Internal vibrational structure of the three-dimensional large bipolaron

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Abstract. The internal vibrational states of the large bipolaron are studied by using the strong coupling Bogolyubov-Tyablikov canonical transformation of coordinates, that takes into account the conservation of the total momentum of the system. The complete spectrum is explicitly calculated and the electronic and vibrational properties of the states are discussed. Moreover the comparison of the bipolaron ground state and the binding energies with the results of the path integral and the Lee-Low and Pines methods shows that the proposed approach provides a correct description of the large bipolaron even in the intermediate regime of the electron-phonon interaction.

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1 Introduction

The polaron problem concerns a slow conduction electron in an ionic crystal or in a polar semiconductor that polarizes the surrounding lattice. This problem has attracted the interest of many theoretical physicists since it is one of the simplest non relativist quantum field problem and can be approached with a variety of methods. After the introduction of the Fröhlich model [1] and the relative electron-phonon coupling constant α the polaron theory has been developed mainly in two asymptotic regimes: the weak and intermediate regimes ($\alpha < 10$) and the adiabatic limit ($\alpha \gg 1$). In the first case the starting point is the Lee, Low and Pines work (LLP) [2,3] based on a variational technique that takes into account the electron recoil due to the emission of virtual phonons. In the second limit the starting point is the Bogolyubov-Tyablikov method (BT) [4–7] based on a canonical transformation of coordinates able to conserve the total momentum of the system even in the strong electron-phonon coupling regime when the system tends to localize. Even today the best available results are provided by the path integral technique developed by Feynman [8] that gives the correct behavior in both the weak and the strong coupling limits and provides a smooth interpolation between them. There is a large amount of reviews where the enormous bibliography on the polaron problem and the relative optical and transport properties are discussed [9–13].

Also the formation of the large bipolaron has been largely studied, starting from Pekar [14]. The accepted conclusion is that the large bipolaron can form in three-

and two-dimensions only if α is sufficiently large and the ratio η between the static and the high frequency dielectric constant is very small [15–25]. With the discovery of superconductors with high critical temperature, the study of the bipolaron formation has aroused new interest as a possible elementary mechanism able to explain such phenomenon [26].

In this work we extend the BT method to calculate the internal vibrational states of the large bipolaron. In the works by Bogolyubov [5] and Tyablikov [6] and in successive refinements of the polaron problem (see for instance [27,28]) the translational invariance of the system was used to substitute the electron position $\mathbf{r}$ with two coordinates, $\mathbf{r} = \mathbf{R} + \mathbf{u}$, whose the first, $\mathbf{R}$, describes the free motion of the polaron and the second $\mathbf{u}$ the oscillation of the electron around $\mathbf{R}$; furthermore each normal mode operator was written as a sum of a number, which indicates a displaced equilibrium position, plus a new operator which describes the ions oscillations around the displaced equilibrium position. Since the electronic freedom degrees of the system are increased by three, a corresponding number of new conditions on $\mathbf{R}$ and $\mathbf{u}$ must be imposed. They are chosen so that in the Hamiltonian appears the conjugate operator of $\mathbf{R}$, but not $\mathbf{R}$. In other words they assure the absence of forces acting at the point $\mathbf{R}$ [28]. The conclusion is that the polaron moves as a free particle and simultaneously the electron oscillates around $\mathbf{R}$. The displaced equilibrium positions are determined with a variational procedure.

In this work regarding the large bipolaron we substitute each electron position $\mathbf{r}_i$ (i=1, 2) as a sum of two vectors $\mathbf{R}_i$ and $\mathbf{x}_i$, whose the first indicates the position

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of a polaron and the second gives the positions of the electron with respect to the polaron; as in the polaron case each ionic displacement vector is substituted by a number plus an operator describing the ion oscillation around the new equilibrium position. In this case it is necessary to write six conditions between the new coordinates. They are chosen so that the final Hamiltonian depends only on the conjugate operator to $\mathbf{R} = \frac{1}{2}(\mathbf{R}_1 + \mathbf{R}_2)$, on $\mathbf{x} = \mathbf{R}_1 - \mathbf{R}_2$, on $\mathbf{x}_i$, but not on $\mathbf{R}$. The problem becomes in this way similar to that of a diatomic homonuclear molecule, in which the polaron positions $\mathbf{R}_i$ play the role of the ions coordinates and $\mathbf{x}_i$ the electron positions. The problem is solved as in the molecular case, determining first the electron wavefunctions and eigenvalues, which contain a parametric dependence on $\mathbf{x}$, and then calculating the oscillation states of the polarons in an effective potential. We find that the minimum of this potential depends on the polarization of the medium and on the quantum number of the vibrational state we are considering. We find also that the bipolaron can be excited, without breaking, in a number of vibrational states depending on α and η. For $\alpha = 7$ and $\eta = 0$ such number is four. This number increases by increasing α and decreases when η increases. Since the ground state energy of the bipolaron has been calculated within many different approximations, we can compare our results with the known data to check the validity of the proposed approach. Other works [20,21] have shown that the lowest value of α for which the bipolaron can form is between 6.0 and 6.8 and the binding energy increases when α increases and decreases when η increases; in other words for any fixed α it exists a η_c such that for $\eta > \eta_c$ the bipolaron cannot form. The value of η_c given in references [20,21] for $\alpha = 7, 10, 15$ are comparable, whereas within the BT method (this work) they are almost twice. When the short range contribution [18] or the correlation terms between the electrons are taken into account [17,19, 22,25] or when the bipolaron is assimilated to the hydrogen molecule (two centers model) [15,16,29], it is found a larger value of η_c, which is 0.14 for α very large. We stress that in our approach both the two centers model and the correlation contribution are taken into account: this justifies the highest values of η_c found. The comparison of the total bipolaron energies with those found mainly in references [20,21] and based on different approximations shows that the results are compatible and the differences can be physically justified. Furthermore we compare also the binding energies. To do this it is necessary to calculate, for each theory, the energy of the system when the electrons are at infinite relative distance. This value is twice the polaron self-energy in references [20,21], but in this work we obtain only the leading term of the limit $\alpha \gg 1$. If the polaron energy were calculated separately at the same approximation order than that of the bipolaron energy, the difference between the present calculation and that in reference [21] tends to disappear. We stress that the above results are obtained with three method completely different: the path-integral technique [21], the extended LLP method [20] and the BT procedures for the bipolaron in the present work. In particular we note that the extended

LLP method and that developed in this work, which are valid in the limit of weak and large α, are very powerful because they give similar results for the stability of the bipolaron even in the intermediate region of α.

For the electrons configuration typical of the ground state of a homonuclear diatomic molecule, we calculate the ground state energy and also the energies of a set of vibrational excited states all with zero orbital angular momentum and for increasing values of the main quantum number n. Such energies do not depend explicitly on n, which determines instead the distance at which the polaron-polaron interaction has a minimum, the vibrational frequency and the displaced ionic equilibrium positions. In other words, the bipolaron excited states are calculated self-consistently taking into account the polarization of the medium.

In Section 2 we outline the calculation procedure and in Section 3 we present and discuss the results.

