left[|1\rangle\langle 1| - |2\rangle\langle 2|\right] \otimes (b_i^+ + b_i) \end{aligned} \tag{1}$$

where T is the bare exciton tunnelling parameter; b_i^+ and b_i, $i = 1,..., M$, are creation and annihilation boson operators for mode i (frequency ω_i) of an aside-molecule which has a substantially larger mass than the exciton and which is placed aside of site positions; g_i is the coupling constant to the i^{th} phonon mode for the tunnelling exciton, $|\mathrm{i}\rangle\langle j|$, $i, j = 1, 2$, is the projective operator from the space generated by the state $|j\rangle$ on the space generated by the state $|i\rangle$. 1_B is the unit operator on the Hilbert space Ω, which is defined lower, and $\hbar = h/2\pi$, where h is the Planck constant.

For further considerations, let us define the Hilbert space $\aleph$, in which the solution of our task will be searched, as

$$\aleph = \{\, \Phi | \Phi(x, Q) = \alpha_1 |1\rangle (x)\Psi_1(Q) + \alpha_2 |2\rangle (x)\Psi_2(Q) \,\},$$

where x is the exciton space coordinate, α_1 and α_2 are real numbers and are regarded as the coefficients of a linear combination, and $\Psi_j \in \Omega$, $j = 1, 2$, where Ω is the Hilbert space consisting of all the real-valued functions of Q that have the following properties. If $\Psi \in \Omega$, then its second power has the Lebesgue integral on the Q space, which is defined as the set of M-dimensional vectors

$$Q = \begin{pmatrix} Q_1 \\ . \\ . \\ . \\ Q_M \end{pmatrix}$$

with $Q_j \in (-\infty, +\infty)$, and the second powers of the functions

$Q_j\Psi(Q)$, $Q_j^2\Psi(Q)$, $\frac{\partial^2}{\partial Q_j^2}\Psi(Q)$, j = 1,...,$M$,

have also the Lebesgue integral on the Q space. The scalar product of the elements $\Psi_j \in \Omega$, $j = 1, 2$, is defined as

$$\langle \Psi_1, \Psi_2 \rangle = \int_{-\infty}^{+\infty} \cdots \int_{-\infty}^{+\infty} \Psi_1(Q)\Psi_2(Q) dQ_1 \cdots dQ_M.$$

As usually presented in the literature, the tensor product of functions $|j\rangle$ and $\Psi \in \Omega$ is defined as $(|j\rangle \otimes \Psi)$ $(x, Q) = |j\rangle\ (x)\Psi(Q)$, for all values of x and Q defined above.

If Ξ is a linear operator defined in the space Ω, i.e. $\Xi(\Phi) \in \Omega$, for an arbitrary$\Phi \in \Omega$, then the linear operator $|i\rangle\langle j| \otimes \Xi$ is defined in the space $\aleph$, $i, j = 1, 2$, as

$$|i\rangle\langle j| \otimes \Xi(\Phi) = |i\rangle\langle j| \otimes \Xi(\alpha_1 |1\rangle \otimes \Psi_1 + \alpha_2 |2\rangle \otimes \Psi_2)$$

$$= \alpha_1 \delta_{j1} |i\rangle \otimes \Xi(\Psi_1) + \alpha_2 \delta_{j2} |i\rangle \otimes \Xi(\Psi_2),$$

where δ_{ji} is the Kronecker delta, α_1 and α_2 are the real numbers, $\Psi_k \in \Omega$, $k = 1, 2$, and $\Phi = \alpha_1 |1\rangle \otimes \Psi_1 + \alpha_2 |2\rangle \otimes \Psi_2$. From the definition of the operator $|i\rangle\langle j| \otimes \Xi$, one obtains the expression

$[|i\rangle\langle j| \pm |k\rangle\langle m|] \otimes \Xi(\Phi) = |i\rangle\langle j| \otimes \Xi(\Phi) \pm |k\rangle\langle m| \otimes \Xi(\Phi), \quad i, j, k, m = 1, 2.$

Sites 1 and 2 can be, for example, two equivalent minima of a potential energy of the two-state exciton between which this exciton hops.

In the next calculations, we employ the relations $\hbar\omega_i \equiv \omega_i$, $i = 1, 2, \ldots, M$. We define the Bloch k-states as

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^{2} e^{i_0 k n} |n\rangle,$$

where $N = 2$, $k = (2\pi/N)\, m$ with $m = 0, 1$, and $i_0 = \sqrt{-1}$. Then the Hamiltonian $-T[|1\rangle\langle 2| + |2\rangle\langle 1|] \otimes 1_B$can be rewritten as

$$-T[|1\rangle\langle 2| + |2\rangle\langle 1|] \otimes 1_B = -T \sum_{k=0,\pi} \cos(k) |k\rangle\langle k| \otimes 1_B.$$

The eigenenergies of this Hamiltonian have the values $E_k = -T\cos(k)$ with $k = 0, \pi$, i.e. $-T$ and $+T$, and the eigenstates (band–type solutions or free states) corresponding to these eigenenergies are

$$|k = 0\rangle \otimes |0\rangle = \left(\frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{2}} |2\rangle\right) \otimes |0\rangle,$$

and $|k = \pi\rangle \otimes |0\rangle = \left(-\frac{1}{\sqrt{2}} |1\rangle + \frac{1}{\sqrt{2}} |2\rangle\right) \otimes |0\rangle$,

respectively; the first one is called a delocalized state and the second is called an excited state. In the above,

$$|0\rangle = \pi^{-M/4} \exp(-0.5\, Q_1^2 \cdots - 0.5\, Q_M^2) = \pi^{-M/4} \exp\left(-0.5 \left\langle\left\langle \hat{\mathbf{I}}\, Q, Q \right\rangle\right\rangle\right), \tag{2}$$

where $\hat{\mathbf{I}}$ is the $M \times M$ unit matrix. The double angular brackets denote the scalar product currently used on the Q space.

In this paper the value of Q_i, i =1, ... ,M, represents the i^{th} normal mode coordinate of the aside-molecule. When using representation of the operators b_i^+ and b_i by means of the variable Q_i, we obtain the following expressions currently used also in the other works:

$$b_i = \frac{1}{\sqrt{2}} \left(Q_i + \frac{\partial}{\partial Q_i}\right) \text{ and } b_i^+ = \frac{1}{\sqrt{2}} \left(Q_i - \frac{\partial}{\partial Q_i}\right), i = 1, \ldots, M. \tag{3}$$

For a free exciton, the value of $-T$ can be associated with the binding energy (the bare exciton inner binding energy) between an excited molecule electron and the hole that arises from this excited electron in a molecule valence band.

For the solution of our task, the concept of a small polaron [7] utilizing the following generalization of the Lang-Firsov unitary operator will be applied

$$S = |1\rangle\langle 1| \otimes e^A + |2\rangle\langle 2| \otimes e^{-A},$$

with $\exp(\pm A) \equiv \overset{B}{\otimes} \prod_{i=1}^{M} \exp(\pm \frac{g_i}{\omega_i}(b_i^+ - b_i))$, where the sign $\overset{B}{\otimes}$ denotes the tensor product of phonon operators of the individual modes.

Applying the unitary operator S, we obtain the following unitary transformation of the Hamiltonian H/T:

$$\begin{aligned} S\,(H/T)\,S^+ &= -\left(|1\rangle\langle 2| \otimes e^{2A} + |2\rangle\langle 1| \otimes e^{-2A}\right) \quad (4) \\ &\quad + [|1\rangle\langle 1| + |2\rangle\langle 2|] \otimes \sum_{i=1}^{M} \frac{\omega_i}{T} b_i^+ b_i \\ &\quad + [|1\rangle\langle 1| + |2\rangle\langle 2|] \otimes \sum_{i=1}^{M} (-\frac{g_i^2}{T\omega_i} 1_B) \quad (5) \\ &= H_{\mathrm{SP}} + H_{\mathrm{ph}} + H_{\mathrm{BE}}, \end{aligned}$$

where S^+ is the Hermitian conjugate of S.

