Ground and excited states of the bipolaron in two and three dimensions

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Abstract

The properties of large bipolarons in two and three dimensions are investigated by averaging over the relative wavefunction of the two electrons and using the Lee-Low-Pines-Huybrechts variational method. We obtain the ground-state (GS) and excited-state energies of the Fröhlich bipolaron for the whole range of electron-phonon coupling constants. Furthermore, we calculate the energies of the first relaxed excited state (RES) and Franck-Condon (FC) excited state of the bipolaron. Compared with the FC state, the first RES has a lower energy. Our results for the GS and RES energies are lower than those obtained before by the Landau-Pekar method in the whole coupling regime.
I. INTRODUCTION

Polaronic and bipolaronic effects are found in many materials such as transition metal oxides [1], polymers [2], and superconducting materials [3]. Since these materials possess low dimensional structures, the effective electron-phonon coupling is very strong owing to the confinement of their low dimensional nature. With this feature, many intriguing phenomena related to polarons and bipolarons can occur in these materials. Electrons in a polar or ionic crystal are influenced by the phonon field giving rise to polaronic effects [4, 5]. When the attractive interaction of the electron-phonon coupling is strong enough to overcome the Coulomb repulsion between two electrons, the two electrons plus their associated phonon field can form a bound state. Such a composite quasi-particle is referred to as a bipolaron. If the bipolaron is extended over many lattice cells, it is called large bipolaron. In contrast, if the bipolaron is localized at one lattice site, it is called small bipolaron [6].

Bipolarons have been extensively discussed both for fundamental theoretical reasons and for their importance in semiconductor materials. With recent advances in the creation of nanocrystals and semiconductor nanostructures, strong electron-phonon coupling is realized due to quantum confinement effects [7, 8, 9, 10, 11, 12, 13], and the properties of bipolarons in low dimensional systems are of growing interest. This problem is also relevant to the proposal of the bipolaronic mechanism for electron pairing in the CuO$_2$ plane in high $T_c$ cuprates [3, 6]. Recently, Schoenes and co-workers [14] reported that some superconductors such as YBa$_2$Cu$_4$O$_8$ have strong electron-phonon coupling, which also boosts the theoretical research on bipolarons.

Though the bipolaron ground state has been extensively discussed in the past decade [15, 16, 17, 18, 19, 20, 21, 22], the excited states have, so far, been studied much less. At the same time, knowledge of the excited states of the bipolaron is related to electron transport, photoluminescence and photoemission [1, 2, 3]. Several works have been devoted to excited states of Fröhlich bipolarons [23, 24, 25, 26, 27]. Huybrechts [23] developed a Lee-Low-Pines variational method and studied the ground and excited states of a single optical polaron. Smondyrev et al. [24] calculated the energy spectra of the one-dimensional bipolaron in the strong-coupling limit. More recently, Sahoo [25] developed the Landau-Pekar variational method to get the ground and first excited states of the Fröhlich bipolaron in a multidimensional ionic crystal in the strong-coupling limit.

In this paper we adopt the Fröhlich Hamiltonian for the large bipolaron which consists of
the kinetic energies of two electrons, their interactions with the phonon field, and the screened Coulomb repulsion between them. We extend the Huybrechts variational approach (LLP-H) to the analysis of the bipolaron ground state in Sec. II. For comparison, different wavefunctions are used to calculate the ground-state energy of the bipolaron in Sec. III, and the best wavefunction of the relative motion is obtained. In Sec. IV, after averaging over the relative motion, the energies of the first relaxed excited state and Franck-Condon excited state of the bipolaron in two and three dimensions are obtained for the whole coupling parameter range, and discussions of these two types of excited states are given. Finally, comparison of our results with previously published data is given in Sec. V. Our conclusions are presented in Sec. VI.

II. CALCULATION OF THE GROUND-STATE ENERGY

The Fröhlich Hamiltonian for the polaron in $N$ dimensions (ND) has been derived by Peeters et al [28]. Accordingly, the Hamiltonian describing a system of two electrons interacting with a longitudinal optical (LO) phonon field may be written as

$$
H = \sum_{i=1,2} \frac{p_i^2}{2m} + \sum_k (V_k a_k e^{i k \cdot r_i} + h.c.) + \sum_k \hbar \omega_k a_k^+ a_k + U(|r_1 - r_2|),
$$

(1)

where all vectors are $N$-dimensional ($N = 2, 3$), $r_i$ ($p_i$) is the position (momentum) operator of the $i$th electron ($i = 1, 2$) and $m$ is the effective electron band mass in the parabolic approximation. $a_k^+$ and $a_k$ are respectively the creation and annihilation operators of the LO phonons with the wave vector $k$. Here we should mention that the impurity-phonon interactions have already been eliminated so that we assume $\omega_k = \omega_{LO}$. For convenience in the following, units are taken where $m = \hbar = \omega_{LO} = 1$, and the Hamiltonian for the ND Fröhlich bipolaron has the form:

$$
H = \sum_{i=1,2} \frac{p_i^2}{2} + \sum_k (V_k a_k e^{i k \cdot r_i} + h.c.) + \sum_k a_k^+ a_k + U(|r_1 - r_2|).
$$