2 Calculation method

We consider the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{2}\sum_{\mathbf{f}} \hbar\omega\left(q_{\mathbf{f}}q_{-\mathbf{f}} + p_{\mathbf{f}}p_{-\mathbf{f}}\right)$$
$$+ \frac{e^2}{\varepsilon_\infty \mid \mathbf{r}_1 - \mathbf{r}_2 \mid} + \sum_{\mathbf{f}}\sum_{j=1,2}\left[V_f q_{\mathbf{f}}\exp(\mathrm{i}\mathbf{f}\cdot\mathbf{r}_j)\right.$$
$$\left. + V_f q_{-\mathbf{f}}\exp(-\mathrm{i}\mathbf{f}\cdot\mathbf{r}_j)\right] \tag{1}$$

where m is the effective mass of the electron, $\mathbf{r}_j$ and ∇_j^2 indicate the position and the Laplacian operator of the j particle, ε_∞ is the high frequency dielectric constant, $\mathbf{f}$ denotes the wavenumber of the optical longitudinal phonon whose non dispersive frequency is ω, $q_{\mathbf{f}}$ and $p_{\mathbf{f}}$ are the conjugate operators of these normal vibrational modes. The coupling between the electron and the phonons is given by

$$V_f = \mathrm{i}\frac{\hbar\omega}{f}\left(\frac{4\pi\alpha}{V}\right)^{\frac{1}{2}}\left(\frac{\hbar}{2m\omega}\right)^{\frac{1}{4}}$$

where

$$\alpha = \frac{e^2}{2\varepsilon^*\hbar\omega}\left(\frac{2m\omega}{\hbar}\right)^{\frac{1}{2}}$$

and

$$\frac{1}{\varepsilon^*} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}$$

with ε_0 the static dielectric constant and V the volume of the system. The kinetic energy of the particle is measured from the bottom of the conduction band.

Following the BT [5,6] procedure we introduce in the Hamiltonian (1) a suitable parameter such that when it is zero the ionic kinetic energy disappears in the Hamiltonian and the problem reduces to that of a particle interacting with an elastic potential whose center of the force is displaced. This can be done substituting $q_{\mathbf{f}}$ with $\frac{q_{\mathbf{f}}}{\xi}$ and $p_{\mathbf{f}}$

with $\xi p_{\mathbf{f}}$. The commutation relations $[q_{\mathbf{f}}, p_{\mathbf{f}}] = i\hbar$ are preserved and the Hamiltonian (1) becomes

$$H = -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{1}{2}\sum_{\mathbf{f}}\hbar\nu\left(q_{\mathbf{f}}q_{-\mathbf{f}} + \xi^4 p_{\mathbf{f}}p_{-\mathbf{f}}\right)$$

$$+ \frac{e^2}{\varepsilon_\infty \mid \mathbf{r}_1 - \mathbf{r}_2 \mid} + \sum_{\mathbf{f}}\sum_{j=1,2}\left[W_f q_{\mathbf{f}}\exp(i\mathbf{f}\cdot\mathbf{r}_j)\right.$$

$$\left. + W_f^* q_{-\mathbf{f}}\exp(-i\mathbf{f}\cdot\mathbf{r}_j)\right] \tag{2}$$

with $\omega = \xi^2\nu$ and $W_f = \frac{V_f}{\sqrt{2\xi}}$. The form (2) of the Hamiltonian is very useful because in the extreme limit $\xi = 0$ the phonon coordinates $q_{\mathbf{f}}$ appear in parametric form (adiabatic approximation). The next step is to define $\mathbf{r}_1 = \mathbf{R}_1 + \mathbf{x}_1$; $\mathbf{r}_2 = \mathbf{R}_2 + \mathbf{x}_2$; $\mathbf{R} = \frac{\mathbf{R}_1 + \mathbf{R}_2}{2}$; $\mathbf{x} = \mathbf{R}_2 - \mathbf{R}_1$, where $\mathbf{R}_j$ indicates the position of the polaron j, $\mathbf{x}_j$ the displacement of the electron with respect to that of the polaron, $\mathbf{R}$ is the position of the center of mass of the bipolaron and $\mathbf{x}$ indicates the relative coordinate of the two polarons. We recall that $\mathbf{R}$ must be chosen so that the final Hamiltonian does not contain $\mathbf{R}$, but only the relative Laplacian operator. If this occurs the translational invariance of the system is verified and consequently the total momentum is conserved. For the phonon coordinates we write furthermore

$$q_{\mathbf{f}}\exp(i\mathbf{f}\cdot\mathbf{R}_1) = u_{\mathbf{f},1} + \xi Q_{\mathbf{f}} \tag{3}$$
$$q_{\mathbf{f}}\exp(i\mathbf{f}\cdot\mathbf{R}_2) = u_{\mathbf{f},2} + \xi Q_{\mathbf{f}}$$

where $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ are the classical components of the phonon field and $Q_{\mathbf{f}}$ indicates the operator which describes the fluctuations of the phonon field. Obviously

$$q_{\mathbf{f}} = \frac{1}{2}\left[(u_{\mathbf{f},1} + \xi Q_{\mathbf{f}})\exp(-i\mathbf{f}\cdot\mathbf{R}_1)\right.$$
$$\left. + (u_{\mathbf{f},2} + \xi Q_{\mathbf{f}})\exp(-i\mathbf{f}\cdot\mathbf{R}_2)\right] \tag{4}$$
$$Q_{\mathbf{f}} = \frac{1}{2\xi}\left[q_{\mathbf{f}}\left(\exp(i\mathbf{f}\cdot\mathbf{R}_1) + \exp(i\mathbf{f}\cdot\mathbf{R}_2)\right) - u_{\mathbf{f},1} - u_{\mathbf{f},2}\right].$$

Six new electronic parameters are introduced so that we must impose six new conditions. They are

$$\sum_{\mathbf{f}} f_\alpha v_{\mathbf{f},1}^*\left\{q_{\mathbf{f}}\exp\left[i\mathbf{f}\cdot(\mathbf{R}+\mathbf{x}) - u_{\mathbf{f},1}\right]\right\} = 0 \tag{5}$$
$$\sum_{\mathbf{f}} f_\alpha v_{\mathbf{f},2}^*\left\{q_{\mathbf{f}}\exp\left[i\mathbf{f}\cdot(\mathbf{R}-\mathbf{x}) - u_{\mathbf{f},2}\right]\right\} = 0$$

with $\alpha = x, y, z$ and $v_{\mathbf{f},i}$ c-numbers such that $v_{\mathbf{f},i}^* = v_{-\mathbf{f},i}$. The relations (5) are the generalization of those we impose in the case of the polaron. As discussed in [28] for the polaron it is convenient, but not essential to impose that $u_{\mathbf{f},i}$ and $v_{\mathbf{f},i}$ satisfy also the orthonormality conditions

