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Ground and Excited States of Bipolarons 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. The ground-state (GS) and excited-state energies of the Fröhlich bipolaron for the whole range of electron-phonon coupling constants can be obtained. The energies of the first relaxed excited state (RES) and Franck–Condon (FC) excited state of the bipolaron are also calculated. It is found that the first RES energy is lower than the FC state energy. The comparison of our GS and RES energies with those in literature is also given.*

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Key words: bipolaron, ground-state energy, excited-state energy, Lee-Low-Pines-Huybrechts variational method

1 Introduction

Bipolarons have been extensively discussed both for fundamental theoretical interest and for their importance in semiconductor materials.[1] With recent advances in the fabrication of nanocrystals and semiconductor nanostructures, strong electron-phonon coupling is realized due to quantum confinement effects, and the properties of bipolarons in low-dimensional systems are of growing interest.[2−6] This problem is also relevant to the proposal of the bipolaronic mechanism for electron pairing in the $\mathrm{CuO_2}$ plane in high-T_c cuprates.[1,7] Recently, Schoenes and co-workers[8] reported that some superconductors such as $\mathrm{YBa_2Cu_4O_8}$ have strong electron-phonon coupling, which also boosts the theoretical research on bipolarons.

Extensive work has already been devoted to the calculation of the bipolaron ground-state (GS) energy in two and three dimensions (an incomplete list is given in Refs. [9] ∼ [13]). Different values of the critical electron-phonon coupling constant α_c above which the bipolaron is stable and the critical ratio of dielectric constants η_c below which the bipolaron is stable are obtained by different approximation approaches. Though the bipolaronic GS state has been extensively investigated in the past decade, only a few works[14−17] have been devoted to the excited states so far. Actually knowledge of the excited states of the bipolaron is also important due to the relevance to electron transport, photoluminescence and photoemission.[1] Smondyrev *et al.*[14] calculated the energy spectra of the one-dimensional bipolaron in the strong-coupling limit. More recently, Sahoo[15] 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. The stability of magnetobipolarons was studied by Kandemir.[16] The system of excited terms of a bipolaron has been established by the method of canonical transformation of coordinate.[17]

In this paper we extend the Huybrechts variational approach (LLP-H)[18] to the analysis of both GS and excited states. Section 2 presents the calculation of GS state. In Sec. 3, we calculate the energies of the first relaxed excited state and Franck–Condon excited state in both two and three dimensions. Discussions of these two types of excited states are given. Finally, comparison of our results with Sahoo's ground-state and excited-state energies is made in Sec. 4. Our conclusions are presented in Sec. 5.

2 Ground-State Energy

The Fröhlich Hamiltonian for the polaron in N dimensions (ND) has been derived by Peeters *et al.*[19] Accordingly, the Hamiltonian describing a system of two electrons interacting with a longitudinal optical (LO) phonon field may be written as (in units of $m = \hbar = \omega_{\mathrm{LO}} = 1$)

$$H = \sum_{i=1,2}\Big[\frac{\boldsymbol{p}_i^2}{2} + \sum_{\boldsymbol{k}}(V_{\boldsymbol{k}} a_{\boldsymbol{k}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i} + \mathrm{h.c.})\Big] + \sum_{\boldsymbol{k}} a_{\boldsymbol{k}}^{\dagger} a_{\boldsymbol{k}} + U(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\,, \qquad (1)$$

where all vectors are N-dimensional ($N = 2, 3$) and $\boldsymbol{r}_i$ ($\boldsymbol{p}_i$) is the position (momentum) operator of the i-th electron ($i = 1, 2$). $a_{\boldsymbol{k}}^{\dagger}$ and $a_{\boldsymbol{k}}$ are respectively the creation and annihilation operators of the LO phonons with the wave vector $\boldsymbol{k}$. Here we should mention that the impurity-phonon interactions have already been eliminated so that