(2)

In this way, energies are in units of $\hbar \omega_{LO}$ and lengths in units of $\sqrt{\hbar/(m \omega_{LO})}$ in this article. The interaction coefficient is

$$
V_k = -i \left\{ \frac{\Gamma[(N-1)/2]2^{N-3/2}\pi^{(N-1)/2}\alpha}{V_N k^{N-1}} \right\}^{1/2},
$$

(3)
where $V_N$ is the ND crystal volume, $\alpha$ is the dimensionless electron-phonon coupling constant

$$\alpha = \frac{1}{\hbar \omega_{LO}} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) \left( \frac{2m\omega_{LO}}{\hbar} \right)^{1/2},$$

and $\varepsilon_\infty (\varepsilon_0)$ is the high-frequency (static) dielectric constant of the medium. $U(r) = U/r$ is the Coulomb interaction potential between the two electrons where the nonscreened electron Coulomb repulsion strength is given by $U = e^2/\varepsilon_\infty$, which may be rewritten as

$$U = \sqrt{2\alpha \frac{1}{1 - \eta}}, \quad \eta = \frac{\varepsilon_\infty}{\varepsilon_0}.$$

Since the bipolaron is a composite particle, it is convenient to introduce center-of-mass and relative coordinates and momenta, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$, $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{p} = (\mathbf{p}_1 - \mathbf{p}_2)/2$, in which the Hamiltonian can be rewritten as

$$H = \frac{\mathbf{P}^2}{4} + 2 \sum_k \cos \left( \frac{k \cdot \mathbf{r}}{2} \right) (V_k a_k e^{ik \cdot \mathbf{R}} + h.c.) + \sum_k a_k^+ a_k + \frac{U}{r}.$$

Up to now, an exact analytical solution for the Hamiltonian (6) is not known. However, we can make progress by averaging (6) over the relative wavefunction $\phi(r)$, which yields an effective Hamiltonian for the center of mass motion,

$$H_{eff} = \frac{\mathbf{P}^2}{4} + \sum_k (B_k a_k e^{ik \cdot \mathbf{R}} + h.c.) + \sum_k a_k^+ a_k + E_r.$$

Here $B_k = 2V_k \langle \cos \left( \frac{k \cdot \mathbf{r}}{2} \rangle \rangle$, $E_r = \langle \mathbf{p}^2 + U/r \rangle$, with $\langle \cdots \rangle$ denoting an averaging over the wavefunction $\phi(r)$. The new Hamiltonian (7) would be equivalent to (6) if the true wavefunction would be known which of course is not the case. Therefore, we will use a variational approach, two specific choices will be discussed in section III.

Note that the effective Hamiltonian (7) corresponding to the center-of-mass motion is in essence equivalent to a single-polaron Hamiltonian. The differences between the Hamiltonian (7) and the usual Hamiltonian of a single polaron are the following: (i) the energy is shifted by the average of the energy of the relative motion $E_r$, and (ii) the electron-phonon interaction coefficient $B_k$ is renormalized.

In this paper, we will follow the modified Lee-Low-Pines variational method proposed by Huybrechts [23] for the polaron problem. This will allow us to obtain very accurate bipolaron energies.
for all coupling regimes and calculate the ground and excited-state energies of the Fröhlich bipolaron. Performing the unitary transformation $U_1$

$$U_1 = \exp \left( -ia \sum_k \mathbf{k} \cdot \mathbf{R} a^+_k a_k \right),$$

the Hamiltonian (7) can be transformed into

$$H_{\text{eff}} = \frac{1}{4} \left( \mathbf{P} - a \sum_k \mathbf{k} a^+_k a_k \right)^2 + \sum_k \left\{ B_k^* a^+_k \exp[-i(1 - a)\mathbf{k} \cdot \mathbf{R}] + \text{h.c.} \right\} + \sum_k a^+_k a_k + E_r,$$

where $a$ is a parameter. In the limit $a \to 0$, the present calculation is identical to the strong-coupling regime, whereas the case $a \to 1$ corresponds to weak electron-phonon interaction.