$$\sum_{\mathbf{f}} f_\alpha f_\beta v_{\mathbf{f},1}^*\left[u_{\mathbf{f},1} + u_{\mathbf{f},2}\exp(i\mathbf{f}\cdot\rho)\right] = \delta_{\alpha\beta} \tag{6}$$
$$\sum_{\mathbf{f}} f_\alpha f_\beta v_{\mathbf{f},2}^*\left[u_{\mathbf{f},2} + u_{\mathbf{f},1}\exp(-i\mathbf{f}\cdot\rho)\right] = \delta_{\alpha\beta}$$

where $\delta_{\alpha\beta}$ is the Kronecker δ function. The next calculation is to express the operators $p_{\mathbf{f}}$ and consequently H as function of the new coordinates [23]; furthermore we develop the Hamiltonian H as a power series of ξ, obtaining

$$H = H_0 + \xi H_1 + \xi^2 H_2 + \xi^3 H_3 + \xi^4 H_4. \tag{7}$$

Each operator H_i depends on $\mathbf{R}$, $\mathbf{x}$, $\mathbf{x}_1$, $\mathbf{x}_2$, $Q_{\mathbf{f}}$ and on the numbers $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$. Their expressions are

$$H_0 = -\frac{\hbar^2}{2m}\left(\nabla_{\mathbf{x}_1}^2 + \nabla_{\mathbf{x}_2}^2\right) + \frac{e^2}{\varepsilon_\infty \mid \mathbf{x} + \mathbf{x}_1 - \mathbf{x}_2 \mid}$$

$$+ \frac{1}{2}\sum_{\mathbf{f}}\hbar\nu\left\{u_{\mathbf{f},1}\left[u_{-\mathbf{f},1} + u_{-\mathbf{f},2}\exp(i\mathbf{f}\cdot\mathbf{x})\right]\right.$$

$$\left. + u_{-\mathbf{f},2}\left[u_{\mathbf{f},1}\exp(-i\mathbf{f}\cdot\mathbf{x}) + u_{\mathbf{f},2}\right]\right\}$$

$$+ \frac{1}{2}\sum_{\mathbf{f}}W_f\left(u_{\mathbf{f},1} + u_{\mathbf{f},2}\exp(i\mathbf{f}\cdot\mathbf{x})\right)\exp(i\mathbf{f}\cdot\mathbf{x}_1)$$

$$+ \frac{1}{2}\sum_{\mathbf{f}}W_f\left(u_{\mathbf{f},2} + u_{\mathbf{f},1}\exp(-i\mathbf{f}\cdot\mathbf{x})\right)\exp(i\mathbf{f}\cdot\mathbf{x}_2)$$

$$+ \frac{1}{2}\sum_{\mathbf{f}}W_f^*\left(u_{-\mathbf{f},1}\right.$$

$$\left. + u_{-\mathbf{f},2}\exp(-i\mathbf{f}\cdot\mathbf{x})\right)\exp(-i\mathbf{f}\cdot\mathbf{x}_1)$$

$$+ \frac{1}{2}\sum_{\mathbf{f}}W_f^*\left(u_{-\mathbf{f},2}\right.$$

$$\left. + u_{-\mathbf{f},1}\exp(i\mathbf{f}\cdot\mathbf{x})\right)\exp(-i\mathbf{f}\cdot\mathbf{x}_2) \tag{8}$$

$$\frac{2}{\xi}H_1 = \sum_{\mathbf{f}}Q_{\mathbf{f}}W_f\left[(1 + \exp(i\mathbf{f}\cdot\mathbf{x}))\exp(i\mathbf{f}\cdot\mathbf{x}_1)\right.$$

$$\left. + (1 + \exp(-i\mathbf{f}\cdot\mathbf{x}))\exp(i\mathbf{f}\cdot\mathbf{x}_2)\right]$$

$$+ \sum_{\mathbf{f}}Q_{-\mathbf{f}}W_f^*\left[(1 + \exp(-i\mathbf{f}\cdot\mathbf{x}))\exp(-i\mathbf{f}\cdot\mathbf{x}_1)\right.$$

$$\left. + (1 + \exp(i\mathbf{f}\cdot\mathbf{x}))\exp(-i\mathbf{f}\cdot\mathbf{x}_2)\right]$$

$$+ \sum_{\mathbf{f}}\hbar\nu Q_{\mathbf{f}}\left[u_{-\mathbf{f},1}(1 + \exp(i\mathbf{f}\cdot\mathbf{x}))\right.$$

$$\left. + u_{\mathbf{f},2}(1 + \exp(-i\mathbf{f}\cdot\mathbf{x}))\right]$$

$$+ \sum_{\mathbf{f}}\hbar\nu Q_{-\mathbf{f}}\left[u_{\mathbf{f},2}(1 + \exp(-i\mathbf{f}\cdot\mathbf{x}))\right.$$

$$\left. + u_{-\mathbf{f},1}(1 + \exp(i\mathbf{f}\cdot\mathbf{x}))\right] \tag{9}$$

$$\frac{8}{\xi^2}H_2 = \sum_{\mathbf{f}}\hbar\nu Q_{\mathbf{f}}Q_{-\mathbf{f}}\left[2 + \exp(i\mathbf{f}\cdot\mathbf{x}) + \exp(-i\mathbf{f}\cdot\mathbf{x})\right]$$

$$+ \sum_{\mathbf{f}}\left[P_{\mathbf{f}}' + \frac{2i}{\hbar}\mathbf{f}\cdot\mathbf{F}_{\mathbf{f}}(\mathbf{R},\mathbf{x})\right]$$

$$\times\left[P_{-\mathbf{f}}' - \frac{2i}{\hbar}\mathbf{f}\cdot\mathbf{F}_{-\mathbf{f}}(\mathbf{R},\mathbf{x})\right] \tag{10}$$

$$\frac{2}{i\xi^3}H_3 = \sum_{\mathbf{f}}\nu\mathbf{f}\cdot\left(P_{\mathbf{f}}' + \frac{2i}{\hbar}\mathbf{f}\cdot\mathbf{F}_{\mathbf{f}}(\mathbf{R},\mathbf{x})\right)\mathbf{G}_{-\mathbf{f}}(\mathbf{x}_1,\mathbf{x}_2)$$

$$- \sum_{\mathbf{f}}\nu\mathbf{f}\cdot\mathbf{G}_{\mathbf{f}}(\mathbf{x}_1,\mathbf{x}_2)\left(P_{-\mathbf{f}}' - \frac{2i}{\hbar}\mathbf{f}\cdot\mathbf{F}_{-\mathbf{f}}(\mathbf{R},\mathbf{x})\right) \tag{11}$$

$$H_4 = \frac{2\xi^4}{\hbar^2} \sum_{\mathbf{f}} \mathbf{f} \cdot \mathbf{G_f}(\mathbf{x}_1, \mathbf{x}_2) \, \mathbf{f} \cdot \mathbf{G_{-f}}(\mathbf{x}_1, \mathbf{x}_2) \qquad (12)$$

where

$$\mathbf{F_f}(\mathbf{R}, \mathbf{x}) = \frac{2\xi\hbar}{i}(S_{\mathbf{f}}^* \nabla_{\mathbf{R}} + Z_{\mathbf{f}}^* \nabla_{\mathbf{x}}) \qquad (13)$$