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we assume $\omega_{\boldsymbol{k}} = \omega_{\mathrm{LO}}$. The interaction coefficient is

$$V_{\boldsymbol{k}} = -\mathrm{i}\Big\{\frac{\Gamma[(N-1)/2]2^{N-3/2}\pi^{(N-1)/2}\alpha}{V_N k^{N-1}}\Big\}^{1/2}, \tag{2}$$

where V_N is the ND crystal volume, α is the dimensionless electron-phonon coupling constant,

$$\alpha = \frac{e^2}{\sqrt{2}}\Big(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\Big), \tag{3}$$

and ε_∞ (ε_0) is the high-frequency (static) dielectric constant of the medium. $U(\boldsymbol{r}) = U/r$ 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

$$U = \frac{\sqrt{2}\alpha}{1-\eta}, \quad \eta = \frac{\varepsilon_\infty}{\varepsilon_0}. \tag{4}$$

Since the bipolaron is a composite particle, it is convenient to introduce center-of-mass and relative coordinates and momenta, $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$, $\boldsymbol{P} = \boldsymbol{p}_1 + \boldsymbol{p}_2$, $\boldsymbol{r} = \boldsymbol{r}_1 - \boldsymbol{r}_2$, $\boldsymbol{p} = (\boldsymbol{p}_1 - \boldsymbol{p}_2)/2$,[20] in which the Hamiltonian can be rewritten as

$$\begin{aligned} H = {} & \frac{\boldsymbol{P}^2}{4} + 2\sum_{\boldsymbol{k}} \cos\Big(\frac{\boldsymbol{k}\cdot\boldsymbol{r}}{2}\Big)(V_{\boldsymbol{k}} a_{\boldsymbol{k}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} + \mathrm{h.c.}) \\ & + \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}} + \boldsymbol{p}^2 + \frac{U}{r}. \end{aligned} \tag{5}$$

To obtain variational estimate of the bipolaron energy, we set the oscillator-type trial wavefunction as

$$\phi^{(o)}(r) = Cr\exp\Big(-\frac{br^2}{4}\Big), \tag{6}$$

where b is a variational parameter. This trial wave function has been shown to be the best one in the estimate of GS in 2D and 3D bipolarons.[11] The next step is to average the Hamiltonian (5) over the wavefunction (6) and obtain the effective Hamiltonian for the center-of-mass motion,

$$H_{\mathrm{eff}} = \frac{\boldsymbol{P}^2}{4} + \sum_{\boldsymbol{k}}(B_{\boldsymbol{k}} a_{\boldsymbol{k}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}} + \mathrm{h.c.}) + \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}} + E_r. \tag{7}$$

Here $B_{\boldsymbol{k}} = 2V_{\boldsymbol{k}}\langle\cos(\boldsymbol{k}\cdot\boldsymbol{r}/2)\rangle$ and $E_r = \langle\,\boldsymbol{p}^2 + U/r\rangle$ with $\langle\cdots\rangle$ denoting an averaging over the wavefunction $\phi^{(o)}(r)$. $B_{\boldsymbol{k}}$ and E_r can be calculated as

$$\frac{B^{\mathrm{ND}}_{\boldsymbol{k}}}{2V_{\boldsymbol{k}}} = 1 - \frac{k^2}{4Nb}, \tag{8}$$

$$E^{3D}_r = \frac{7b}{12} + \frac{4}{3}\sqrt{\frac{b}{2\pi}}U, \quad E^{2D}_r = \frac{b}{2} + \frac{\sqrt{2b\pi}}{4}U. \tag{9}$$

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 $B_{\boldsymbol{k}}$ is renormalized.

We will follow the LLP-H variational method proposed by Huybrechts[18] for the single polaron problem. First, we perform the following LLP-H transformation,

$$U = \exp\Big(-\mathrm{i}a\sum_{\boldsymbol{k}} \boldsymbol{k}\cdot\boldsymbol{R} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}}\Big), \tag{10}$$

where a is a variational 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. The Hamiltonian (7) can be transformed into

$$H_{\mathrm{eff}} = \frac{1}{4}\Big(\boldsymbol{P} - a\sum_{\boldsymbol{k}} \boldsymbol{k} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}}\Big)^2 + \sum_{\boldsymbol{k}}\{B^*_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} \exp[-\mathrm{i}(1-a)\boldsymbol{k}\cdot R] + \mathrm{h.c.}\} + \sum_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}} + E_r. \tag{11}$$