Following Huybrechts, we introduce the creation and annihilation operators $b^+_j$ and $b_j$ for electrons

$$P_j = (\lambda)^{1/2}(b^+_j + b_j),$$

$$R_j = i \left( \frac{1}{4\lambda} \right)^{1/2} (b_j - b^+_j),$$

where the index $j$ refers to the $N$ space directions and $\lambda$ is a variational parameter. Rewriting the Hamiltonian (9) using (10) one gets

$$H'_{\text{eff}} = H'_1 + H'_2 + E_r,$$

$$H'_1 = \frac{\lambda}{2} \sum_j (b^+_j b_j + \frac{N}{2}) + \sum_k \left( 1 + \frac{a^2 k^2}{4} \right) a^+_k a_k$$

$$+ \sum_k \left\{ B_k^* a^+_k \exp \left[ -\frac{(1 - a)^2 k^2}{8\lambda} \right] \times \exp \left[ -(1 - a) \sqrt{\frac{1}{4\lambda}} \sum_j k_j b^+_j \right] \times \exp \left[ (1 - a) \sqrt{\frac{1}{4\lambda}} \sum_j k_j b_j \right] + \text{h.c.} \right\}$$

$$+ \frac{\lambda}{4} \sum_j (b^+_j b^+_j + b_j b_j),$$

(12)
\[ H'_2 = \frac{a^2}{4} \sum_{k,k'} k \cdot k' a_k^+ a_{k'} a_k a_{k'} \]
\[ -a \sqrt{\lambda} \frac{\lambda}{2} \sum_k \sum_j k_j (b_j^+ + b_j) a_k^+ a_k. \]  

(13)

Performing now the second Lee-Low-Pines transformation:

\[ U_2 = \exp \left[ \sum_k (f_k a_k^+ - f_k^* a_k) \right], \]  

(14)

one obtains

\[ H'' = \frac{\lambda}{2} \sum_j b_j^+ b_j + \frac{N \lambda (1-a)^2}{4} \]
\[ + \sum_k \left( 1 + \frac{a^2 k^2}{4} \right) (a_k^+ + f_k^*) (a_k + f_k) \]
\[ + \sum_k \left\{ B_k^* (a_k^+ + f_k^*) \exp \left[ -\frac{(1-a)^2 k^2}{8 \lambda} \right] \right. \]
\[ \times \exp \left[ -(1-a) \sqrt{\frac{1}{4 \lambda} \sum_j k_j b_j^+} \right] \]
\[ \times \exp \left[ (1-a) \sqrt{\frac{1}{4 \lambda} \sum_j k_j b_j} \right] + h.c. \right\} \]
\[ + H''_1 + E_r, \]  

(15)

where the part \( H''_1 \) of the Hamiltonian (15) contains terms of no importance for the further calculation and will be omitted. The wavefunction describes the polaron system \( \Psi(r) \) including an electron wavefunction \( \phi(r) \) and a phonon field wavefunction \( |f\rangle \), \( \Psi(r) = \phi(r) |f\rangle \). For the ground state, one has

\[ \Psi_0(r) = \phi_0(r) |f\rangle, \]  

(16)

with

\[ b_j \phi_0(r) = 0, \quad \phi_0(r) = c \exp(-\lambda \sum_j R_j^2), \]  

(17)

where \( b_j \) and \( \lambda \) are defined in equation (10), \( \phi_0(r) \) corresponds to the ground-state wavefunction for the electron and \( j \) refers to the \( j \)th direction of \( N \) space. For the field function in the ground state one has

\[ |f\rangle = U_2 |0\rangle, \quad a_k |0\rangle = 0, \]  

(18)
where $U_2$ is defined in equation (14) and $f_k$ in $U_2$ will be obtained by minimizing the ground-state energy of the bipolaron,

$$\frac{\partial E_{0,ND}^{BP}}{\partial f_k^*} = 0.$$  (19)

Then we can directly present the bipolaron ground-state energy $E_{0,ND}^{BP}$ as

$$E_{0,ND}^{BP} = \frac{N}{4} \lambda (1 - a)^2 + \sum_k \left( 1 + \frac{a^2 k^2}{4} \right) | f_k |^2$$

$$+ \sum_k \left\{ B_k^* f_k^* \exp \left[ -\frac{(1 - a)^2 k^2}{8 \lambda} \right] + h.c. \right\}$$

$$+ E_r,$$  (20)

with

$$f_k = \frac{-B_k^* \exp\left[-(1 - a)^2 k^2/(8 \lambda)\right]}{1 + a^2 k^2/4}.$$  (21)

Using (21) in (20) we obtain the ground-state energy of the bipolaron in $N$ dimensions with an arbitrary electron-phonon coupling constant:

$$E_{0,ND}^{BP} = \frac{N}{4} \lambda (1 - a)^2 - \sum_k B_k^2 \exp\left[-(1 - a)^2 k^2/(4 \lambda)\right]$$

$$+ E_r.$$  (22)

The effective electron mass of ND materials which is modified by bipolaronic effect is given by (for details see Ref. [29])

$$m^* = 2 + \frac{1}{D} \sum_k (k)^2 B_k^2 \exp\left[-(1 - a)^2 k^2/(4 \lambda)\right]$$

$$\frac{1}{(1 + a^2 k^2/4)^3}.$$  (23)

To obtain explicit results for the ground-state energy and the effective mass we now compute the relative wavefunction of the electron pair.