$$\mathbf{G_f}(\mathbf{x}_1, \mathbf{x}_2) = \frac{2\xi\hbar}{i}(Y_{\mathbf{f}}^* \nabla_{\mathbf{x}_1} + X_{\mathbf{f}}^* \nabla_{\mathbf{x}_2})$$

$$S_{\mathbf{f}}^* = \frac{1}{2}\left(v_{\mathbf{f},1}^* \exp\left(-\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right) + v_{\mathbf{f},2}^* \exp\left(\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right)\right)$$

$$Z_{\mathbf{f}}^* = v_{\mathbf{f},1}^* \exp\left(-\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right) - v_{\mathbf{f},2}^* \exp\left(\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right)$$

$$Y_{\mathbf{f}}^* = v_{\mathbf{f},1}^* \exp\left(-i\frac{\mathbf{f}\cdot\mathbf{x}}{2}\right)$$

$$X_{\mathbf{f}}^* = v_{\mathbf{f},2}^* \exp\left(i\frac{\mathbf{f}\cdot\mathbf{x}}{2}\right)$$

$$P_{\mathbf{f}} = \frac{1}{i}\frac{\partial}{\partial Q_{\mathbf{f}}}$$

$$P_{\mathbf{f}}' = \exp\left(\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right)\left\{ P_{\mathbf{f}} - \mathbf{f}\cdot v_{\mathbf{f},1}^* \sum_{\mathbf{k}} \mathbf{k}\,[u_{\mathbf{k},1} \right.$$

$$\left. + u_{\mathbf{k},2} \exp(i\mathbf{k}\cdot\mathbf{x})]\, P_{\mathbf{k}} \right\}$$

$$+ \exp\left(-\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right)\left\{ P_{\mathbf{f}} - \mathbf{f}\cdot v_{\mathbf{f},2}^* \sum_{\mathbf{k}} \mathbf{k}\,[u_{\mathbf{k},2} \right.$$

$$\left. + u_{\mathbf{k},1} \exp(-i\mathbf{k}\cdot\mathbf{x})]\, P_{\mathbf{k}} \right\} + ...$$

$$= \exp\left(\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right) P_{\mathbf{f},1}' + \exp\left(-\frac{i\mathbf{f}\cdot\mathbf{x}}{2}\right) P_{\mathbf{f},2}' + ...$$

The final form of the Hamiltonian (7) is very convenient:

a) the zero order term H_0 describes the motion of two electrons interacting with a Coulomb potential screened by ε_∞ and a classical polarization field whose strength depends on the parameters $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$; moreover it contains operators in the coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$, whereas the relative position of the polarons $\mathbf{x}$ appears as a parameter. This means that H_0 gives the extreme adiabatic description of the bipolaron and the other terms the corrections to this limit;

b) once the solution of H_0 has been found, we will see that the numbers $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ can be chosen so that the operator H_1 is zero; this means that the successive correction to H_0 is given by H_2;

c) the same choice for $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ and the orthogonality conditions (5, 6) allow to write in a simple and physically meaningful form the equation for the correction H_2 to the adiabatic limit.

We proceed considering in the equation (7) the parameter ξ as a small number, so that we can apply the perturbation theory to solve the Schrödinger equation

$$(H - E)\Psi(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}, \mathbf{R}, Q_{\mathbf{f}}) = 0. \qquad (14)$$

We write

$$\Psi = \Psi_0 + \xi\Psi_1 + \xi^2\Psi_2.... \qquad (15)$$
$$E = E_0 + \xi E_1 + \xi^2 E_2....$$

and determine $(E_0, E_1, E_2...)$ and $(\Psi_0, \Psi_1, \Psi_2...)$ through the equations

$$(H_0 - E_0)\Psi_0 = 0 \qquad (16)$$
$$(H_0 - E_0)\Psi_1 = (E_1 - H_1)\Psi_0$$
$$(H_0 - E_0)\Psi_2 = (E_2 - H_2)\Psi_0 + (E_1 - H_1)\Psi_1$$
$$...$$

The zero order equation gives non trivial informations on the system. Since the operator H_0 does not contain neither the operator $Q_{\mathbf{f}}$ nor the vector $\mathbf{R}$ and depends parametrically on the vector $\mathbf{x}$, we write

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}, \mathbf{R}, Q_{\mathbf{f}}) = \chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})\,\Phi(\mathbf{x}, \mathbf{R}, Q_{\mathbf{f}}) \qquad (17)$$

with $\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})$ solution of the equation

$$(H_0 - E_0(\mathbf{x}))\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}) = 0. \qquad (18)$$

This last equation describes the motion of two electrons, which interact with a Coulomb force, in the phonon field with classical coordinates $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$; moreover the relative position of the two polarons appears in the equation as a parameter. This makes the equation (18) similar to that of a diatomic molecule, in which the polaron positions play the same role of the ions. Furthermore it is worth to stress that the interaction between the electrons depends also on the polarization field, which contains also $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ as parameters. These last are fixed by the minimization of the energy $\langle \chi_0 \mid H_0 \mid \chi_0 \rangle$ through the conditions

$$\frac{\delta\langle \chi_0 \mid H_0 \mid \chi_0 \rangle}{\delta w_{\mathbf{f},1}} = \frac{\delta\langle \chi_0 \mid H_0 \mid \chi_0 \rangle}{\delta w_{\mathbf{f},2}} = 0 \qquad (19)$$

where

$$w_{\mathbf{f},1} = u_{-\mathbf{f},1} + u_{-\mathbf{f},2} \exp(-i\mathbf{f}\cdot\mathbf{x})$$
$$w_{\mathbf{f},2} = u_{-\mathbf{f},2} + u_{-\mathbf{f},1} \exp(i\mathbf{f}\cdot\mathbf{x}).$$

It is found

$$u_{\mathbf{f},1} = -\frac{4W_f^*}{\hbar\nu}\langle \chi_0 \mid \exp(-i\mathbf{f}\cdot\mathbf{x}_1) \mid \chi_0 \rangle \qquad (20)$$

$$u_{\mathbf{f},2} = -\frac{4W_f^*}{\hbar\nu}\langle \chi_0 \mid \exp(-i\mathbf{f}\cdot\mathbf{x}_2) \mid \chi_0 \rangle.$$