Thus, the Hamiltonian (1) of the tunnelling exciton-phonons system has been transformed by the unitary transformation S into a sum of three Hamiltonians. The first of the three is the Hamiltonian $H_{\mathrm{SP}} = -\left(|1\rangle\langle 2| \otimes e^{2A} + |2\rangle\langle 1| \otimes e^{-2A}\right)$ of the small polaron, while the second one is the Hamiltonian

$$H_{\mathrm{ph}} = [|2\rangle\langle 2| + |1\rangle\langle 1|] \otimes \sum_{i=1}^{M} \frac{\omega_i}{T} b_i^+ b_i$$

of phonons, and the third one is the Hamiltonian

$$H_{BE} = [|2\rangle\langle 2| + |1\rangle\langle 1|] \otimes \sum_{i=1}^{M} \left(-\frac{g_i^2}{T\omega_i} 1_B\right)$$

that represents a decrease of the total energy of the tunnelling exciton-phonons system due to the binding between the exciton and all the phonons.

In our case, the small polaron is a stable object created as a consequence of the coupling between the tunnelling exciton and the aside-molecule phonons.

From the physical point of view, the most interesting cases are those in which the values of ω_j, $j = 1, \ldots, M$, and T are comparable (i.e. the values of T/ω_j, $\quad j = 1, \ldots, M$, are not too much different from the value of 1, the parameter ω_j/T is sometimes called a non-adiabaticity parameter with respect to the j^{th} phonon mode), i.e. it's about such cases in which the bare exciton inner binding energy determining the stability of the exciton and the energies ω_j of phonons that try to destroy the exciton stable system have comparable values, and such cases will be also involved in a model presented in this paper. For such cases and for the weak exciton-phonons binding (coupling), i.e. for $\Lambda_j = g_j^2/T\omega_j << 1$, $j = 1, \ldots, M$, utilizing the identities:

$$\left(\frac{g_j}{\omega_j}\right)^2 = \frac{g_j^2}{T\omega_j} \cdot \frac{T}{\omega_j}, \quad j = 1, \ldots, M,$$

we get the result

$$\left(\frac{g_j}{\omega_j}\right)^2 = \frac{g_j^2}{T\omega_j} . \frac{T}{\omega_j} << 1 \quad \Rightarrow \quad \frac{g_j}{\omega_j} << 1,$$

which leads to the approximation

$$|1\rangle\langle 2| \otimes e^{2A} + |2\rangle\langle 1| \otimes e^{-2A} \approx |1\rangle\langle 2| \otimes 1_B + |2\rangle\langle 1| \otimes 1_B.$$

Regardless of the number of phonons of j^{th} mode, the value of $-\Lambda_j$ represents the decrease (expressed in units of T) of total energy of the tunnelling exciton-phonons system that is due to the "adherence" of the tunnelling exciton to all the phonons of the j^{th} mode. (The value of $-\Lambda_j$ is defined similarly in other works).

Thus, in this case, the approximation of the Hamiltonian (4) can be expresed as

$$S\left(H/T\right)S^{+} \approx -\left[\left|1\right\rangle\left\langle 2\right| + \left|2\right\rangle\left\langle 1\right|\right] \otimes 1_B \; + \; \left[\left|1\right\rangle\left\langle 1\right| + \left|2\right\rangle\left\langle 2\right|\right] \otimes \sum_{i=1}^{M} \tfrac{\omega_i}{T} b_i^{+} b_i$$
$$+ \left[\left|1\right\rangle\left\langle 1\right| + \left|2\right\rangle\left\langle 2\right|\right] \otimes \sum_{i=1}^{M} \left(-\tfrac{g_i^2}{T\omega_i} 1_B\right).$$

It means that, in this case, the ground state for the Hamiltonian (4) has approximately the form

$$\frac{1}{\sqrt{2}}\left|1\right\rangle \otimes \left|0\right\rangle + \frac{1}{\sqrt{2}}\left|2\right\rangle \otimes \left|0\right\rangle,$$

which is the ground state of the approximating operator stated a few lines above, and $|0\rangle$ is the phonon vacuum state defined in equation (2). This ground state represents the free exciton state. Thus, in the case of the weak exciton-phonons interaction, the ground state of the exciton-phonons system can be regarded as nearly the free exciton state.

It is known that for strong exciton-phonons binding one gets the inequality $1 << \Lambda_j$, $j = 1, \ldots, M$. As the operator

$$\left|1\right\rangle\left\langle 2\right| \otimes e^{2A} + \left|2\right\rangle\left\langle 1\right| \otimes e^{-2A}$$

is unitary, its norm is equal to 1. For proof of this statement, at first, let us prove that this operator is an isomorphism on the Hilbert space $\aleph$. As an arbitrary element $f \in \aleph$ has the form $f(x,Q) = \alpha_1 \left|1\right\rangle(x)\Psi_1(Q) + \alpha_2 \left|2\right\rangle(x)\Psi_2(Q)$, where the real values of α_1 and α_2 are the real-valued coefficients of a linear combination, and $\Psi_j \in \Omega$, $j = 1, 2$, the element

$$\Phi(x,Q) = \alpha_1 \left|2\right\rangle(x)\Psi_1\left(Q + 2\sqrt{2}\vec{D}\right) + \alpha_2 \left|1\right\rangle(x)\Psi_2\left(Q - 2\sqrt{2}\vec{D}\right),$$

with $\vec{D} = \begin{pmatrix} g_1/\omega_1 \\ . \\ . \\ . \\ g_M/\omega_M \end{pmatrix}$,

has the properties $\Phi \in \aleph$ and $\left(\left|1\right\rangle\left\langle 2\right| \otimes e^{2A} + \left|2\right\rangle\left\langle 1\right| \otimes e^{-2A}\right)(\Phi) = f$, where the expression

$$\exp(2A)\Psi(Q) = \Psi(Q - 2\sqrt{2}\vec{D}),$$

for an arbitrary element $\Psi \in \Omega$, has been applied.

Further, the linear operator $\left|1\right\rangle\left\langle 2\right| \otimes e^{2A} + \left|2\right\rangle\left\langle 1\right| \otimes e^{-2A}$ is the Hermitian one on the space $\aleph$ and

$$\left(\left|1\right\rangle\left\langle 2\right| \otimes e^{2A} + \left|2\right\rangle\left\langle 1\right| \otimes e^{-2A}\right)\left(\left|1\right\rangle\left\langle 2\right| \otimes e^{2A} + \left|2\right\rangle\left\langle 1\right| \otimes e^{-2A}\right) = 1_{\aleph},$$

where $1_{\aleph}$ is the unit operator on the space $\aleph$. Therefore,

$$\left\|\left|1\right\rangle\left\langle 2\right| \otimes e^{2A} + \left|2\right\rangle\left\langle 1\right| \otimes e^{-2A}\right\| = 1 << \sum_{j=1}^{M} \Lambda_j = \Lambda, \tag{6}$$

where sign$\|\|$ denotes the norm of bounded linear operators defined on the Hilbert space $\aleph$ on which the following scalar product is defined:

$$(f,h) = \alpha_1\beta_1 \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} \Psi_1(Q)\,\Phi_1(Q)\,dQ_1 \ldots dQ_M + \alpha_2\beta_2 \int_{-\infty}^{+\infty} \ldots \int_{-\infty}^{+\infty} \Psi_2(Q)\,\Phi_2(Q)\,dQ_1 \ldots dQ_M,$$

where

$$f(x,Q)=\alpha_1\left|1\right\rangle(x)\Psi_1(Q)+\alpha_2\left|2\right\rangle(x)\Psi_2(Q),$$

$$h(x,Q)=\beta_1\left|1\right\rangle(x)\Phi_1(Q)+\beta_2\left|2\right\rangle(x)\Phi_2(Q),$$

And the real values of $\alpha_1,\beta_1,\alpha_2,\beta_2$ are the coefficients of the linear combination, and $\Psi_j,\Phi_j\in\Omega$, $j=1,2$.

Parameter Λ represents a decrease of the total energy of the tunnelling exciton-phonons system that is due to the coupling of the exciton to all the phonons (regardless of the number of these phonons in all the modes).