### III. CHOICE OF THE BEST WAVEFUNCTION FOR RELATIVE MOTION

In order to calculate the energy related to the relative motion $E_r$ and the coefficient $B_k$, we have to choose a trial wavefunction $\phi(r)$. In the following two different functional forms will be chosen: (a) Coulombic type

$$\phi_n^{(c)}(r) = C r^n \exp(-\Omega r/4),$$  (24)
and (b) oscillator type

$$\phi^{(o)}_n(r) = Cr^n \exp(-br^2/4),$$  \hspace{1cm} (25)

where $b$ and $\Omega$ are variational parameters and $n = 0, 1, 2, ...$. Using the wavefunctions (24) or (25) to calculate $E_r$ and $B_k$, we obtain the ground-state energy of the bipolaron from equation (22). Comparing the results obtained with wave functions (a) and (b) allows us to determine which one leads to the best approximation of the relative motion.

In Fig. 1(a), the ground-state energy $E^{0,3D}_{BP}$ of a 3D system is plotted versus $\alpha$ for different Coulombic wave functions (24) for the case $n = 0, 1, 2, 3$. Interestingly, the energy obtained with the function $\phi^{(c)}_2$ ($n = 2$) is smaller than those obtained by the others with $n = 0, 1, 3$. From the viewpoint of the variational principle, the relative motion is best described by the function $r^2 \exp(-\Omega r/4)$ among the different Coulombic wave functions.

In Fig. 1(b), we plot $E^{0,3D}_{BP}$ (3D) as a function of $\alpha$ for different oscillator wavefunctions (25) for $n = 0, 1, 2$. Here, the energy obtained with $\phi^{(o)}_1$ is lower than those by others, indicating that $r \exp(-br^2/4)$ is superior to other oscillator wavefunctions in describing the relative motion. Furthermore, we find that $E^{0,3D}_{BP}$ calculated with the oscillator wavefunction $\phi^{(o)}_1$ is smaller than that obtained by using the best Coulombic wavefunction $\phi^{(c)}_2$. So we conclude that the oscillator wavefunction $\phi^{(o)}_1$ reflects the relative motion best in 3D materials.

Next consider the 2D case. Fig. 2(a) and Fig. 2(b) present $E^{0,2D}_{BP}$ as a function of $\alpha$ for Coulombic and oscillator wavefunctions, respectively. In Fig. 2(a), we find that the energy obtained by $\phi^{(c)}_1$ is lower than those by $\phi^{(c)}_0$ and $\phi^{(c)}_2$. Fig. 2(b) shows that the energy obtained from $\phi^{(o)}_1$ is lower than those following from $\phi^{(o)}_0$ and $\phi^{(o)}_2$. Compared with $E^{0,2D}_{BP}$ of $\phi^{(c)}_1$, $E^{0,2D}_{BP}$ of $\phi^{(o)}_1$ is a
little smaller, which demonstrates that the oscillator wavefunction $\phi^{(o)}_1$ reflects the relative motion best in 2D systems as well.

Finally we calculate the energy of the relative motion $E_r$ by using the best wavefunction $\phi^{(o)}_1$ in equation (22) and obtain the ground-state energies of the bipolaron in 3D and 2D materials as follows

$$E^{0,3D}_{BP} = \frac{3\lambda}{4} (1 - a)^2 - \frac{4\sqrt{2}\alpha}{\pi} \int_0^\infty dk \left( 1 - \frac{k^2}{6b} + \frac{k^4}{144b^2} \right) \times \frac{\exp(-gk^2)}{1 + a^2k^2/4} + \frac{7b}{12} + \frac{4}{3} \sqrt{\frac{b}{2\pi}} U, \quad (26)$$

$$E^{0,2D}_{BP} = \frac{\lambda}{2} (1 - a)^2 - 2\sqrt{2}\alpha \int_0^\infty dk \left( 1 - \frac{k^2}{4b} + \frac{k^4}{64b^2} \right) \times \frac{\exp(-gk^2)}{1 + a^2k^2/4} + \frac{b}{2} + \frac{\sqrt{2b\pi}}{4} U, \quad (27)$$

with

$$g = \frac{1}{4b} + \frac{(1 - a)^2}{4\lambda}, \quad (28)$$

and $a, b$ and $\lambda$ being usual variational parameters. Comparing our bipolaron ground-state energy ($E^{0,ND}_{BP}$) with the ground-state energy ($E^{0,ND}_p$) of a single polaron [28], we find that the bipolaron is stable for $\alpha \geq \alpha_c = 8.1(3.6)$ in 3D (2D). It is interesting to note that our results are very close to the estimate $\alpha_c = 8.1$ in 3D and $\alpha_c = 3.5$ in 2D in Ref. [18] by Luczak et al., who obtained the bipolaron ground-state energy by a totally different variational scheme.