We note that the equations (20) for the displaced positions of the harmonic oscillators have the same form of the polaron case, but they contain an implicit dependence on $\mathbf{x}$. Using the equations (20) we find that the coefficients of $Q_{\mathbf{f}}$ and $Q_{-\mathbf{f}}$ in H_1 are zero so that the first correction to H_0 is given by H_2. Using the equations (20) and choosing $v_{\mathbf{f},1}$ and $v_{\mathbf{f},2}$ in such a way that the conditions (5, 6) are satisfied, H_2 becomes [23]

$$\xi^2 H_2 = -\frac{\hbar^2}{2M_R}\nabla_{\mathbf{R}}^2 - \frac{\hbar^2}{2M_x}\nabla_{\mathbf{x}}^2$$

$$+ \frac{1}{2}\sum_{\mathbf{f}} \hbar\omega\left(Q_{\mathbf{f}}' Q_{-\mathbf{f}}' + \Pi_{\mathbf{f}}\Pi_{-\mathbf{f}}\right) \qquad (21)$$

where

$$M_R = \frac{\hbar^2}{3} \sum_{\mathbf{f}} \frac{f^2}{\omega} \left[u_{-\mathbf{f},2} + u_{-\mathbf{f},1} \exp\left(\mathrm{i}\mathbf{f}\cdot\mathbf{x}\right)\right]$$
$$\times \left[u^*_{-\mathbf{f},2} + u^*_{-\mathbf{f},1} \exp\left(-\mathrm{i}\mathbf{f}\cdot\mathbf{x}\right)\right] \qquad (22)$$

$$M_\rho = \frac{1}{4} M_R$$

$$Q'_{\mathbf{f}} = Q_{\mathbf{f}} \left(1 + \exp\left(\mathrm{i}\mathbf{f}\cdot\mathbf{x}\right)\right)$$

$$\Pi_{\mathbf{f}} = \frac{1}{2}\left[\pi'_{\mathbf{f},1} \exp\left(\frac{\mathrm{i}\mathbf{f}\cdot\mathbf{x}}{2}\right) + \pi'_{\mathbf{f},2} \exp\left(-\frac{\mathrm{i}\mathbf{f}\cdot\mathbf{x}}{2}\right)\right]$$

$$\pi'_{\mathbf{f},1} = \pi_{\mathbf{f}} - v^*_{\mathbf{f},1}\mathbf{f}\cdot\sum_{\mathbf{k}} \mathbf{k}\left[u_{\mathbf{k},1} + u_{\mathbf{k},2} \exp\left(\mathrm{i}\mathbf{k}\cdot\mathbf{x}\right)\right]\pi_{\mathbf{k}}$$

$$\pi'_{\mathbf{f},2} = \pi_{\mathbf{f}} - v^*_{\mathbf{f},2}\mathbf{f}\cdot\sum_{\mathbf{k}} \mathbf{k}\left[u_{\mathbf{k},2} + u_{\mathbf{k},1} \exp\left(-\mathrm{i}\mathbf{k}\cdot\mathbf{x}\right)\right]\pi_{\mathbf{k}}$$

$\pi_{\mathbf{f}} = P_{\mathbf{f}} - a_{\mathbf{f}}$ and $a_{\mathbf{f}}$ a number to be fixed in such a way that the linear terms coefficients of the operator $\pi_{\mathbf{f}}$ of the phonon kinetic energy is zero. It is worth to note that in H_2 it appears the conjugate operator to $\mathbf{R}$, but not $\mathbf{R}$. Taking into account the equations (16, 17, 20), the expression (21) for $\xi^2 H_2$ and considering that $\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})$ is the eigenstate of H_0 with eigenvalue $E_0(\mathbf{x})$, we obtain

$$\left[-\frac{\hbar^2}{2M_R}\nabla^2_{\mathbf{R}} - \frac{\hbar^2}{2M_x}\nabla^2_{\mathbf{x}} + \frac{1}{2}\sum_{\mathbf{f}} \hbar\omega\left(Q'_{\mathbf{f}}Q'_{-\mathbf{f}} + \Pi_{\mathbf{f}}\Pi_{-\mathbf{f}}\right)\right.$$
$$\left. + E_0(\mathbf{x})\right]\Phi\left(\mathbf{x}, \mathbf{R}, Q_{\mathbf{f}}\right) = U\Phi\left(\mathbf{x}, \mathbf{R}, Q_{\mathbf{f}}\right) \quad (23)$$

where $U = \xi^2 E_2$. Since in equation (23), the coordinate $\mathbf{R}$ appears only in the kinetic energy operator, we can write

$$\Phi\left(\mathbf{x}, \mathbf{R}, Q_{\mathbf{f}}\right) = \Phi_0\left(\mathbf{x}, Q_{\mathbf{f}}\right)\exp\left(\mathrm{i}\mathbf{Q}\cdot\mathbf{R}\right) \qquad (24)$$

where $\hbar\mathbf{Q}$ is the total momentum of the system and

$$\left[-\frac{\hbar^2}{2M_x}\nabla^2_{\mathbf{x}} + \frac{1}{2}\sum_{\mathbf{f}} \hbar\omega\left(Q'_{\mathbf{f}}Q'_{-\mathbf{f}} + \Pi_{\mathbf{f}}\Pi_{-\mathbf{f}}\right)\right.$$
$$\left. + E_0(\mathbf{x})\right]\Phi_0\left(\mathbf{x}, Q_{\mathbf{f}}\right) = \left(U - \frac{\hbar^2 Q^2}{2M_R}\right)\Phi_0\left(\mathbf{x}, Q_{\mathbf{f}}\right). \quad (25)$$

In this work we consider only the case $Q = 0$.

As already stressed equation (18) describes the motion of the electrons in a potential depending on the polarization of the medium and containing as parameter the relative distance between the polarons, as it occurs in a diatomic homonuclear molecule. The equation (25) describes the relative motion of the polarons through the kinetic energy operator depending on $\mathbf{x}$ and the ionic oscillations through the operators $Q'_{\mathbf{f}}$ and $\Pi_{\mathbf{f}}$ which now are also depending on $\mathbf{x}$. The eigenvalue $E_0(\mathbf{x})$ of equation (18) enters in the equation (25) as the potential energy of the two polarons. We note that the reduced bipolaron mass M_x depends on the polarization of the medium and on the relative distance of the polarons. This

fact and the dependence of the operators $Q'_{\mathbf{f}}$ and $\Pi_{\mathbf{f}}$ on $\mathbf{x}$ in the equation (25) prevents that it can be solved easily. Since we will see that the function $E_0(\mathbf{x})$ is a very smooth function around the position of the minimum and that this last occurs at distance larger than the lattice parameter, the sum over the wavevector $\mathbf{f}$ verifies the condition $fx \gg 1$ for almost all the vectors $\mathbf{f}$ in the Brillouin zone. The consequence is that $\exp\left(\mathrm{i}\mathbf{f}\cdot\mathbf{x}\right)$ is rapidly oscillating and therefore $Q'_{\mathbf{f}} \approx Q_{\mathbf{f}}$ and $\Pi_{\mathbf{f}} \approx \pi_{\mathbf{f}}$, the phonon operators in (25) become then independent of $\mathbf{x}$ and we can write $\Phi_0\left(\mathbf{x}, Q_{\mathbf{f}}\right) = \mu(\mathbf{x})\theta(Q_{\mathbf{f}})$ where

$$\left(-\frac{\hbar^2}{2M_x}\nabla^2_{\mathbf{x}} + E_0(\mathbf{x})\right)\mu(\mathbf{x}) = W\mu(\mathbf{x}) \qquad (26)$$

$\theta(Q_{\mathbf{f}})$ gives the phonon replicas of the spectrum given by equation (26).

The equations (18) and (26) are the main ones of this work. The first describes the electrons motion in the Coulomb and polarization fields as in a diatomic homonuclear molecule and the second the relative motion of the polarons in a potential depending on the electronic configuration. There are also the phonon replicas of the bipolaron states, all with the same unrenormalized phonon frequency.