Thus, relation (5) leads to the approximation

$$S(H/T)S^{+}\approx[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|]\otimes\sum_{i=1}^{M}\frac{\omega_i}{T}b_i^{+}b_i+[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|]\otimes\sum_{i=1}^{M}\left(-\frac{g_i^2}{T\omega_i}1_B\right). \tag{7}$$

Equation (6) means that the ground state of the Hamiltonian $S(H/T)S^{+}$ has approximately the form

$$\frac{1}{\sqrt{2}}\left|1\right\rangle\otimes\left|0\right\rangle+\frac{1}{\sqrt{2}}\left|2\right\rangle\otimes\left|0\right\rangle.$$

Then, in both cases mentioned above, i.e. both for weak and strong exciton-phonons bindings, the ground state of the Hamiltonian (1) has approximately the form

$$S^{+}\left(\frac{1}{\sqrt{2}}\left|1\right\rangle\otimes\left|0\right\rangle+\frac{1}{\sqrt{2}}\left|2\right\rangle\otimes\left|0\right\rangle\right)=\frac{1}{\sqrt{2}}\left|1\right\rangle\otimes e^{A}\left|0\right\rangle+\frac{1}{\sqrt{2}}\left|2\right\rangle\otimes e^{-A}\left|0\right\rangle, \tag{8}$$

where $\exp(\pm A)\equiv\overset{B}{\otimes}\prod_{i=1}^{M}\exp\left(\pm\frac{g_i}{\omega_i}(b_i^{+}-b_i)\right)$.

As the case of the weak exciton-phonons binding is characterized by the inequalities $0\leq g_i/\omega_i<<1$, $i=1,\ldots,M$, which lead to the approximation $S^{+}\approx 1_{\aleph}$, we come to the conclusion that, in this case, the ground state of Hamiltonian (1) has approximately the form

$$\frac{1}{\sqrt{2}}\left|1\right\rangle\otimes\left|0\right\rangle+\frac{1}{\sqrt{2}}\left|2\right\rangle\otimes\left|0\right\rangle.$$

In the case of strong exciton-phonons binding, expression (7) represents a linear combination of two displaced harmonic oscillators from which the first one is displaced in one direction when the tunnelling exciton is in the state $\left|1\right\rangle$ and the second one is displaced in the opposite direction when the tunnelling exciton is in the state $\left|2\right\rangle$.

A so-called intermediate region of the parameters T,g_j,ω_j, $j=1,\ldots,M$, is such one in which the values of $\Lambda$and $\left\|\left|1\right\rangle\left\langle 2\right|\otimes e^{2A}+\left|2\right\rangle\left\langle 1\right|\otimes e^{-2A}\right\|=1$ are comparable, and it is this region has been studied in the literature the most intensively.

As stated above, of late, a variational approach proves a convenient method for finding the approximations of the ground state wave functions. We shall also apply the variational approach to find the analytical wave functions that approximate the ground state wave functions of the Hamiltonian $S(H/T)S^{+}$for the weak, intermediate, and strong exciton-phonon interactions.

First of all, let us notice that the operators $S(H/T)S^{+}$ and $\Re=[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|]\otimes G$, where

$G=\overset{B}{\otimes}\prod_{k=1}^{M}G_k, G_k=e^{i_0\pi b_k^{+}b_k},\quad G_k^2=1_{B,k},\quad k=1,...,M,$

where $1_{B,k}$ is the unit operator on the linear space generated by the wave functions of the k^{th} phonon mode, fulfil commutation relation

$$\left[S(H/T)S^{+},\Re\right]=0. \tag{9}$$

Using expressions (3), Hamiltonian (4) can be rewritten as

$$\begin{aligned} S\left(H/T\right)S^{+} &= -\left[\begin{array}{l} \left|1\right\rangle\left\langle 2\right| \otimes \left(\overset{B}{\otimes}\prod_{i=1}^{M}\exp\left(-2\sqrt{2}\frac{g_i}{\omega_i}\frac{\partial}{\partial Q_i}\right)\right) \\ +\left|2\right\rangle\left\langle 1\right| \otimes \left(\overset{B}{\otimes}\prod_{i=1}^{M}\exp\left(2\sqrt{2}\frac{g_i}{\omega_i}\frac{\partial}{\partial Q_i}\right)\right) \end{array}\right] \\ &+\left[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right]\otimes\sum_{i=1}^{M}\left[\frac{\omega_i}{T}\frac{1}{2}\left(Q_i^2-\frac{\partial^2}{\partial Q_i^2}-1_B\right)\right] \\ &+\left[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right]\otimes\sum_{i=1}^{M}\left[-(g_i^2/T\omega_i)1_B\right]. \end{aligned} \tag{10}$$

For any real-valued phonon wave function $\Phi_{\mathrm{ph}} \in \Omega$ for which

$$\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}(\Phi_{\mathrm{ph}}(Q))^2 dQ_1\cdots dQ_M = 1,$$

and for $\tilde{\Psi}(x,Q) = \left(\frac{1}{\sqrt{2}}\left(1_{e\otimes B}+\Re\right)\left|1\right\rangle\otimes\Phi_{\mathrm{ph}}\right)(x,Q) = \frac{1}{\sqrt{2}}\left|1\right\rangle(x)\Phi_{\mathrm{ph}}(Q) + \frac{1}{\sqrt{2}}\left|2\right\rangle(x)\Phi_{\mathrm{ph}}(-Q)$, where $1_{e\otimes B} = \left(\left[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right]\right)\otimes 1_B$, we obtain the expression

$$\begin{aligned} \Re\tilde{\Psi}(x,Q) &= \Re\left(\frac{1}{\sqrt{2}}\left(1_{e\otimes B}+\Re\right)\left|1\right\rangle\otimes\Phi_{\mathrm{ph}}\right)(x,Q) = \left(\frac{1}{\sqrt{2}}\left(\Re+\Re^2\right)\left|1\right\rangle\otimes\Phi_{ph}\right)(x,Q) \\ &= \left(\frac{1}{\sqrt{2}}(\Re+1_{e\otimes B})\right)\left(\left|1\right\rangle\otimes\Phi_{\mathrm{ph}}\right)(x,Q) \\ &= \frac{1}{\sqrt{2}}\Re\left(\left|1\right\rangle\otimes\Phi_{\mathrm{ph}}\right)(x,Q)+\frac{1}{\sqrt{2}}1_{e\otimes B}\left(\left|1\right\rangle\otimes\Phi_{\mathrm{ph}}\right)(x,Q) \\ &= \frac{1}{\sqrt{2}}\left(\left[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right]\left|1\right\rangle\otimes G\Phi_{\mathrm{ph}}\right)(x,Q)+\frac{1}{\sqrt{2}}\left(\left[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right]\left|1\right\rangle\otimes 1_B\Phi_{\mathrm{ph}}\right)(x,Q) \\ &= \frac{1}{\sqrt{2}}\left|2\right\rangle(x)G\Phi_{\mathrm{ph}}(Q)+\frac{1}{\sqrt{2}}\left|1\right\rangle(x)\Phi_{\mathrm{ph}}(Q) \\ &= \frac{1}{\sqrt{2}}\left|1\right\rangle(x)\Phi_{\mathrm{ph}}(Q)+\frac{1}{\sqrt{2}}\left|2\right\rangle(x)\Phi_{\mathrm{ph}}(-Q) = \tilde{\Psi}(x,Q). \end{aligned} \tag{11}$$

In the equation (10) we have used the relations

$$G^2 = \overset{B}{\otimes}\prod_{k=1}^{M}G_k^2 = \overset{B}{\otimes}\prod_{k=1}^{M}1_{B,k} = 1_B, \text{ and } G\Phi_{\mathrm{ph}}(Q) = \Phi_{\mathrm{ph}}(-Q),$$

and

$$\begin{aligned} \Re 1_{e\otimes B} &= \left(\left[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right]\right)\otimes G\left(\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right)\otimes 1_B \\ &= \left(\left[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right]\right)\left(\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right)\otimes G1_B = \left(\left[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right]\right)\otimes G = \Re, \\ \Re^2 &= \left(\left[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right]\right)\otimes G\left(\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right)\otimes G = \left(\left[\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right]\right)\left(\left|1\right\rangle\left\langle 2\right|+\left|2\right\rangle\left\langle 1\right|\right)\otimes G^2 \\ &= \left(\left[\left|1\right\rangle\left\langle 1\right|+\left|2\right\rangle\left\langle 2\right|\right]\right)\otimes 1_B = 1_{e\otimes B}, \end{aligned}$$

(see [7]; the operator G is often called a reflection operator on the phonon space). Thus, expression (10) gives

$$\Re\tilde{\Psi}(x,Q) = \tilde{\Psi}(x,Q),$$

or in other words, wave function $\tilde{\Psi}(x,Q)$ is an eigenfunction of the operator $\Re$. Relations (8), (9) and (10) lead to the conclusion that the wave function (10) can be regarded as an eigenfunction of Hamiltonian (9). The main aim of our study is to find the phonon wave function $\Phi_{\rm ph}(Q)$ so as to be reached the minimum of the energy functional $(\tilde{\Psi}, S(H/T)S^{+}\tilde{\Psi})$, where $\tilde{\Psi}$ is defined by (10) and the brackets denote the scalar product on the space $\aleph$. We shall construct this phonon wave function $\Phi_{\rm ph}(Q)$ utilizing some physical conclusions following from a physical view on a studied problem.