Furthermore, the effective mass and root mean square separation $r_{12}$ of two electrons can be
FIG. 3: Effective electron mass in two and three dimensions as a function of the coupling constant at $\eta = 0.08$ (units of bipolaron effective mass: free electron mass $m_e$).

The effective mass as a function of the coupling constant is shown in Fig. 3. Due to the interaction of electron and phonon field, the effective mass greatly increases with the coupling constant. It also can be seen from Fig. 3 that the effective mass in 2D materials is larger than that in 3D materials, which indicates that the electron-phonon interaction is increased as the dimension of the material is reduced. Similarly, in one-dimensional materials [24], the bipolaron has a much larger effective mass than our results of 2D materials.

calculated as

$$m^{*3D} = 2 + \frac{4\sqrt{2}\alpha}{3\pi} \int_{0}^{\infty} dk \left( 1 - \frac{k^2}{6b} + \frac{k^4}{144b^2} \right) \times \frac{k^2 \exp(-gk^2)}{(1 + a^2k^2/4)^3},$$

(29)

$$m^{*2D} = 2 + \sqrt{2}\alpha \int_{0}^{\infty} dk \left( 1 - \frac{k^2}{4b} + \frac{k^4}{64b^2} \right) \times \frac{k^2 \exp(-gk^2)}{(1 + a^2k^2/4)^3},$$

(30)

$$r_{12}^{3D} = \left[ \frac{5}{b} \right]^{1/2},$$

(31)

$$r_{12}^{2D} = \left[ \frac{4}{b} \right]^{1/2}.$$  

(32)
TABLE I: The values of the variational parameters $\lambda$, $a$ and $b$ which are used in the GS and FC state energies for 3D and 2D materials.

| $\alpha$ | $\lambda^{3D}$ | $a^{3D}$ | $b^{3D}$ | $\lambda^{2D}$ | $a^{2D}$ | $b^{2D}$ |
|---|---|---|---|---|---|---|
| 1.0 | 0.628 | 0.802 | 0.7297 | 1.58 | 0.635 | 1.795 |
| 2.0 | 1.52 | 0.638 | 1.659 | 4.26 | 0.376 | 4.743 |
| 3.0 | 2.60 | 0.507 | 2.715 | 8.51 | 0.217 | 9.396 |
| 4.0 | 3.93 | 0.398 | 3.990 | 14.6 | 0.132 | 16.11 |
| 5.0 | 5.58 | 0.310 | 5.574 | 22.6 | 0.0871 | 24.88 |
| 6.0 | 7.61 | 0.241 | 7.530 | 32.4 | 0.0612 | 35.68 |
| 7.0 | 10.1 | 0.188 | 9.889 | 44.1 | 0.0452 | 48.47 |
| 8.0 | 12.9 | 0.150 | 12.66 | 57.5 | 0.0347 | 63.25 |
| 9.0 | 16.2 | 0.121 | 15.84 | 72.7 | 0.0274 | 80.02 |
| 10.0 | 19.9 | 0.0991 | 19.42 | 89.8 | 0.0222 | 98.76 |
| 11.0 | 23.96 | 0.0826 | 23.40 | 108.6 | 0.0184 | 119.5 |
| 12.0 | 28.4 | 0.0698 | 27.77 | 129.2 | 0.0155 | 142.2 |
| 13.0 | 33.3 | 0.0597 | 32.53 | 151.7 | 0.0132 | 166.8 |
| 14.0 | 38.6 | 0.0516 | 37.68 | 175.9 | 0.0114 | 193.5 |
| 15.0 | 44.3 | 0.0450 | 43.22 | 201.9 | 0.0099 | 222.1 |

IV. INTERNAL EXCITED STATES

Following the definition given by Devreese [4], we compute the relaxed excited state (RES) and Franck-Condon excited state (FC) energies of the bipolaron. The RES is created if the electron in the polaron is excited while the lattice readapts to the new electronic configuration. One can imagine that the electron goes from a 1s- to a 2p-state, while the lattice polarization in the final state is adapted to the 2p-state of the electron. If, on the contrary, the lattice corresponds to the electron ground state, while the electron is excited, one speaks of a FC state.