Our next step regards the solution of equation (18) with the calculation of $E_0(\mathbf{x})$ and then the solution of the equation (26). It can be shown that the equation (18) with the relations (20) satisfied can be obtained minimizing the functional [23,30]

$$E_0(\mathbf{x}) = T(\mathbf{x}) - U_1(\mathbf{x}) + U_2(\mathbf{x}) \qquad (27)$$

$$T(\mathbf{x}) = -\frac{\hbar^2}{2m}\int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})$$
$$\times\left(\nabla^2_{\mathbf{x}_1} + \nabla^2_{\mathbf{x}_2}\right)\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})$$

$$U_1(\mathbf{x}) = \frac{e^2}{2\varepsilon^*}\int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\mathrm{d}\mathbf{x}'_1\,\mathrm{d}\mathbf{x}'_2\,\chi^2_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})$$
$$\times \chi^2_0(\mathbf{x}'_1, \mathbf{x}'_2; \mathbf{x})\left[\frac{1}{|\mathbf{x}_1 - \mathbf{x}'_1|} + \frac{1}{|\mathbf{x}_2 - \mathbf{x}'_2|}\right.$$
$$\left. + \frac{1}{|\mathbf{x}_1 - \mathbf{x}'_1 - \mathbf{x}|} + \frac{1}{|\mathbf{x}_2 - \mathbf{x}'_2 - \mathbf{x}|}\right]$$

$$U_2(\mathbf{x}) = \frac{e^2}{\varepsilon_\infty}\int \mathrm{d}\mathbf{x}_1\,\mathrm{d}\mathbf{x}_2\,\chi^2_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})\frac{1}{|\mathbf{x}_1 - \mathbf{x}_2 + \mathbf{x}|}$$

with respect to the molecular orbital $\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x})$. The solution of the equation (18) and the conditions (20) are equivalent to the variational problem (27). Two particular features can be found for $x = 0$ and $x \to \infty$: $E_0(\mathbf{x})$ has its largest value (finite and positive) at $x = 0$ and is behaves as $\left(\frac{1}{1-\eta} - 1\right)\frac{1}{x}$ when $x \to \infty$ apart the constant term $-\frac{2}{3\pi}\alpha^2\hbar\omega$.

The calculation of $E_0(\mathbf{x})$ can be done as in the case of the diatomic molecule taking the trial orbital

$$\chi_0(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}) = N\left(\chi_a(\mathbf{x}_1)\chi_b(\mathbf{x}_2) + \chi_b(\mathbf{x}_1)\chi_a(\mathbf{x}_2)\right) \quad (28)$$
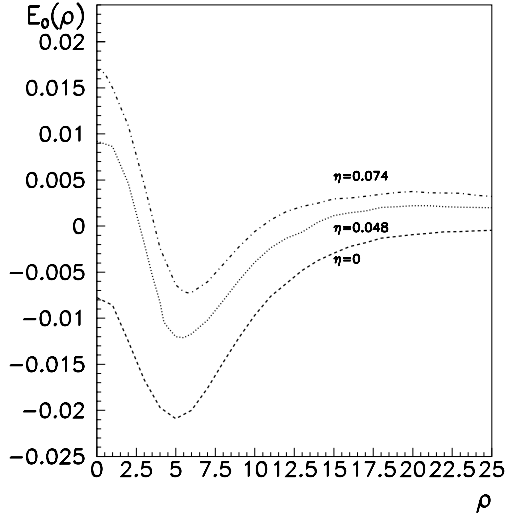
Fig. 1. The effective polaron-polaron interaction $\Delta E_0(\rho)$ in units $2\alpha^2\hbar\omega$ as function of the polarons distance ρ in units $a_{\mathrm{B}} = \frac{\varepsilon^*\hbar^2}{e^2 m}$.

where χ_a and χ_b indicate single-particle wavefunctions localized around the polaron positions $\mathbf{R}_1$ and $\mathbf{R}_2$ respectively, $N = \left(2(1+S^2)\right)^{-1/2}$ is the normalization constant and $S = \langle \chi_a \mid \chi_b \rangle$ is the overlap integral. Furthermore each function χ is taken as

$$\chi(x_i) = N_0(1 + \gamma x_i) \exp(-\gamma x_i) \qquad (29)$$

where N_0 is the normalization coefficient and γ a variational parameter. The minimization of the functional (27) gives values of γ that we must take in such a way the virial theorem

$$2T(x) + U_1(x) + x\frac{\mathrm{d}E_0(x)}{\mathrm{d}x} + U_2(x) = 0 \qquad (30)$$

is satisfied [23,30]. Since the method gives also the energy of two non interacting particles (limit $x \to \infty$), the binding bipolaron energy is defined as

$$\Delta E(x) = E_0(x) - 2E_0(x = \infty) \qquad (31)$$

$\Delta E(x)$ is depending only on the parameter η if the length unit is the effective Bohr radius $a_{\mathrm{B}} = \frac{\varepsilon^*\hbar^2}{e^2 m}$ and the energy is measured in unit

$$2\alpha^2\hbar\omega = \frac{e^4 m}{\varepsilon^{*2}\hbar^2} \cdot \qquad (32)$$

In Figure 1 we show $\Delta E(x)$ for $\eta = 0.0$, 0.048, 0.074. We see that each curve has a value x_0 for which $\Delta E(x_0)$ assumes the minimum value.

The next step is to calculate the spectrum of this equation.

Table 1. The coefficients which allow the approximate calculation of $\Delta E_0(\rho)$ in unit $2\alpha^2\hbar\omega$ as function of the polarons distance ρ in unit $a_{\mathrm{B}} = \frac{\varepsilon^*\hbar^2}{e^2 m}$.

	$\eta = 0$	$\eta = 0.048$	$\eta = 0.074$
$\delta a_{\mathrm{B}}^{-1}$	0.18	0.19	0.20
A_0	-0.00775	0.0	0.0
$A_1 a_{\mathrm{B}}^{-1}$	-9.591×10^{-4}	3.106×10^{-3}	1.01×10^{-2}
$A_2 a_{\mathrm{B}}^{-2}$	-2.328×10^{-3}	-4.902×10^{-3}	-1.021×10^{-2}
$A_3 a_{\mathrm{B}}^{-3}$	-1.134×10^{-5}	7.097×10^{-4}	2.104×10^{-3}
$A_4 a_{\mathrm{B}}^{-4}$	5.428×10^{-5}	-4.179×10^{-5}	-2.384×10^{-4}
$A_5 a_{\mathrm{B}}^{-5}$	-3.189×10^{-6}	1.156×10^{-6}	1.769×10^{-5}
$A_6 a_{\mathrm{B}}^{-6}$	-1.662×10^{-7}	-1.149×10^{-8}	-8.402×10^{-7}
$A_7 a_{\mathrm{B}}^{-7}$	1.831×10^{-8}	-9.772×10^{-11}	2.254×10^{-8}
$A_8 a_{\mathrm{B}}^{-8}$	-4.000×10^{-10}	2.168×10^{-12}	-2.546×10^{-10}
$M_\rho(\alpha^4 m)^{-1}$	0.0232	0.0195	0.0181