The shape of wave function (10) resembles a linear combination of two orthogonal localized states $|1\rangle(x)\Phi_{\rm ph}(Q)$ and $|2\rangle(x)\Phi_{\rm ph}(-Q)$, where $\Phi_{\rm ph}(Q)$ and $\Phi_{\rm ph}(-Q)$ are the states of the aside-molecule provided that the tunnelling exciton is in state $|1\rangle$ or $|2\rangle$, respectively. For the construction of the term $|1\rangle(x)\Phi_{\rm ph}(Q)$, first of all let us introduce the concept of "a zero-equilibrium position of the aside-molecule." The aside-molecule oscillates around the zero-equilibrium position as long until the coupling between the tunnelling exciton and the aside-molecule phonons starts to have an effect. Further, let us imagine that the tunnelling exciton is for a while in the state $|1\rangle$ and simultaneously is also in site 1 or 2. Then the aside-molecule is shifted from the zero-equilibrium position (which has in the Q space a coordinate $Q=0$) to a new equilibrium position which has in the Q space a coordinate $Q=\alpha^{(1)}$or $Q=\alpha^{(2)}$, respectively, where

$$\alpha^{(k)}=\begin{pmatrix}\alpha_1^{(k)}\\ .\\ .\\ .\\ \alpha_M^{(k)}\end{pmatrix},$$

$\alpha_i^{(k)}, i=1,2,...,M$ and $k=1,2$, are the real-valued variational parameters independent on all the normal mode coordinates Q_i, $i=1,2,...,M$. The simultaneous occurrence of the tunnelling exciton both in state $|1\rangle$ and in site 1 or 2 results in the existence of two phonon fields corresponding to two shifts of the aside-molecule. It is obvious to assume that both these phonon fields are similar to two ground state fields of two displaced linear quantum harmonic oscillators. This assumed similarity allows us to presume that the wave functions of these two phonon fields have the form

$$D(\alpha^{(k)})\Psi_{\rm vac}(B,Q)=\Psi_{\rm vac}(B,Q+\alpha^{(k)}), \tag{12}$$

where

$$D(\alpha^{(k)})=\overset{B}{\otimes}\prod_{i=1}^{M}\exp((\alpha_i^{(k)}/\sqrt{2})(b_i-b_i^{+}))=\overset{B}{\otimes}\prod_{i=1}^{M}\exp(\alpha_i^{(k)}\partial/\partial Q_i), k\ =\ 1,2,$$

are the displacement operators, and

$$\Psi_{\rm vac}(B,Q)=\sqrt[4]{\frac{2^M|B|}{\pi^M}}\exp(-\langle\langle BQ,Q\rangle\rangle), \tag{13}$$

where $|B|$ is a determinant of the $M\times M$symmetrical matrix B which has the elements b_{ij} regarded as the real-valued variational parameters that are independent of Q, $i,j=1,...,M$, and are introduced in order to embrace the correlation effect between the i^{th} and j^{th} phonon modes into our model. On account of the equality $\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}(\Psi_{\rm vac}(B,Q))^2\,dQ_1\cdots dQ_M=1$, the matrix B must fulfil the condition $\langle\langle BQ,Q\rangle\rangle\ \ >0$ for an arbitrary non-zero vector Q.

For the two-mode case, the vacuum state in (12), deduced from the results of studies in [6, 8, 9], has been utilized in [10] for the approximation of the ground state wave functions and energies of the linear Jahn-Teller system.

For the one-mode case, i.e. for $M=1$, the definition of the vacuum state (12) coincides with the definition of the squeezed vacuum state that has been used in many works [4, 5, 6, 8]. Namely, in this case,

the squeezing of the vacuum state (12) is characterized by an inequality $|b_{11}| < 2^{-1}$ which says the maximum of function (12), as a function of Q_1, is reached at the point $Q_1 = 0$ and is not larger than the maximum of the function $|0\rangle = \pi^{-1/4}\exp(-0.5Q_1^2)$, as a function of Q_1. The generalization of these facts for an arbitrary whole number M gives us, for the squeezing of the vacuum state (12), the condition

$$|B| < 2^{-M},$$

which leads to the fact that the maximum of the function $|0\rangle$ is not smaller than the maximum of function (12), as it is in the single-mode case discussed above.

Following from one of the fundamental principles of quantum theory, in which a linear combination of possible states of the phonon field is also a possible state for the phonon field, one can construct the phonon ground state wave function $\Phi_{\rm ph}(Q)$ from the linear combination of the two states defined in (11) as

$$\begin{aligned}\Phi_{\rm ph}(Q) &= \tilde{C}_0\sum_{k=1}^{2}\varepsilon_k D(\alpha^{(k)})\Psi_{\rm vac}(B,Q) = \tilde{C}_0\sum_{k=1}^{2}\varepsilon_k\Psi_{\rm vac}(B,Q+\alpha^{(k)})\\ &= \tilde{C}\sum_{k=1}^{2}\varepsilon_k\exp(-\left\langle\left\langle B(Q+\alpha^{(k)}),(Q+\alpha^{(k)})\right\rangle\right\rangle) \equiv \Psi_{\rm ph}(\alpha,B,\varepsilon,Q),\end{aligned}$$

where

$$\tilde{C} = \sqrt[4]{\frac{2^M|B|}{\pi^M}}(\sum_{k=1}^{2}\sum_{l=1}^{2}\varepsilon_k\varepsilon_l F(\alpha,B,k,l))^{-\frac{1}{2}}.$$

Here,

$$F(\alpha,B,k,l) = \exp(-0.5\sum_{i=1}^{M}\sum_{j=1}^{M}b_{ij}(\alpha_i^{(k)}-\alpha_i^{(l)})(\alpha_j^{(k)}-\alpha_j^{(l)})),$$

$$\varepsilon = \begin{pmatrix}\varepsilon_1\\ \varepsilon_2\end{pmatrix},$$

where ε_k, $k = 1, 2$, are the real-valued numbers regarded as the variational parameters (coefficients of the linear combination, independent of Q), $\alpha = \left(\alpha^{(1)},\alpha^{(2)}\right)$ is a $M\times 2$ matrix, and

$$\tilde{C}_0\sqrt[4]{\frac{2^M|B|}{\pi^M}} = \tilde{C}$$

following from the normalizing condition

$$\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}(\Psi_{\rm ph}(\alpha,B,\varepsilon,Q))^2 dQ_1\cdots dQ_M = 1,$$

but has no influence on the solution of our task.