Here we use a method of Huybrechts [23] who computed the FC state energy [30] of a single polaron. In this section, we will develop Huybrechts method to calculate the RES energy of the bipolaron by adjusting $a$, $b$, $\lambda$ and $f_k$ to the relaxed excited state. Finally the FC state and RES energies we obtain are fit for the whole electron-phonon coupling regime.
The wavefunction for the excited polaron system is as follows

\[ \Psi_1(r) = \phi_1(r) |f\rangle, \]  

(33)

with

\[ b_j^+ \phi_0(r) = \phi_1(r), \quad \phi_1(r) = cR_j \exp(-\lambda \sum_j R_j^2). \]  

(34)

In the FC model, the electrons can be excited to a higher level in the same potential well built up by the field of virtual phonons in the ground state so that \( \lambda \) has the same value as that in Tab. 1. For the RES, \( \lambda \) is different from that in Tab. 1 and it can be obtained by minimizing the first excited-state energy. The potential well should adjust to the first excited state, Consequently, the lattice polarization in the final state is adapted.

For the field wavefunction in the excited state one has

\[ |f\rangle = U_2 |0\rangle, \quad a_k |0\rangle = 0. \]  

(35)

For the FC state \( f_k \) in \( U_2 \) is the same as that in equation (21). For the RES \( f_k \) can be obtained by minimizing the excited-state energy according to

\[ \frac{\partial E_{BP}^{1,ND}}{\partial f_k^*} = 0. \]  

(36)

In order to obtain the energy of the first internal excited state of the bipolaron we calculate the average

\[ \langle 0 \mid \phi_1(r) \mid H'' \mid \phi_1(r) \mid 0 \rangle. \]  

(37)

After some elementary calculus, we get the excited-state energy \( E_{BP}^{1,ND} \) for the bipolaron in N dimensions

\[ E_{BP}^{1,ND} = \frac{\lambda}{2} + \frac{N \lambda (1 - a)^2}{4} + \sum_k \left( 1 + \frac{a^2 k^2}{4} \right) |f_k|^2 \]

\[ + \sum_k \left\{ B_k^* f_k \left[ 1 - (1 - a)^2 \frac{k^2}{4\lambda N} \right] \right\} \times \exp \left[ -\frac{(1 - a)^2 k^2}{8\lambda} \right] + \text{h.c.} + E_r, \]  

(38)

with

\[ f_k^{FC} = \frac{-B_k^* \exp[-(1 - a)^2 k^2/(8\lambda)]}{1 + a^2 k^2 / 4}, \]  

(39)
for the FC state and for the RES one has

\[
 f_{k}^{\text{RES}} = \frac{-B_k^* \exp\left[-(1-a)^2k^2/(8\lambda)\right]}{1+a^2k^2/4} \times \left[ 1 - (1-a)^2 \frac{1}{4\lambda N} \right].
\]

(40)

Then we calculate the energy of the relative motion by using the best relative wavefunction \(\phi_1^{(o)}\) in equation (25) and inserting \(f_k^{FC}\) and \(f_k^{RES}\) into equation (38). Finally we obtain the FC state and RES energies of the bipolaron in 3D and 2D materials as follows

\[
 E_{BP}^{\text{FC},3D} = \frac{\lambda}{2} + \frac{3\lambda}{4}(1-a)^2 \right.
\]

\[
 \left. -\frac{4\sqrt{2}\alpha}{\pi} \int_0^\infty dk \left( 1 - \frac{k^2}{6b} + \frac{k^4}{144b^2} \right) \exp\left(-gk^2\right) \right. \]

\[
 \left. \times \left[ 1 - \frac{(1-a)^2k^2}{8\lambda} \right] + \frac{7b}{12} + \frac{4\sqrt{2b\pi}}{3} U, \right.
\]

(41)

\[
 E_{BP}^{\text{FC},2D} = \frac{\lambda}{2} + \frac{\lambda}{2}(1-a)^2 \right.
\]

\[
 \left. -\frac{2\sqrt{2}\alpha}{\pi} \int_0^\infty dk \left( 1 - \frac{k^2}{4b} + \frac{k^4}{64b^2} \right) \exp\left(-gk^2\right) \right. \]

\[
 \left. \times \left[ 1 - \frac{(1-a)^2k^2}{8\lambda} \right] + \frac{b}{2} + \frac{\sqrt{2b\pi}}{4} U, \right.
\]

(42)

\[
 E_{BP}^{\text{RES},3D} = \frac{\lambda}{2} + \frac{3\lambda}{4}(1-a)^2 \right.
\]

\[
 \left. -\frac{4\sqrt{2}\alpha}{\pi} \int_0^\infty dk \left( 1 - \frac{k^2}{6b} + \frac{k^4}{144b^2} \right) \exp\left(-gk^2\right) \right. \]

\[
 \left. \times \left[ 1 - \frac{(1-a)^2k^2}{8\lambda} \right] + \frac{7b}{12} + \frac{4\sqrt{2b\pi}}{3} U, \right.
\]