3 Calculation of the bipolaron vibrational states

The variational calculation of $E_0(x)$ by the functional (27) allows to approximate $\Delta E_0(x)$ by the analytical form

$$\Delta E_0(x) = \left(\frac{B}{\rho} + \exp(-\delta x)\sum_{n=-1}^{8} A_n x^n\right)\frac{e^4 m}{\varepsilon^{*2}\hbar^2} \qquad (33)$$

where, to assure that $\Delta E_0(x)$ has a finite value for $x = 0$, we must have

$$B = -A_{-1} = \left(1 - \frac{1}{1-\eta}\right) a_{\mathrm{B}}. \qquad (34)$$

In Table 1 the values of the coefficients δ and A_n are given. The radial part of equation (26)

$$\left[-\frac{\hbar^2}{2M_x}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{(\bar{k}-1)(\bar{k}-3)}{8M_\rho x^2} + \Delta E_0(x)\right]R_{n,l} = E_{n,l}R_{n,l} \qquad (35)$$

where $\bar{k} = N + 2l$ (N is the number of spatial dimension and $l(l + N - 2)\hbar^2$ the eigenvalue of the square of the momentum angular operator) cannot be solved exactly. However a satisfactory approximation to determine the radial solution is the so called $\frac{1}{N}$ shifted expansion [31] which can be applied when the potential is smooth. The whole spectrum is obtained. In this method the expansion parameter is k^{-1}, with $k = N + 2l - a$ and a a shifted expansion parameter not given *a priori*. The radial Schrödinger equation is written

$$\left\{-\frac{\hbar^2}{2M_x}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + k^2\left[\frac{\hbar^2\left(1 - \frac{1-a}{k}\right)\left(1 - \frac{3-a}{k}\right)}{8M_x x^2}\right.\right.$$
$$\left.\left. + \frac{\Delta E_0(x)}{Q}\right]\right\}R_{n,l} = E_{n,l}R_{n,l} \qquad (36)$$

where $k = \sqrt{Q}$ to assure the identity of the equation (36) with (35). If k is a large parameter, the leading term

of the potential is given by

$$V_{\text{eff}}(x) = k^2 \left(\frac{\hbar^2}{8M_x x^2} + \frac{\Delta E_0(x)}{Q} \right) \qquad (37)$$

and Q is fixed by the condition $\frac{\mathrm{d}V_{\text{eff}}(x)}{\mathrm{d}x} = 0$. If x_0 satisfies such condition, we obtain

$$Q = \frac{4M_x x_0^3 E_0^{(1)}(x_0)}{\hbar^2} \qquad (38)$$

where $E_0^{(n)}(x) = \frac{\mathrm{d}^n E_0(x)}{\mathrm{d}x^n}$. Furthermore, developing $V_{\text{eff}}(x)$ to second order around x_0, we obtain the oscillation frequency

$$\Omega = \frac{\hbar^2}{2M_x x_0^2} \left(3 + x_0 \frac{E_0^{(2)}(x_0)}{E_0^{(1)}(x_0)} \right)^{\frac{1}{2}}. \qquad (39)$$

The next step is to develop the potential in the radial equation (36) in the adimensional coordinate

$$u = \frac{k^{\frac{1}{2}}}{x_0}(x - x_0).$$

Equation (36) becomes

$$\left[-\frac{\hbar^2}{2M_x} \frac{\mathrm{d}^2}{\mathrm{d}u^2} + \frac{k\hbar^2}{8M_x} \left(1 + \frac{3u^2}{k} - \frac{4u^3}{k^{\frac{3}{2}}} + \frac{5u^4}{k^2} \cdots \right) \right] R_{n,l}$$
$$+ \left(\frac{(1-a)(3-a)\hbar^2}{8kM_x} - \frac{(2-a)\hbar^2}{4M_x} \right) \left(1 - \frac{2u}{k^{\frac{1}{2}}} + \frac{3u^2}{k} \right.$$
$$\left. - \frac{4u^3}{k^{\frac{3}{2}}} \cdots \right) R_{n,l} + \frac{x_0^2 k}{Q} \left(\Delta E_0(x_0) + \frac{1}{2k} E_0^{(2)}(x_0) x_0^2 u^2 \right.$$
$$\left. + \frac{1}{6k^{\frac{3}{2}}} E_0^{(3)}(x_0) x_0^3 u^3 \cdots \right) R_{n,l} = \frac{1}{k} E_{\text{nl}} x_0^2 R_{n,l}. \quad (40)$$

We see from (40) that the leading term ($\propto k^2$) gives a constant contribution to the energy; those $\propto k$ give the harmonic oscillator Hamiltonian whose frequency is Ω plus the constant term $-\frac{(2-a)\hbar^2}{4M_\rho x_0^2}$. The quantity a is obtained through the condition

$$\left(n + \frac{1}{2} \right) \hbar\Omega - \frac{(2-a)\hbar^2}{4M_x x_0^2} = 0. \qquad (41)$$

Substituting the value of a obtained through this equation in the definition of k and taking into account that $Q = k^2$, we obtain the equation

$$2l + N - 2 + (2n+1) \left(3 + x_0 \frac{E_0^{(2)}(x_0)}{E_0^{(1)}(x_0)} \right)^{\frac{1}{2}} =$$
$$\left(4M_\rho x_0^3 \frac{E_0^{(1)}(x_0)}{\hbar^2} \right)^{\frac{1}{2}} \qquad (42)$$

Table 2. The binding energies of the large bipolaron in unit $2\alpha^2\hbar\omega$ for $\alpha = 7$ and $\eta = 0, 0.048, 0.074$.

n	$\eta = 0.0$	$\eta = 0.048$	$\eta = 0.074$
0	-1.466×10^{-2}	-8.043×10^{-3}	-3.760×10^{-3}
1	-1.020×10^{-2}	-3.877×10^{-3}	$--$
2	-6.171×10^{-3}	-4.239×10^{-3}	$--$
3	-2.354×10^{-3}	$--$	$--$

Table 3. The binding energies of the large bipolaron in unit $2\alpha^2\hbar\omega$ for $\alpha = 10$ and $\eta = 0, 0.048, 0.074$.

n	$\eta = 0.0$	$\eta = 0.048$	$\eta = 0.074$
0	-1.588×10^{-2}	-9.212×10^{-3}	-4.990×10^{-3}
1	-1.355×10^{-2}	-6.983×10^{-3}	-2.669×10^{-3}
2	-9.438×10^{-3}	-4.976×10^{-3}	-6.284×10^{-4}
3	-7.511×10^{-3}	-3.135×10^{-3}	$--$
4	-5.624×10^{-3}	-1.446×10^{-3}	$--$
5	-3.754×10^{-3}	$--$	$--$
6	-1.977×10^{-3}	$--$	$--$
7	-6.035×10^{-4}	$--$	$--$

which allows, for any fixed n and l, to determine x_0. The other corrections to the energy are obtained with the standard perturbation theory. Finally we obtain the spectrum

$$E_{\text{nl}} = \frac{k^2}{x_0^2} \left[\frac{\hbar^2}{8M_x} + x_0^2 \frac{\Delta E_0(x_0)}{Q} + \frac{\gamma^{(1)}}{k^2} + \frac{\gamma^{(2)}}{k^3} + O\left(\frac{1}{k^4} \right) \right] \qquad (43)$$

where $\gamma^{(1)}$ and $\gamma^{(2)}$ give the first and the second perturbative correction to the energy. We see that the leading part of the spectrum is obtained from first and second terms of the equation (43).