As

$$\begin{aligned} D(\alpha^{(k)})\Psi_{\rm vac}(B,-Q) &= \Psi_{\rm vac}(B,-Q+\alpha^{(k)}) \\ &= \sqrt[4]{\frac{2^M\,|B|}{\pi^M}}\exp\left(-\left\langle\left\langle B(-Q+\alpha^{(k)}),(-Q+\alpha^{(k)})\right\rangle\right\rangle\right) \\ &= \sqrt[4]{\frac{2^M\,|B|}{\pi^M}}\exp\left(-\sum_{i=1}^{M}\sum_{j=1}^{M}b_{ij}(-Q_i+\alpha_i^{(k)})(-Q_j+\alpha_j^{(k)})\right) \\ &= \sqrt[4]{\frac{2^M\,|B|}{\pi^M}}\exp\left(-\sum_{i=1}^{M}\sum_{j=1}^{M}b_{ij}(Q_i-\alpha_i^{(k)})(Q_j-\alpha_j^{(k)})\right) \\ &= D(-\alpha^{(k)})\Psi_{\rm vac}(B,Q), \end{aligned}$$

we come to the result

$$\Phi_{\rm ph}(-Q)=\tilde{C}\sum_{k=1}^{2}\varepsilon_k D(\alpha^{(k)})\Psi_{\rm vac}(B,-Q)=\tilde{C}\sum_{k=1}^{2}\varepsilon_k\Psi_{\rm vac}(B,Q-\alpha^{(k)})\equiv\Psi_{\rm ph}(-\alpha,B,\varepsilon,Q).$$

Then, expression (10) can be written as

$$\tilde{\Psi}(x,Q)=\frac{1}{\sqrt{2}}\left|1\right\rangle(x)\Psi_{\rm ph}(\alpha,B,\varepsilon,Q)+\frac{1}{\sqrt{2}}\left|2\right\rangle(x)\Psi_{\rm ph}(-\alpha,B,\varepsilon,Q). \tag{14}$$

The expectation value of (9) in the trial ground state wave function (13) amounts to

$$\begin{aligned} \frac{\Im}{T} &= (\tilde{\Psi},S\,(H/T)\,S^{+}\tilde{\Psi})=-DW(\alpha,B,\varepsilon)-\sum_{i=1}^{M}\Lambda_i \\ &+\sum_{i=1}^{M}\frac{\omega_i}{2T}\left(\frac{1}{4}(B^{-1})_{ii}+b_{ii}-1\right) \\ &+\left(\sum_{k=1}^{2}\sum_{l=1}^{2}\varepsilon_k\varepsilon_l F(\alpha,B,k,l)\right)^{-1}\times \\ &\times\sum_{k=1}^{2}\sum_{l=1}^{2}\sum_{i=1}^{M}\varepsilon_k\varepsilon_l\frac{\omega_i}{2T}F(\alpha,B,k,l)\left[\frac{1}{4}(\alpha_i^{(k)})^2+\frac{1}{4}(\alpha_i^{(l)})^2-\left(\sum_{j=1}^{M}b_{ij}(\alpha_j^{(k)}-\alpha_j^{(l)})\right)^2\right], \end{aligned} \tag{15}$$

where

$$DW(\alpha,B,\varepsilon)=F0(\alpha,B,\varepsilon)(\sum_{k=1}^{2}\sum_{l=1}^{2}\varepsilon_k\varepsilon_l F(\alpha,B,k,l))^{-1},$$

with

$$F0(\alpha,B,\varepsilon)=\sum_{k=1}^{2}\sum_{l=1}^{2}\varepsilon_k\varepsilon_l\exp\left[-0.5\sum_{i=1}^{M}\sum_{j=1}^{M}b_{ij}\left(-2\sqrt{2\Lambda_i}\sqrt{\frac{T}{\omega_i}}-\alpha_i^{(k)}-\alpha_i^{(l)}\right)\left(-2\sqrt{2\Lambda_j}\sqrt{\frac{T}{\omega_j}}-\alpha_j^{(k)}-\alpha_j^{(l)}\right)\right],$$

the values of $F(\alpha,B,k,l)$, $k,\,l=1,\,2$, defined above, $\Lambda_i=\frac{g_i^2}{T\omega_i}$, $i=1,\,\ldots\,,M$, are stated above, and $(B^{-1})_{ii}$, $i=1,\,\ldots\,,M$, is the i^{th} diagonal element of the matrix B^{-1}.

Thus, $\frac{\Im}{T}=\frac{\Im}{T}\left(\alpha,B,\varepsilon,\Lambda_1,\Lambda_2,...,\Lambda_M,\frac{\omega_1}{T},\frac{\omega_2}{T},...,\frac{\omega_M}{T}\right)$, and provided that $\frac{\omega_i}{T}$ and Λ_i, $i=1,\,\ldots\,,M$, are constants, we search for the stable minimum of the energy functional (14), as the function of the

variable quantities $b_{ij}, \alpha_i^{(k)}, \varepsilon_k$, with $i,\ j\ =\ 1,...,M$ and $k\ =\ 1,\ 2$, that is reached at the optimum values of $b_{ij}, \alpha_i^{(k)}, \varepsilon_k$ i.e. $b_{ij}^{(m)}, \alpha_i^{(k)(m)}, \varepsilon_k^{(m)}$, $i,\ j\ =\ 1,...,M$ and $k\ =\ 1,\ 2$, with respect to the condition $|B| \leq 2^{-M}$. Without any restrictions concerning the results of our task, we suppose $\varepsilon_1^{(m)} = 1$. The parameters $\Lambda_1, \Lambda_2, \ldots, \Lambda_M, \omega_1/T, \omega_2/T, \ldots, \omega_M/T$ can be called material parameters.

Regarding the system described by Hamiltonian (1), the ground state model taking into account the correlation effect among all the phonon modes into consideration has not been yet presented in any literature.

It is evident that the ground state wave function $\Psi_m$of the Hamiltonian H has the form

$$\begin{aligned}\Psi_m &= S^+\tilde{\Psi}_m(x,Q) \\ &= \frac{1}{\sqrt{2}}\left|1\right\rangle(x)\Psi_{\mathrm{ph}}(\alpha_m+\vec{A},B_m,\varepsilon_m,Q)+\frac{1}{\sqrt{2}}\left|2\right\rangle(x)\Psi_{\mathrm{ph}}(-\alpha_m-\vec{A},B_m,\varepsilon_m,Q),\end{aligned} \tag{16}$$

where $\tilde{\Psi}_m$ is obtained by substituting the values of $\alpha_m, B_m, \varepsilon_m$for the values of α, B, ε in the definition of the function $\tilde{\Psi}$ given by the expression (13),

$$\Psi_{\mathrm{ph}}(\pm\alpha_m\pm\vec{A},B_m,\varepsilon_m,Q)=\tilde{C}_m\sum_{k=1}^{2}\varepsilon_k^{(m)}\exp\left(-\left\langle\left\langle B(Q\pm\alpha^{(k)(m)}\pm\vec{A}_k),(Q\pm\alpha^{(k)(m)}\pm\vec{A}_k)\right\rangle\right\rangle\right), \tag{17}$$

where the value of $\tilde{C}_m$is obtained by substituting the values of α_m, B_m for the values of α, B in the expression defining the value of $\tilde{C}$ stated above, the $M \times 2$ matrix α_m is defined as

$$\alpha_m=\left(\alpha^{(1)(m)},\alpha^{(2)(m)}\right);\quad \alpha^{(k)(m)}=\begin{pmatrix}\alpha_1^{(k)(m)}\\ \vdots \\ \alpha_M^{(k)(m)}\end{pmatrix},$$

$k = 1, 2$, the $M \times M$ matrix $B_m$and the vector ε_m have the forms

$$B_m=\begin{pmatrix}b_{11}^{(m)} & \cdots & b_{1M}^{(m)}\\ \vdots & & \vdots \\ b_{M1}^{(m)} & \cdots & b_{MM}^{(m)}\end{pmatrix},\qquad \varepsilon_m=\begin{pmatrix}1\\ \varepsilon_2^{(m)}\end{pmatrix},$$

the $M \times 2$ matrix $\vec{A}$ has the elements $\left(\vec{A}\right)_{ij} = \sqrt{2}g_i/\omega_i$, $i = 1, \ldots, M$ and $j = 1, 2$, and $\vec{A} = \left(\vec{A}_1, \vec{A}_2\right)$, where $\vec{A}_1$ and $\vec{A}_2$ are the first and the second column of the matrix $\vec{A}$, respectively, whereupon $\vec{A}_1 = \vec{A}_2$.