For convenience we write the Hamiltonian (11) in the following more detailed form:

$$\begin{aligned} H_{\mathrm{eff}} = {} & \frac{1}{4}\boldsymbol{P}^2 - \frac{a}{2}\sum_{\boldsymbol{k}} \boldsymbol{P}\cdot\boldsymbol{k} a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}} + \sum_{\boldsymbol{k}}\Big(1 + \frac{a^2k^2}{4}\Big)a^\dagger_{\boldsymbol{k}} a_{\boldsymbol{k}} + \sum_{\boldsymbol{k}}\{B^*_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} \exp[-\mathrm{i}(1-a)\boldsymbol{k}\cdot\boldsymbol{R}] + \mathrm{h.c.}\} \\ & + E_r + \frac{a^2}{4}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2} \boldsymbol{k}_1\cdot\boldsymbol{k}_2 a^\dagger_{\boldsymbol{k}_1} a^\dagger_{\boldsymbol{k}_2} a_{\boldsymbol{k}_1} a_{\boldsymbol{k}_2}. \end{aligned} \tag{12}$$

The trial wave function in the new representation is assumed to take the following form,

$$|\cdots\rangle = \phi(R)|A\rangle, \tag{13}$$

where the wave function of the electron part is chosen as the following Gaussian type,

$$\phi_0(R) = c\exp\Big(-\lambda\sum_j R^2_j\Big), \tag{14}$$

with λ being a variational parameter to be determined. $|A\rangle$ is the phonon coherent state,

$$|A\rangle = \exp\Big[\sum_{\boldsymbol{k}}(f_{\boldsymbol{k}} a^\dagger_{\boldsymbol{k}} - f^*_{\boldsymbol{k}} a_{\boldsymbol{k}})\Big]|0\rangle, \tag{15}$$

here $f_{\boldsymbol{k}}$ and $f^*_{\boldsymbol{k}}$ are assumed to be a function of k only and to be determined variationally, $|0\rangle$ is the unperturbed zero phonon state satisfying $a_{\boldsymbol{k}}|0\rangle = 0$ for all k.

In the next step, we average the Hamiltonian (12) over the wave function (13) and directly present the bipolaron ground-state energy $E_{\rm BP}^{0,\rm ND}$ as

$$E_{\rm BP}^{0,\rm ND} = \frac{N}{4}\lambda - \frac{a}{2}\sum_{\boldsymbol{k}} \boldsymbol{P}\cdot\boldsymbol{k} f_{\boldsymbol{k}}^* f_{\boldsymbol{k}} + \sum_k \Big(1+\frac{a^2k^2}{4}\Big)|f_k|^2 + \sum_k \Big\{ B_{\boldsymbol{k}}^* f_{\boldsymbol{k}}^* \exp\Big[-\frac{(1-a)^2k^2}{8\lambda}\Big] + \text{h.c.}\Big\} + E_r + \frac{a^2}{4}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2} \boldsymbol{k}_1\cdot\boldsymbol{k}_2 f_{\boldsymbol{k}_1}^* f_{\boldsymbol{k}_2}^* f_{\boldsymbol{k}_1} f_{\boldsymbol{k}_2}\,. \tag{16}$$

It can be noticed that the $\boldsymbol{P}\cdot\boldsymbol{k}$ term and the last term in $E_{\rm BP}^{0,\rm ND}$ vanish exactly if we perform the angular integration first. Therefore the neglect of these terms in the Hamiltonian (16) does not violate the variational principle. Minimizing $E_{\rm BP}^{0,\rm ND}$ with respect to $f_{\boldsymbol{k}}$ and $f_{\boldsymbol{k}}^*$ yields

$$f_k = \frac{-B_{\boldsymbol{k}}^* \exp[-(1-a)^2k^2/(8\lambda)]}{1+a^2k^2/4}\,, \tag{17}$$

$$f_k^* = \frac{-B_{\boldsymbol{k}} \exp[-(1-a)^2k^2/(8\lambda)]}{1+a^2k^2/4}\,. \tag{18}$$