In Tables 2, 3 and 4 are shown the binding energy (in unit $2\alpha^2\hbar\varpi$) of the bipolaron vibrational states for $\eta = 0.0, \eta = 0.048$ and $\eta = 0.074$ for $\alpha = 7, 10, 15$ respectively.

The box without numbers mean that, for the values of η and α considered, do not exist bound states.

4 Discussion of the results

In this work we have calculated the spectrum of the internal vibrational bound states of the bipolaron using the Bogolyubov-Tyablikov method. It results that the bipolaron states are the product of the free wavefunction of the center of mass of the polarons pair and of vibrational states describing the relative motion of the polarons around equilibrium positions. As found also by other authors [20,21] the bipolaron can form only if α is larger than a critical value $\alpha_c \sim 6$ for $\eta = 0$. When this occurs the energy difference between two successive states is smaller than the unrenormalized phonon energy and the energy difference between the ground and the highest excited state is larger than the phonon energy (*i.e.* there are phonon replicas of the ground state with energy lower than the highest excited state). Consequently the bipolaron absorption coefficient and conductivity has a very

Table 4. The binding energies of the large bipolaron in unit $2\alpha^2\hbar\omega$ for $\alpha = 15$ and $\eta = 0, 0.048, 0.074$.

n	$\eta = 0.0$	$\eta = 0.048$	$\eta = 0.074$
0	-1.657×10^{-2}	-9.865×10^{-3}	-5.682×10^{-3}
1	-1.546×10^{-2}	-8.812×10^{-3}	-4.572×10^{-3}
2	-1.442×10^{-2}	-7.811×10^{-3}	-3.528×10^{-3}
3	-1.343×10^{-2}	-6.864×10^{-3}	-2.546×10^{-3}
4	-1.249×10^{-2}	-5.962×10^{-3}	-1.624×10^{-3}
5	-1.158×10^{-2}	-5.098×10^{-3}	-7.479×10^{-4}
6	-1.069×10^{-2}	-4.266×10^{-3}	$--$
7	-9.824×10^{-3}	-3.463×10^{-3}	$--$
8	-8.967×10^{-3}	-2.689×10^{-3}	$--$
9	-8.121×10^{-3}	-1.943×10^{-3}	$--$
10	-7.283×10^{-3}	-1.543×10^{-3}	$--$
11	-6.451×10^{-3}	-5.471×10^{-4}	$--$
12	-5.621×10^{-3}	$--$	$--$
13	-4.793×10^{-3}	$--$	$--$
14	-3.964×10^{-3}	$--$	$--$
15	-3.138×10^{-3}	$--$	$--$
16	-2.325×10^{-3}	$--$	$--$
17	-1.554×10^{-3}	$--$	$--$
18	-8.797×10^{-4}	$--$	$--$
19	-4.081×10^{-4}	$--$	$--$
20	-3.242×10^{-4}	$--$	$--$

complicated structure. The number of the bound states increases when α increases and decreases when η increases. Each state of the spectrum is characterized by two parameters: the relative equilibrium position of the polarons x_0 and the quantities $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ which describe the displaced equilibrium position of the ionic vibrations. The first quantity x_0 depends self-consistently on the quantum numbers of the bipolaron state we are considering and on the effective polaron-polaron interaction; it increases when the quantum numbers and η increase and it is independent of α. The quantities $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ are different from zero and depend on f only in a range around $f = 0$; this range and the values of $u_{\mathbf{f},1}$ and $u_{\mathbf{f},2}$ become larger when α increases and smaller when x_0 or η increases. Since, for fixed α and η, x_0 increases when the principal quantum number n of the state increases and the displacement of the equilibrium position of the ions decrease, the conclusion is that the bipolaron forms because there is a local polarization of the medium depending on the state we are considering. The polarization becomes smaller and its extension increases when n increases.

We stress that the electrons wavefunction is taken of the ground state type of the homonuclear diatomic molecule; obviously we could also consider electron states with a different structure as it occurs in the physics of the molecules.

The next logical step is the comparison of our results with those obtained with the path-integral technique [21] and the variational approach by Lee-Low and Pines [2]. The comparison shows:

a) the values of η_c calculated in the present work are almost twice than those in references [20,21], which

are $\eta_c = 0.02, 0.04, 0.06$ and $\eta_c = 0.004, 0.05, 0.066$ respectively for $\alpha = 7, 10, 15$. Highest values of η_c are found or including correlation effects between the electrons or considering the bipolaron as a two centers system [15–19,22,25]. We stress that both effects are taken into account in this work;

b) for $\eta = 0$, the smallest value of α for which the bipolaron begins to form is very near to that found in previous works using approaches very different [20,21] $\alpha \simeq 6$;

c) the bipolaron total energies calculated in this work for $\alpha = 7, 10, 15$ and $\eta = 0$ are $(-11.825\hbar\omega, -24.376\hbar\omega, -55.156\hbar\omega)$, those in reference [20] are $(-14.056\hbar\omega, -20.240\hbar\omega, -30.736\hbar\omega)$ and those in [21] are $(-16.283\hbar\omega, -28.631\hbar\omega, -59.058\hbar\omega)$. This indicates that the three theories give coherent values even in the intermediate regime of α;

d) for $\eta = 0$ and $\alpha = 7, 10, 15$, the binding energies of the lowest bound states in this work are $(-1.437\hbar\omega, -3.176\hbar\omega, -7.456\hbar\omega)$. In references [20,21] for $\alpha = 7, 10, 15$ it was found $(-0.056\hbar\omega, -0.24\hbar\omega, -0.736\hbar\omega)$ and $(-0.058\hbar\omega, -1.650\hbar\omega, -5.608\hbar\omega)$ respectively. To find the binding energy in our case we have taken the polaron energy $-\frac{2}{3\pi}\alpha^2\hbar\omega = E_0(\rho = \infty)$. We stress that the calculation in this work does not allow the comparison between the bipolaron and polaron energies at the same order of approximation. If this were done the binding energy found in this work becomes more near to that found in references [20,21]. Finally we must again remember that the present calculation is done considering the bipolaron as two centers system and that the correlation between electrons is taken into account.

In summary we have calculated the internal vibrational states of the large bipolaron by making use of the BT method. The features of the states both for what it concerns the electronic and the ionic parts of the wavefunction have been discussed. Moreover the comparison of our results with those obtained within different approaches shows that the theory developed in this work, although in principle valid for very high values of α, gives good results even in the range of the intermediate values of α. This provides an important check of the proposed approach. The knowledge of the spectrum for intermediate values of the electron-phonon coupling constant can be the starting point for the calculation of quantities of experimental interest.

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