The mean value of the ground state energy (in units of T) of the small polaron, which has the Hamiltonian H_{SP}, is equal to the expectation value of the Hamiltonian H_{SP} in the ground state $\tilde{\Psi}_m$ of the Hamiltonian (4), and amounts to

$$\left(\tilde{\Psi}_m, H_{SP}\tilde{\Psi}_m\right) = -DW(\alpha_m, B_m, \varepsilon_m) \equiv -DW_m < 0,$$

where

$$DW(\alpha_m,B_m,\varepsilon_m)=\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}\Psi_{ph}\left(\alpha_m+\vec{A},B_m,\varepsilon_m,Q\right)\Psi_{\mathrm{ph}}\left(-\alpha_m-\vec{A},B_m,\varepsilon_m,Q\right)dQ_1\cdots dQ_M.$$

This reality follows from one of the principles of quantum mechanics that says: if the quantum system wave function in the y-representation is known (denoted it as $f(y)$, where y is the space coordinate) then the expectation value (sometimes called as the mean value) $\left\langle\widehat{\Theta}\right\rangle$ of the physical quantity of the given quantum system, which is represented by the operator $\widehat{\Theta}$,has the form

$$\left\langle\widehat{\Theta}\right\rangle=\int f^*(y)\,\widehat{\Theta}f(y)\,dy,$$

where f^* is a conjugate of the wave function f. In our case we have $y \equiv Q$, $f \equiv \tilde{\Psi}_m$, and $\widehat{\Theta} \equiv H_{\mathrm{SP}}$.

The value of $\left(\tilde{\Psi}_m, H_{SP}\tilde{\Psi}_m\right)$ will be in the further text called the ground state energy (in units of T) of the small polaron.

The value of $-DW_mT$ determines the inner binding energy (this inner binding energy has origin in the inner binding energy of the bare exciton that is equal to –T) of the small polaron. It is obvious that more the negative value of $-DW_mT$, more stable is the small polaron.

Sometimes the value of DW_m is called a tunnelling reduction factor and it is obtained by substituting the optimum values of $\alpha_m, B_m, \varepsilon_m$for the values of α, B, ε in the expression $DW(\alpha, B, \varepsilon)$ stated in the description of expression (14). It is obvious that the value of DW_m is dependent on the concrete values of $\Lambda_1, \Lambda_2 \ldots, \Lambda_M$, ω_1/T, $\omega_2/T, \ldots, \omega_M/T$.

3. Numerical Results and Conclusions

Up to now, the only published work dealing with the ground state of Hamiltonian (1) with value of M greater than 1, namely $M = 2$, is Lo and Sollie in [6]. We compare the results of our model with the numerical results presented in [6], namely for the case $g_1 = g_2 = g$, $\omega_1 = \omega_2 = \omega$, and $M = 2$. For the given values of Λ_i, $i = 1, \ldots, M$, the energy function (14), considered only as the function of T and ω_i, with $i = 1, \ldots, M$, is dependent only on the quotients $\omega_i/T \equiv 1/\Delta_i$. Parameters Δ_i are often called the non-adiabatic parameters. Therefore, in the case that $\omega_1 = \omega_2 = \omega$, when using the parameter $1/\Delta \equiv \omega/T$, and defining the functional E/Δ by means of a modification of the energy functional (14), namely as follows $E/\Delta = \Im/T = \Im/(\omega\Delta)$, we can compare the results of our model with the analogous descriptions from [6] according to a degree of non-adiabaticity given by the value of Δ. When considering the case $g_1 = g_2 = g$, $\omega_1 = \omega_2 = \omega$, and $M = 2$, calling this a symmetrical two-mode case, we obtain the expressions $\Delta_1 = \Delta_2 = \Delta$ and $\Lambda_1 = \Lambda_2 = \frac{g^2}{\Delta\omega}$. Regarding the values of Δ,Λ_1, Λ_2 as constants, we search for the stable minimum of the functional E/Δ in a region of parameters α, B, ε fulfilling the conditions $|B| \leq 2^{-2}$and $\varepsilon_1 = 1$, i.e. in a region corresponding to a linear combination of the displacements of the vacuum states (12) that are regarded as a generalization of squeezed vacuum states [4–8]. In this case the stable minimum E_m/Δ of the functional E/Δ is defined as

$$\frac{E_m}{\Delta} \equiv \frac{E_m}{\Delta}\left(\Lambda_1, \Lambda_2, \frac{1}{\Delta_1}, \frac{1}{\Delta_2}\right) \equiv \min_{\alpha,B,\varepsilon} \frac{E}{\Delta}\left(\alpha, B, \varepsilon, \Lambda_1, \Lambda_2, \frac{1}{\Delta_1}, \frac{1}{\Delta_2}\right),$$

in the region $|B| \leq 2^{-2}$,$\varepsilon_1 = 1$, $\Lambda_1 = \Lambda_2$, $\Delta_1 = \Delta_2 = \Delta$.

The optimum values of $\alpha_m, B_m, \varepsilon_m$in which this minimum is reached will be the supporting points for the conclusions following from our model.

We now present the numerical results of our model for two typical values of the non-adiabatic parameter Δ, namely for the weak non-adiabatic case we have chosen $\Delta = 10$ and for the strong non-adiabatic case $\Delta = 0.1$, whereupon the parameters g and ω are regarded as the same for both cases. In this case, $\Lambda = \Lambda_1 + \Lambda_2 = 2\frac{g^2}{\Delta\omega}$, i.e. $\Lambda$is a function of g, Δ, and ω, and between the value of $\Lambda$for $\Delta = 10$ being denoted as Λ_{10} and the value of Λ for $\Delta = 0.1$ being denoted as $\Lambda_{0.1}$ one can obtain the following relation $\Lambda_{10} = 2\frac{g^2}{10\omega} = 2\frac{g^2}{0.1\omega}0.01 = 0.01\Lambda_{0.1}$.

Let us verify the correctness of our assumption concerning the approximation of two phonon fields that have arisen as a result of the interaction between the tunnelling exciton and the aside-molecule phonons, provided that the tunnelling exciton is in the state $|1\rangle$ and simultaneously also in site 1 or 2. The correctness of this assumption can be verified by the results shown in Figure 1, where the elements $b_{ij}^{(m)}$ of the matrix B_m, i, $j = 1, 2$, are presented for the weak, intermediate and strong exciton-phonons binding parameters Λ for$\Delta = 10$, and $\Delta = 0.1$. It is evident that the conditions $g_1 = g_2 = g$, $\omega_1 = \omega_2 = \omega$, and $M = 2$ lead to the equalities $b_{11}^{(m)} = b_{22}^{(m)}$ and $b_{12}^{(m)} = b_{21}^{(m)}$.

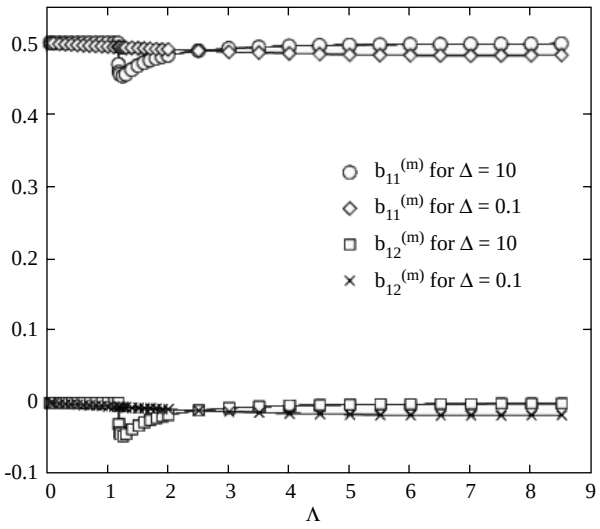

Figure 1. The optimum values of $b_{11}^{(m)}$ and $b_{12}^{(m)}$as the functions of $\Lambda = \Lambda_1 + \Lambda_2$ in the case that $\Delta = 0.1$,and $\Delta = 10$.

As Figure 1 shows, for sufficiently small and also sufficiently large values of Λ, in comparison with the number 1, the optimum values of $b_{11}^{(m)}$are practically equal to 0.5, and the greatest deviation from 0.5 is only for the weak non-adiabatic case with the intermediate values of Λ, i.e. with the values of Λcomparable with the number 1. But, this deviation is negligible in comparison with 0.5. The values of $b_{12}^{(m)}$are practically equal to zero for both studied cases (i.e. for $\Delta = 10$ and $\Delta = 0.1$), only for the intermediate values of Λthese ones have a slight deviation from the zero, namely only for the weak non-adiabatic case.