Using Eqs. (17) and (18), in Eq. (16) we obtain the ground-state energy of the bipolaron in N dimensions with an arbitrary electron-phonon coupling constant:

$$E_{\rm BP}^{0,\rm ND} = \frac{N}{4}\lambda - \sum_k B_{\boldsymbol{k}}^2 \frac{\exp[-(1-a)^2k^2/(4\lambda)]}{1+a^2k^2/4} + E_r\,. \tag{19}$$

Finally we calculate the ground-state energies of the bipolaron in 3D and 2D materials as follows:

$$E_{\rm BP}^{0,\rm 3D} = \frac{3\lambda}{4} - \frac{4\sqrt{2}\alpha}{\pi}\int_0^\infty {\rm d}k\Big(1-\frac{k^2}{6b}+\frac{k^4}{144b^2}\Big) \times \frac{\exp(-gk^2)}{1+a^2k^2/4} + \frac{7b}{12} + \frac{4}{3}\sqrt{\frac{b}{2\pi}}U\,, \tag{20}$$

$$E_{\rm BP}^{0,\rm 2D} = \frac{\lambda}{2} - 2\sqrt{2}\alpha\int_0^\infty {\rm d}k\Big(1-\frac{k^2}{4b}+\frac{k^4}{64b^2}\Big) \times \frac{\exp(-gk^2)}{1+a^2k^2/4} + \frac{b}{2} + \frac{\sqrt{2b\pi}}{4}U \tag{21}$$

with

$$g = \frac{1}{4b} + \frac{(1-a)^2}{4\lambda}\,. \tag{22}$$

Thus the ground-state energy of this system can be obtained by minimizing Eqs. (20) and (21) with respect to a, b, and λ. Although one can further integrate the k variable analytically on the right-hand side of Eqs. (20) and (21) and get a very complicated form including the complementary error function ${\rm erf}\,c(x)$, which is of no use for practical calculations.

3 Internal Excited-State Energy

Following the definition given by Devreese,[21] 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 an FC state.

Here we use a method of Huybrechts,[18] who computed the FC state energy[22] of a single polaron. In this section, we will extend Huybrechts method to calculate the RES energy of the bipolaron by adjusting a, b, λ, and f_k to the relaxed excited state.

The wavefunction of the electron part for the first excited state is N-fold degenerate,

$$\phi_1(R) = cR_j \exp\Big(-\lambda\sum_j R_j^2\Big)\,. \tag{23}$$

By Eqs. (23) and (15) the Hamiltonian (12) can be calculated as

$$E_{\rm BP}^{1,\rm ND} = \frac{\lambda}{2} + \frac{N}{4}\lambda - \frac{a}{2}\sum_{\boldsymbol{k}} \boldsymbol{P}\cdot\boldsymbol{k} f_{\boldsymbol{k}}^* f_{\boldsymbol{k}} + \sum_{\boldsymbol{k}} \Big(1+\frac{a^2k^2}{4}\Big)|f_k|^2 + \sum_{\boldsymbol{k}} \Big\{ B_{\boldsymbol{k}}{}^* f_{\boldsymbol{k}}^* \exp\Big[-\frac{(1-a)^2k^2}{8\lambda}\Big]\Big[1-(1-a)^2\frac{k_j^2}{4\lambda}\Big] + \text{h.c.}\Big\} + E_r + \frac{a^2}{4}\sum_{\boldsymbol{k}_1,\boldsymbol{k}_2} \boldsymbol{k}_1\cdot\boldsymbol{k}_2 f_{\boldsymbol{k}_1}^* f_{\boldsymbol{k}_2}^* f_{\boldsymbol{k}_1} f_{\boldsymbol{k}_2}\,. \tag{24}$$