(43)

\[
 E_{BP}^{\text{RES},2D} = \frac{\lambda}{2} + \frac{\lambda}{2}(1-a)^2 \right.
\]

\[
 \left. -\frac{2\sqrt{2}\alpha}{\pi} \int_0^\infty dk \left( 1 - \frac{k^2}{4b} + \frac{k^4}{64b^2} \right) \exp\left(-gk^2\right) \right. \]

\[
 \left. \times \left[ 1 - \frac{(1-a)^2k^2}{8\lambda} \right] + \frac{b}{2} + \frac{\sqrt{2b\pi}}{4} U, \right.
\]

(44)

where \(E_{BP}^{1,ND}\) is expressed in units of \(\hbar\omega_{LO}\). For the FC state the values of the parameters \(a, b\) and \(\lambda\) are taken from the calculation of the ground state energy \(E_{BP}^{0,ND}\) (Tab. 1). For the RES the values
of the parameters $\lambda$, $a$ and $b$ are obtained by minimizing the excited-state energy $E_{\text{RES,ND}}^{BP}$ of Eq. (36) through numerical calculation, which are presented in tables 2. From Tabs. 1 and 2, we can see that $\lambda$ in the RES is smaller than in the ground state which means that there is weaker potential well built up by the phonon field in the RES.

In Fig. 4(a) and Fig. 4(b), the ground-state energy ($E_{\text{BP,ND}}^{0}$), first RES energy ($E_{\text{BP,ND}}^{\text{RES}}$) and FC state energy ($E_{\text{BP,ND}}^{\text{FC}}$) of the bipolaron are displayed as functions of the electron-phonon coupling constants for 3D and 2D materials. We find that in the whole range of electron-phonon coupling constants, the RES energies are negative. On the other hand, the FC state energies in 3D and 2D materials are negative when $\alpha > 0.4$ and $\alpha > 0.2$, respectively. The difference in energy, $\Delta E_{\text{ND}} = E_{\text{BP,ND}}^{1} - E_{\text{BP,ND}}^{0}$, yields the excitation energy, which is related to optical absorption of bipolarons in semiconductor materials [3, 31].

In all cases, we find that the RES energy is smaller than the FC state energy, see Fig. 4, which

TABLE II: The values of the variational parameters $\lambda$, $a$ and $b$ which are used in the RES energy for 3D and 2D materials.

| $\alpha$ | $\lambda^{3D}$ | $a^{3D}$ | $b^{3D}$ | $\lambda^{2D}$ | $a^{2D}$ | $b^{2D}$ |
|---------|----------------|---------|---------|----------------|---------|---------|
| 1.0     | $1.13 \times 10^{-9}$ | 0.999 0.631 | $1.01 \times 10^{-9}$ | 0.999 1.227 |
| 2.0     | $3.71 \times 10^{-9}$ | 0.999 1.170 | $1.81 \times 10^{-9}$ | 0.999 2.097 |
| 3.0     | $2.59 \times 10^{-9}$ | 0.999 1.556 | 1.34 0.717 | 3.193  |
| 4.0     | 0.726 0.792 | 2.085 3.25 | 0.515 4.671 |
| 5.0     | 1.54 0.651 | 2.685 5.53 | 0.387 6.478 |
| 6.0     | 2.42 0.551 | 3.337 8.31 | 0.296 8.694 |
| 7.0     | 3.39 0.472 | 4.065 11.6 | 0.230 11.36 |
| 8.0     | 4.49 0.406 | 4.886 15.5 | 0.182 14.48 |
| 9.0     | 5.74 0.350 | 5.812 19.9 | 0.147 18.06 |
| 10.0    | 7.13 0.302 | 6.855 24.9 | 0.121 22.09 |
| 11.0    | 8.67 0.262 | 8.020 30.3 | 0.100 26.57 |
| 12.0    | 10.4 0.228 | 9.312 36.4 | 0.0847 31.50 |
| 13.0    | 12.2 0.199 | 10.73 42.9 | 0.0724 36.86 |
| 14.0    | 14.3 0.175 | 12.28 50.0 | 0.0625 42.67 |
| 15.0    | 16.5 0.155 | 13.95 57.7 | 0.0545 48.91 |
FIG. 4: (a) Ground-state energy ($E_{BP}^{0,3D}$), first RES energy ($E_{BP}^{RES,3D}$) and FC state energy ($E_{BP}^{FC,3D}$) of the bipolaron are displayed as functions of the electron-phonon coupling constants for 3D materials. The bipolaron is stable for $\alpha \geq \alpha_{c}^{3D} = 8.1$. (b) Ground-state energy ($E_{BP}^{0,2D}$), first RES energy ($E_{BP}^{RES,2D}$) and FC state energy ($E_{BP}^{FC,2D}$) of the bipolaron are displayed as functions of the electron-phonon coupling constants for 2D materials. The bipolaron is stable for $\alpha \geq \alpha_{c}^{2D} = 3.6$.

is well known from absorption spectrum calculations [4, 32, 33]: The absorption peak due to a transition from the ground state to the first relaxed excited state corresponds to the zero-phonon peak. In contrast, an absorption transition from the GS to the FC state is accompanied with phonon emission. If the bipolaron system is excited to the FC state, the lattice will relax towards the RES by emission of phonons.