Thus, from the magnitude of the values of $b_{11}^{(m)}$and $b_{12}^{(m)}$, we can state that the vacuum state $\Psi_{\text{vac}}(B_m, Q)$ (see also (12)) differs only slightly from the vacuum state $|0\rangle(Q)$ (see the equation (2)) both for weak and for strong non-adiabatic cases in all the region of the parameters for Λ. These considerations lead to the following approximations (see expressions (11) and (12):

$$D(\alpha_m^{(k)})\Psi_{\text{vac}}(B_m, Q) \approx |0\rangle \left(Q + \alpha_m^{(k)}\right), \quad k = 1, 2 \tag{18}$$

for all the values of Q and Λ, and both for weak and for strong non-adiabatic cases.

As the states $|0\rangle \left(Q + \alpha_m^{(k)}\right)$, $k = 1, 2$, are the ground states of two shifted linear quantum harmonic oscillators, the approximations (17) prove our assumption concerning the approximations of two phonon fields mentioned above by means of ground state wave functions of two shifted linear quantum harmonic oscillators.

Still, there is a certain controversy whether the quantities the ground state energy and the tunnelling reduction factor, as the functions of the parameter Λ have any sharp change or even a discontinuous jump at some critical values of Λ. This question is studied further.

Let us compare the values of DW_m presented in Table 1 for $\Delta = 10$ and $\Delta = 0.1$. From the values shown in Table 1 one can verify the reality that the tunnelling reduction factor of the tunnelling small polaron for the case $\Delta = 10$ is greater than for the case $\Delta = 0.1$, whereupon the values of g and ω are considered to be the same for both these cases. It can be proved as follows. When choosing any value of $\Lambda \equiv \Lambda_{0.1}$, for example $\Lambda_{0.1} = 5$, then we can find its corresponding value of DW_m in Table 1, for this example it is $DW_m = 0.520$. The value of DW_m corresponding to the case $\Delta = 10$ is this one that corresponds to the value of $\Lambda \equiv \Lambda_{10} = 0.01\Lambda_{0.1} = 0.01 \times 5 = 0.05$. For the value of $\Lambda_{10} = 0.05$, as Table 1 shows, the value of DW_m is 0.9994, what is the value greater than 0.520. Thus, we can state that the tunnelling reduction factor DW_m, considered only as a function of Δ, increases. What is not valid in the case of the model presented in

[6] for the symmetrical two-mode case. Here, this model gives zero values for the tunnelling reduction factor for sufficiently large values of $\Lambda \equiv \Lambda_{10}$, namely for $\Lambda \equiv \Lambda_{10} > 1.75$; at $\Lambda \equiv \Lambda_{10} \approx 1.75$ there is a sudden jump of this factor to zero.

When introducing $v_k^{(m)} = \vec{A}_k + \alpha^{(k)(m)}$, $k = 1, 2$, $\left\langle \left\langle B_m \nu_k^{(m)}, \nu_k^{(m)} \right\rangle \right\rangle \equiv \left\| v_k^{(m)} \right\|^2$, $k = 1, 2$, and $v_1^{(m)} = -cv_2^{(m)}$ for some positive constant c generally dependent on the value of Λ (this condition follows from a physical view on the studied problem and is also fully supported by our numerical efforts and not only for the symmetrical two-mode cases), one can rewrite the tunnelling reduction factor DW_m as

$$DW_m = \frac{\exp\left(-2\left\|v_1^{(m)}\right\|^2\right) + \left(\varepsilon_2^{(m)}\right)^2 \exp\left(-2\left\|v_2^{(m)}\right\|^2\right) + 2\varepsilon_2^{(m)} \exp\left(-0.5\left(\left\|v_1^{(m)}\right\| - \left\|v_2^{(m)}\right\|\right)^2\right)}{1 + \left(\varepsilon_2^{(m)}\right)^2 + 2\varepsilon_2^{(m)} \exp\left(-0.5\left(\left\|v_1^{(m)}\right\| + \left\|v_2^{(m)}\right\|\right)^2\right)}. \quad (19)$$

In our symmetrical two-mode case, with $\Delta = 0.1$, the optimum values in which the minima of functional (14) are reached can be characterized as follow. The magnitudes of $\alpha_1^{(2)(m)} = \alpha_2^{(2)(m)}$ are from a few hundredths (for the values of Λcorresponding to weak exciton-phonons bindings) to one tenth (for the rest values of Λ), and the optimum values of $\varepsilon_2^{(m)}$ are practically equal to zero. When inserting these values in (18), the values of DW_m can be expressed by the approximation

$$\begin{aligned} DW_m &\cong \exp\left(-2\left\langle\left\langle B_m \vec{A}_1, \vec{A}_1\right\rangle\right\rangle\right) \cong \exp\left(-\left(2\Lambda_1 \frac{T}{\omega} + 2\Lambda_2 \frac{T}{\omega}\right)\right) = \exp\left(-2\Delta\Lambda\right) \\ &= \exp\left(-2\left(\frac{g}{\omega}\right)^2\right), \end{aligned}$$

because $b_{11}^{(m)} = b_{22}^{(m)} \cong 0.5$, $b_{12}^{(m)} = b_{21}^{(m)} \cong 0$ for all the values of Λ(see Figure 1). It means that, in our studied symmetrical two-mode case with $\Delta = 0.1$, the tunnelling reduction factor is practically independent of T.

If $\Delta = 10$, the numerical results show that larger the value of $\Lambda = (1/\Delta\omega)\left(g_1^2 + g_2^2\right)$, less the difference between norms $\left\|v_1^{(m)}\right\|$ and $\left\|v_2^{(m)}\right\|$; and as it has been proved by our numerical efforts this statement is valid not only for the symmetrical two-mode case (i.e. for the case $g_1 = g_2$) but also for a non–symmetrical two-mode case (i.e. for the case $g_1 \neq g_2$). For small values of Λ, the ground state phonon wave functions $\Psi_{\rm ph}(\alpha_m + \vec{A}, B_m, \varepsilon_m, Q)$ and $\Psi_{\rm ph}(-\alpha_m - \vec{A}, B_m, \varepsilon_m, Q)$ (see expression (15)) are practically equal and symmetrical with respect to the origin of the Q space (see Figure 2).

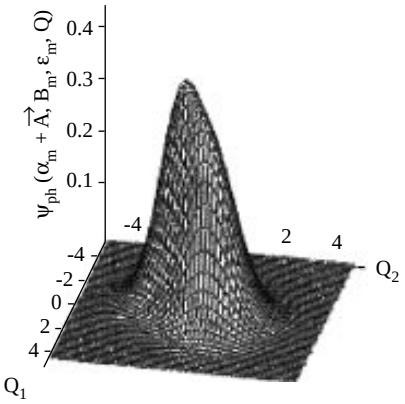

Figure 2. The shape of the ground state phonon wave function $\Psi_{\rm ph}(\alpha_m + \vec{A}, B_m, \varepsilon_m, Q)$ in the case that $\Lambda_1 = \Lambda_2 = 1.0$, and $\Delta = 10$.

The relation $\varepsilon_2^{(m)} \cong 1$ is valid only for the values of Λ from the zero to the intermediate region, and the value of $\varepsilon_2^{(m)}$, as the function of Λ, increases.

From the data of Table 1, one can state some essential conclusions concerning the ground state properties of the symmetrical two-mode case. These conclusions are presented below.

Table 1. Comparison of the optimum values of $-E_m/\Delta$, DW_m, and N_m, for $\Delta = 0.1$ and 10, presented in Reference [6] and in our work.