The $\boldsymbol{P}\cdot\boldsymbol{k}$ term and the last term in $E_{\rm BP}^{1,\rm ND}$ also vanish exactly if performing the angular integration. For the FC state, $f_{\boldsymbol{k}}$ and $f_{\boldsymbol{k}}^*$ in $E_{\rm BP}^{1,\rm ND}$ is the same as that in Eqs. (17) and (18). For the RES, $f_{\boldsymbol{k}}$ and $f_{\boldsymbol{k}}^*$ can be obtained by minimizing the excited-state energy according to

$$\frac{\partial E_{\rm BP}^{1,\rm ND}}{\partial f_k^*} = 0\,, \quad \frac{\partial E_{\rm BP}^{1,\rm ND}}{\partial f_k} = 0\,. \tag{25}$$

Then we get the excited-state energy $E_{\rm BP}^{1,\rm ND}$ for the bipolaron in N dimensions,

$$E_{\rm BP}^{1,\rm ND} = \frac{\lambda}{2} + \frac{N\lambda}{4} + \sum_k \Big(1+\frac{a^2k^2}{4}\Big)|f_k|^2 + \sum_{\boldsymbol{k}} \Big\{ B_{\boldsymbol{k}}^* f_{\boldsymbol{k}}^* \Big[1-\frac{(1-a)^2k_j^2}{4\lambda}\Big] \exp\Big[-\frac{(1-a)^2k^2}{8\lambda}\Big] + \text{h.c.}\Big\} + E_r\,, \tag{26}$$

with

$$f_{\boldsymbol{k}}^{\rm FC} = \frac{-B_{\boldsymbol{k}}^{*}\exp[-(1-a)^2k^2/(8\lambda)]}{1+a^2k^2/4} \tag{27}$$

for the FC state and

$$f_{\boldsymbol{k}}^{\rm RES} = \frac{-B_{\boldsymbol{k}}^{*}\exp[-(1-a)^2k^2/(8\lambda)]}{1+a^2k^2/4}\Big[1-\frac{(1-a)^2k_j^2}{4\lambda}\Big] \tag{28}$$

for the RES.

The energy of the relative motion can be obtained by Eqs. (8) and (9) and insert $f_{\boldsymbol{k}}^{\rm FC}$ and $f_{\boldsymbol{k}}^{\rm RES}$ into Eq. (26). Finally we obtain the FC state and RES energies of the bipolaron in 3D and 2D, respectively,

$$E_{\rm BP}^{\rm FC,3D} = \frac{5\lambda}{4}+\frac{7b}{12}+\frac{4}{3}\sqrt{\frac{b}{2\pi}}U-\frac{4\sqrt{2}\alpha}{\pi}\int_0^\infty {\rm d}k\Big(1-\frac{k^2}{6b}+\frac{k^4}{144b^2}\Big)\frac{\exp(-gk^2)}{1+a^2k^2/4}\Big[1-\frac{(1-a)^2k^2}{12\lambda}\Big]\,, \tag{29}$$

$$E_{\rm BP}^{\rm FC,2D} = \lambda+\frac{b}{2}+\frac{\sqrt{2b\pi}}{4}U-2\sqrt{2}\alpha\int_0^\infty {\rm d}k\Big(1-\frac{k^2}{4b}+\frac{k^4}{64b^2}\Big)\frac{\exp(-gk^2)}{1+a^2k^2/4}\Big[1-\frac{(1-a)^2k^2}{8\lambda}\Big]\,, \tag{30}$$

$$E_{\rm BP}^{\rm RES,3D} = \frac{5\lambda}{4}+\frac{7b}{12}+\frac{4}{3}\sqrt{\frac{b}{2\pi}}U-\frac{4\sqrt{2}\alpha}{\pi}\int_0^\infty {\rm d}k\Big(1-\frac{k^2}{6b}+\frac{k^4}{144b^2}\Big)\frac{\exp(-gk^2)}{1+a^2k^2/4}\Big[1-\frac{(1-a)^2k^2}{6\lambda}+\frac{(1-a)^4k^4}{80\lambda^2}\Big]\,, \tag{31}$$

$$E_{\rm BP}^{\rm RES,2D} = \lambda+\frac{b}{2}+\frac{\sqrt{2b\pi}}{4}U-2\sqrt{2}\alpha\int_0^\infty {\rm d}k\Big(1-\frac{k^2}{4b}+\frac{k^4}{64b^2}\Big)\frac{\exp(-gk^2)}{1+a^2k^2/4}\Big[1-\frac{(1-a)^2k^2}{4\lambda}+\frac{3(1-a)^4k^4}{128\lambda^2}\Big]\,. \tag{32}$$