V. COMPARISON WITH STRONG-COUPLING CALCULATIONS

In order to assess the heuristic value of our approach, we compare the present GS and RES energies with those obtained by Sahoo [25], who adopted the wavefunction $\phi_{0}^{(o)}(r)$ and developed a Landau-Pekar variational method to get the ground-state and RES energies of the Fröhlich bipolaron in the strong-coupling limit. For the case of $N$ dimensions we obtain from Eqs. (22, 25, 38, 40) the following results when $\phi_{0}^{(o)}(r)$ is used

$$E_{osc,ND}^{0,N}(0, a) = \frac{N\lambda}{4} (1 - a)^{2} + \frac{Nb}{4} + \sqrt{b/2U} \frac{\Gamma(N-1)}{\Gamma(N/2)}$$

$$- \frac{2\sqrt{2\alpha}}{\sqrt{\pi}} \frac{\Gamma(N-1)}{\Gamma(N/2)} \int_{0}^{\infty} \frac{\exp(-gk^2)}{1 + a^2 k^2/4} dk,$$

(45)
with $a$, $b$ and $\lambda$ being usual variational parameters, and $g$ being defined in equation (28). If we set $a = 0$ and use the units $2m = \hbar = \omega = 1$ equations (45, 46) reduce to the results of Sahoo [25].

To perform a comparison with our results, we define the relative deviation

$$
\xi = \left| \frac{E_{osc,ND}^{0,0}(0,0) - E_{osc,ND}^{0,0}(0,0)}{E_{osc,ND}^{0,0}(0,0)} \right|,
$$

with $E_{osc,ND}^{0,0}(0,0)$ referring to the GS energies obtained by Sahoo [25] and $E_{osc,ND}^{0,0}(0,0)$ given by Eqs. (26, 27). Also, we define

$$
\delta = \left| \frac{E_{RES,ND}^{0,0}(0,0) - E_{RES,ND}^{0,0}(0,0)}{E_{RES,ND}^{0,0}(0,0)} \right|,
$$

with $E_{RES,ND}^{0,0}(0,0)$ referring to the RES energies obtained by Sahoo [25] and $E_{RES,ND}^{0,0}(0,0)$ denoting our results (43, 44).

In Fig. 5, we plot $\xi$ and $\delta$ as functions of $\alpha$ for 3D and 2D materials at $\eta = 0$. $\xi$ and $\delta$ are positive in the whole coupling regime, indicating that our GS and RES energies are smaller than those of Sahoo. It is well known that the Landau-Pekar method works well only in the strong-coupling regime, indeed $\xi$ and $\delta$ decrease monotonously with the increase of $\alpha$. At large $\alpha$, $E_{osc,ND}^{0,0}(0,0)$ and $E_{RES,ND}^{0,0}(0,0)$ are very close to our results, which demonstrates the reliability of our approach. These numerical results demonstrate that our results which are obtained by the LLP-H method give improved GS and RES energies compared to previous strong-coupling models [25]. Moreover, our results apply to the whole electron-phonon coupling regime which is due to the additional parameter $a$ in equation (8).

VI. CONCLUSIONS

We have extended the Huybrechts variational approach (LLP-H) to the analysis of bipolarons. By performing an average over the wavefunction of the relative motion of the two electrons, the ground and first excited-state energies of the bipolaron in two and three dimensions are obtained. Numerical results show that the RES energy is smaller than the FC state energy.

The energies we obtain are applicable to arbitrary values of the electron-phonon coupling constants. Our ground-state and RES energies are lower than the previously reported results from Landau-Pekar method [25], which is due to the use of a more appropriate relative wave function and the additional parameter $a$ in LLP-H method. Based on analytical and numerical results, we
FIG. 5: Relative deviation of our ground-state energy and Sahoo’s result ($\xi = \left( E_{osc}^{0, ND} (0, 0) - E_{BP}^{0, ND} \right) / \left| E_{osc}^{0, ND} (0, 0) \right|$) as a function of $\alpha$ for 3D and 2D materials at $\eta = 0$; Relative deviation of our RES energy and Sahoo’s result ($\delta = \left( E_{osc}^{RES, ND} (0, 0) - E_{BP}^{RES, ND} \right) / \left| E_{osc}^{RES, ND} (0, 0) \right|$) as a function of $\alpha$ for 3D and 2D materials at $\eta = 0$.

conclude that the best relative wavefunction is the oscillator-type function $\phi_{1}^{(o)}$ both for the ground state and the first excited state of the bipolaron. Our results could be of relevance for high-$T_c$ superconductors where bipolarons are expected to play an important role [6].

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