Λ	0.05	0.2	0.4	0.6	0.8	1.0	1.2	1.3	1.5	1.7	3.0	5.0	Notes
$-E_m/10$	1.002	1.011	1.025	1.048	1.094	1.164	1.254	1.306	1.421	1.550	3	5	Ref.[6]
$-E_m/10$	1.026	1.102	1.205	1.309	1.413	1.518	1.627	1.693	1.839	1.999	3.168	5.101	Ours
$-E_m/0.1$	1.042	1.167	1.335	1.504	1.674	1.845	2.016	2.102	2.275	2.448	3.594	5.410	Ref.[6]
$-E_m/0.1$	1.043	1.172	1.344	1.516	1.690	1.863	2.038	2.125	2.300	2.475	3.628	5.442	Ours
$DW_m, \Delta = 10$	0.998	0.989	0.968	0.915	0.816	0.713	0.613	0.563	0.460	0.338	0	0	Ref.[6]
$DW_m, \Delta = 10$	0.999	0.997	0.994	0.989	0.983	0.971	0.866	0.788	0.680	0.598	0.336	0.201	Ours
$DW_m, \Delta = 0.1$	0.993	0.972	0.945	0.919	0.893	0.867	0.842	0.829	0.805	0.781	0.637	0.453	Ref.[6]
$DW_m, \Delta = 0.1$	0.995	0.980	0.960	0.939	0.919	0.898	0.878	0.868	0.848	0.828	0.700	0.520	Ours
$N_m, \Delta = 10$	0.452	1.782	3.437	4.667	5.224	5.491	5.585	5.571	5.397	4.885	0	0	Ref.[6]
$N_m, \Delta = 10$	0.238	0.948	1.886	2.807	3.699	4.527	4.891	3.955	3.403	2.992	1.681	1.005	Ours
$10^3 N_m, \Delta = 0.1$	0.137	0.533	1.022	1.469	1.876	2.246	2.581	2.736	3.020	3.274	4.281	4.311	Ref.[6]
$10^3 N_m, \Delta = 0.1$	0.200	0.790	1.532	2.237	2.886	3.490	4.050	4.310	4.810	5.260	7.271	7.760	Ours

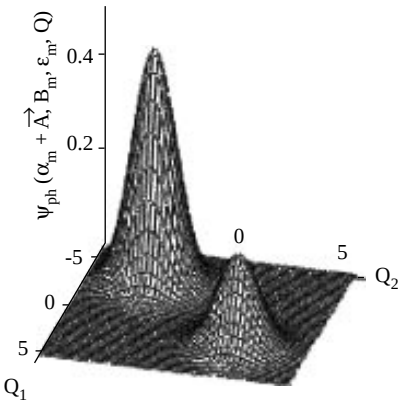

Figure 3. The shape of the ground state phonon wave function $\Psi_{\rm ph}(\alpha_m + \vec{A}, B_m, \varepsilon_m, Q)$ in the case that $\Lambda_1 = \Lambda_2 = 1.5$, and $\Delta = 10$.

We look now at the mean number of phonons N_m in the ground state of Hamiltonian (4) for the symmetrical two-mode case. This can be directly derived from expression (4) as

$$E_m + \Delta DW_m + \Delta\Lambda = \sum_{i=1}^{2} < \tilde{\Psi}_m, b_i^+ b_i \tilde{\Psi}_m > \equiv N_m,$$

where all the expressions of this equation have been defined above.

Table 2 shows values of $v_1^{(m)}$, $v_2^{(m)}$, and $\varepsilon_2^{(m)}$ in some typical cases of parameter Λ, namely for the weak, intermediate, and strong exciton-phonons bindings for the symmetrical two-mode case, with $\Delta = 10$. The shapes of the ground state phonon wave functions $\Psi_{\rm ph}(\alpha_m + \vec{A}, B_m, \varepsilon_m, Q)$, corresponding to the optimum values of $v_1^{(m)}$, $v_2^{(m)}$, and $\varepsilon_2^{(m)}$ for Λ= 1.0 and 1.5, are shown in Figures 2 and 3, respectively.

Table 2. The first and second elements $v_{1,1}^{(m)}$ and $v_{1,2}^{(m)}$, $v_{2,1}^{(m)}$ and $v_{2,2}^{(m)}$ of the vectors $v_1^{(m)}$ and $v_2^{(m)}$, respectively, and the values of the parameter $\varepsilon_2^{(m)}$ for the symmetrical two-mode case with Λ= 0.1, 0.3, 0.5, 1.0, 1.2, 1.4, 1.5, 2.5, 5, and $\Delta = 10$.

Λ	$v_{1,1}^{(m)} = v_{1,2}^{(m)}$	$v_{2,1}^{(m)} = v_{2,2}^{(m)}$	$\varepsilon_2^{(m)}$
0.1	0.1308	−0.1851	1.0332
0.3	0.2481	−0.3301	1.0620
0.5	0.3443	−0.4500	1.0998
1.0	0.6459	−0.7948	1.2527
1.2	1.5156	−1.6951	1.6906
1.4	2.3914	−2.5515	2.2703
1.5	2.6862	−2.8367	2.5158
2.5	4.4675	−4.5730	4.7088
5.0	6.8549	−6.9267	9.8222

Consider the case with $\Delta = 10$. As Table 1 shows for this case, both for our model and for the model presented in [6], the mean number of ground state phonons N_m (or the mean value of the ground state energy of the phonon field being equal to $\hbar\omega N_m$) is greatest in the intermediate region, leading to the following conclusions. Although the size of the intermediate region is relatively small, namely this region is represented by the values of Λ that are comparable with 1, the mean number of phonons that couple with the exciton is more than two times greater than for other parameters of Λ. More stable the small polaron (i.e. more negative the value of $-DW_m$), larger is the free path of the polaron, i.e. larger the mobility of this small polaron (or, larger is the lifetime of such a polaron), because a larger binding energy between an excited molecule electron and a molecule valence band hole causes a larger resistance of the exciton both against the collisions with phonons, and against the exciton-phonon binding that try to destroy the exciton-stable system. As the value of Λ is practically constant in the intermediate region, we can state that in this region small polaron mobility is influenced more by exciton scatterings (collisions), with an increased number of phonons, than by the magnitude of coupling between the exciton and all the phonons. Therefore, the mobility of the small polaron rapidly decreases in this region as a consequence of an enlarged number of phonons (see in Table 1 the values of $DW_m$with $\Delta = 10$ for the intermediate parameters of Λ). For parameters of Λ larger than the intermediate values, the small polaron mobility is, in a predominant extent, influenced by the magnitude of the coupling between the exciton and phonons, because in this region both the mean number of phonons and the small polaron mobility, as a functions of Λ, decrease (see in Table 1 the values of $DW_m$for small and large values of Λ). The reality that, in the region of small parameters, the mean number of phonons is also relatively great, and yet the small polaron mobility is approximately equal to 1, can be explained as a consequence of the weak exciton binding with these phonons.

The small polaron mobility, expressed by DW_m, is greater in our model than in [6], and is caused by a smaller mean number of the ground state phonons N_m that collide with the excitons and so decrease the mobility of the small polaron (a comparison of value from the present work with those reported in [6] is shown in Table 1). As our numerical results show, the mean number of phonons is equal to zero for the model in [6] if $\Lambda > 1.75$. However, the condition $N_m = 0$ contradicts the condition $\Lambda > 0$, because the value $-\Lambda$ is the energy decrease (expressed in units of T) which is caused by the coupling of the exciton to all the phonons; but if the system has no phonons, the coupling between the exciton and phonons in this system doesn't exist, it means that the energy decrease caused by the coupling is none, that is $-\Lambda = 0$, contradicting the relation $\Lambda > 1.75$. Thus, in the case of the model in [6] the implication $\Lambda > 0 \Rightarrow N_m > 0$ is not fulfilled.

For the case with $\Delta = 0.1$, the effect of a rapid decrease of the small polaron mobility connected with an increasing number of phonons has not arisen because, in this case, the mean number of the ground state phonons is practically equal to zero (but not a fully zero number) for all the values of Λ; and thus, the small

polaron mobility can not be in a predominant extent influenced only by the number of collisions with the phonons in any region of the parameters Λ.

Comparing the ground state energies of both models, we shall use the reality that the non–dimensional ground state energies E_m of the tunnelling exciton-phonons system is in the symmetrical two-mode case composed of three terms

$$E_m = -DW_m\Delta - \Lambda\Delta + N_m.$$

Because, for given values of Λ and Δ, the value of N_m, representing the mean number of ground state phonons and also the value of $-DW_m\Delta$, representing the ground state energy of the small polaron, are in our model lower than these ones in the model presented in [6], and simultaneously these both quantities as the functions of Λ are in our model continuous (i.e. there is no jump of these quantities to zero values), the ground state energy of the tunnelling exciton-phonons system is also continuous as a function of Λ and simultaneously is lower than in [6]. From the conclusions presented above, we can state that our model give a relatively good picture of the tunnelling exciton-phonons system up to now not being presented in any literature.

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