For the FC state, the values of the parameters a, b, and λ are taken from the calculation of the ground state energy $E_{\rm BP}^{0,\rm ND}$. For the RES, the values of the parameters λ, a, and b are obtained by minimizing the excited-state energy $E_{\rm BP}^{\rm RES,ND}$ of Eqs. (31) and (32) through numerical calculation.

In Figs. 1(a) and 1(b), the ground-state energy ($E_{\rm BP}^{0,\rm ND}$), first RES energy ($E_{\rm BP}^{\rm RES,ND}$), and FC state energy ($E_{\rm BP}^{\rm FC,ND}$) of the bipolaron are displayed as functions of the electron-phonon coupling constants for 3D and 2D materials. Comparing the energy of two single polarons by LLP-H method, we find the bipolaron is stable when $\alpha \geq 6.3$ (2.9) in three and two dimensions. We start from $\alpha = 6.3$ (2.9) in Figs. 1(a) and 1(b) for 3D and 2D bipolarons. We find that in the whole range of electron-phonon coupling constants, the FC state and RES energies are negative. The difference in energy, $\Delta E^{\rm ND} = E_{\rm BP}^{1,\rm ND} - E_{\rm BP}^{0,\rm ND}$, yields the excitation energy, which is related to optical absorption of bipolarons in semiconductor materials.[1,23]

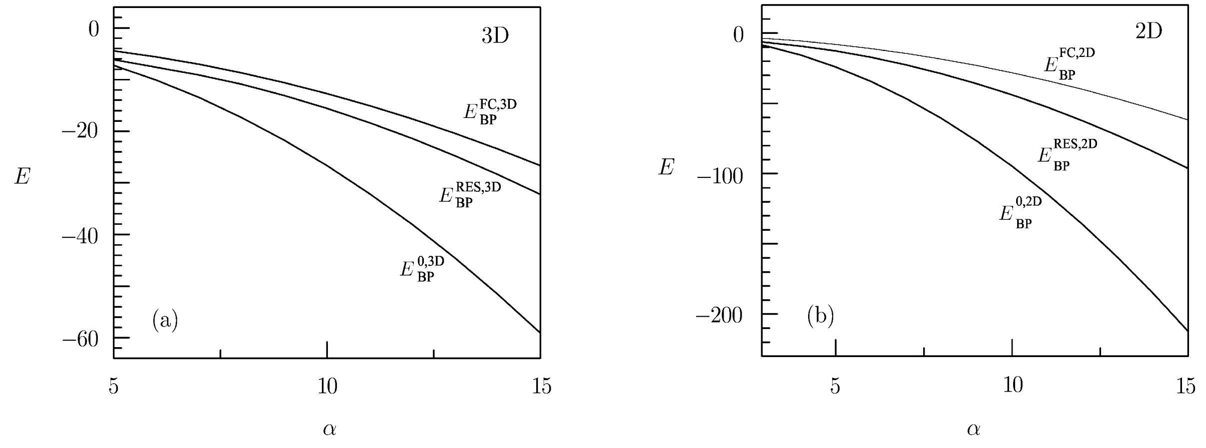

Fig. 1 (a) Ground-state energy ($E_{\rm BP}^{0,3\rm D}$), first RES energy ($E_{\rm BP}^{\rm RES,3D}$), and FC state energy ($E_{\rm BP}^{\rm FC,3D}$) of the bipolaron are displayed as functions of the electron-phonon coupling constants for 3D materials. The bipolaron is stable for $\alpha \geq \alpha_c^{3D} = 6.3$ at $\eta = 0.0$. (b) Ground-state energy ($E_{\rm BP}^{0,2\rm D}$), first RES energy ($E_{\rm BP}^{\rm RES,2D}$), and FC state energy ($E_{\rm BP}^{\rm FC,2D}$) of the bipolaron are displayed as functions of the electron-phonon coupling constants for 2D materials. The bipolaron is stable for $\alpha \geq \alpha_c^{2D} = 2.9$ at $\eta = 0.0$.

As shown in Figs. 1(a) and 1(b), we find that the RES energy is always lower than the FC state energy. This is well known from absorption spectrum calculations.[21,24,25] 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.

4 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,[15] who adopted the wavefunction $\phi_0^{(o)}(r)$ $(C\exp(-br^2/4))$ for relative coordinates and developed a Landau–Pekar variational method to get the ground-state and RES energies of the Fröhlich bipolaron in the strong-coupling limit. To perform a comparison with our results, we define the relative deviation $\xi = (E_s^{0,\mathrm{ND}} - E_{\mathrm{BP}}^{0,\mathrm{ND}})/|E_s^{0,\mathrm{ND}}|$, with $E_s^{0,\mathrm{ND}}$ referring to the GS energies obtained by Sahoo[15] and $E_{\mathrm{BP}}^{0,\mathrm{ND}}$ given by Eqs. (20) and (21). Also, we define $\delta = (E_s^{\mathrm{RES,ND}} - E_{\mathrm{BP}}^{\mathrm{RES,ND}})/|E_s^{\mathrm{RES,ND}}|$, $E_s^{\mathrm{RES,ND}}$ referring to the RES energies obtained by Sahoo[15] and $E_{\mathrm{BP}}^{\mathrm{RES,ND}}$ denoting our results (31) and (32).

In Fig. 2, we plot ξ and δ as functions of α for 3D and 2D materials at $\eta = 0$. ξ and δ are positive in the whole coupling regime, demonstrating that our GS and RES energies are smaller than those by Sahoo. It is well known that the Landau–Pekar method works well only in the strong-coupling regime, indeed ξ and δ decrease monotonously with the increase of α. $E_s^{0,\mathrm{ND}}$ and $E_{\mathrm{BP}}^{\mathrm{RES,ND}}$ are very close to our results at large α, which demonstrates the reliability of our approach. It is shown that the present approach can give better results for GS and RES energies, comparing with previous strong-coupling models.[15]

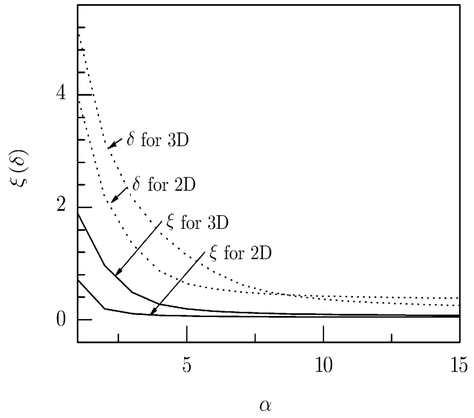

Fig. 2 Relative deviation of our ground-state energy and Sahoo's result ($\xi = (E_s^{0,\mathrm{ND}} - E_{\mathrm{BP}}^{0,\mathrm{ND}})/|E_s^{0,\mathrm{ND}}|$) as a function of α for 3D and 2D materials at $\eta = 0.0$. Relative deviation of our RES energy and Sahoo's result ($\delta = (E_s^{\mathrm{RES,ND}} - E_{\mathrm{BP}}^{\mathrm{RES,ND}})/|E_s^{\mathrm{RES,ND}}|$) as a function of α for 3D and 2D materials at $\eta = 0.0$.

5 Conclusions

We have extended the Huybrechts variational approach (LLP-H) to the analysis of the properties of bipolarons. By averaging 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 lower than the FC state energy.

Our ground-state and RES energies are lower than the previously reported results from Landau–Pekar method,[15] which is due to the use of a more appropriate relative wave function and the additional parameter a in LLP-H method. Our results may be of relevance for high-T_c superconductors where bipolarons are expected to play an important role.[7]

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