Ground and excited states of the Fröhlich bipolaron in a multidimensional system

Satyabrata Sahoo*
Department of Physics, Raidighi College, Raidighi, South 24-Parganas, Pin Code 743383, WB, India
(Received 6 November 1998; revised manuscript received 7 June 1999)

A variational calculation is performed to obtain the ground state and the first excited state of the Fröhlich bipolaron in a multidimensional polar crystal. Numerical and analytical results are derived for the ground state and the first excited state. Results for the excitation energy are discussed with reference to the spectroscopic absorption data in the oxide superconductors. [S0163-1829(99)10139-5]

The study of the bipolaron has long been of general interest both for academic reasons and for its importance in semiconductor technology. In 1975 Anderson[1] advocated the bipolaron concept in negative U centers to study the electronic properties of the amorphous semiconductor. Lakkis *et al.*[2] extended the idea of Anderson to propose intersite bipolarons to explain the mechanism of two successive metal-insulator transitions in titanium oxide (Ti_4O_7). But perhaps the greatest impetus to the renewed interest in the bipolaron came from its possible connection with the high T_c superconductivity, where singlet bipolarons, such as bosons in Bose condensation, have been conjectured as a possible mechanism for high T_c superconductivity.[3–6] However, all these important developments do not help to resolve the question of the first-principles existence of bipolarons in a solid. This probably sparked the recent state of interest in the study of the stability of a bipolaron. Regarding the question of the stability of the bipolaron, a general concensus, however, seems to be lacking; the majority of workers[7–16] have maintained that the Fröhlich bipolaron can indeed exist in polar crystals, provided that certain conditions are satisfied by the material parameters. Nevertheless, despite these developments, the Fröhlich bipolaron is far from completely solved. It may be remarked that the excited states of the bipolaron have so far been studied less. Though the stability of the bipolaron has been predicted by a majority of authors addressing this problem, the experimental evidence of the bipolaron still remains controversial. Several key investigations on the optical properties of the oxide superconductors have been performed by Herr *et al.*[17] and many other groups.[18–20] The mid-ir feature observed on spectroscopic data has been interpreted by different groups in different ways. Some of them have tentatively ascribed it to a photo-induced electronic transition from polarons or bipolarons.[19,20] Knowledge of the excited states of the bipolaron is thus required for the interpretation of spectroscopic absorption data in the oxide superconductors if they are assumed to be the charge carrier in the relevant materials. In the framework of the intensively developing bipolaron theory there has been a recent analysis[21] of the optical absorption spectrum of large bipolarons in the presence and absence of the magnetic field. The peculiarities of the absorption spectrum of the bipolaron as a function of the electromagnetic field are attributed to the transitions involving scattering states or internal excited states of the bipolaron. But much less is known so far about the excited states of the bipolaron, though there has been a recent interest in this topic due the possible role they play in material revealing high T_c superconductivity. The energy spectrum of the two-dimensional large bipolaron is investigated in the high magnetic field in the framework of the adiabatic theory by Fomin and Devreese.[22] More recently, Smondyrev and co-workers[23] reported the energy spectrum of the one-dimensional bipolaron in the strong-coupling limit. It is of urgent experimental relevance, as well as academic interest, to investigate the complex energy spectrum of the large bipolaron.

In the present paper we suitably develop the Landau-Pekar variational method to get an approximation to the energy of the ground state and the first excited state of the Fröhlich bipolaron in a multidimensional ionic crystal in the strong-coupling limit, and compare our result for the excitation energy from the ground state to the first excited state with the value estimated from the optical absorption data in the oxide superconductors.

The Fröhlich Hamiltonian for the polaron in N dimensions is generalized by Peeters, Xiaoguang, and Devreese.[24] Accordingly, the relevant Hamiltonian for the case of two electrons in the N-dimensional (ND) polar crystal consists of the kinetic energies of two electrons, their interactions with the optical modes of the ionic lattice, and the screened Coulomb repulsion between them. Assuming the phonon frequency to be dispersionless, the Hamiltonian for the ND Fröhlich bipolaron may be written as

$$\tilde{H} = -\frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}'_1} - \frac{\hbar^2}{2m}\nabla^2_{\mathbf{r}'_2} + \frac{e^2}{\epsilon_\infty|\mathbf{r}'_1-\mathbf{r}'_2|} + \hbar\omega\sum_{\mathbf{q}'} b^\dagger_{\mathbf{q}'}b_{\mathbf{q}'} + \sum_{i=1}^{2}\sum_{\mathbf{q}'}[\tilde{\xi}_{\mathbf{q}'}e^{-i\mathbf{q}'\cdot\mathbf{r}'_i}b^\dagger_{\mathbf{q}'} + \text{H.c.}], \quad (1)$$

where all vectors are N-dimensional, $\mathbf{r}'_1, \mathbf{r}'_2$ being the position vectors of the electrons and m their band effective mass. ϵ_∞ is the high-frequency dielectric constant of the medium. ω is the longitudinal optical phonon frequency. $b^\dagger_{\mathbf{q}'}(b_{\mathbf{q}'})$ is the creation (annihilation) operator for a phonon of wave vector $\mathbf{q}'$. $\tilde{\xi}_{\mathbf{q}'}$ is the electron phonon interaction coefficient. The explicit form of the interaction coefficient in N dimensions has been derived in Ref. 24.

If the two electrons are capable of forming a bipolaron, the obvious dynamical variables are the relative and center-of-mass (c.m.) coordinates defined by

$$\boldsymbol{\rho}' = \mathbf{r}_1' - \mathbf{r}_2', \tag{2}$$

$$\mathbf{R}' = \frac{(\mathbf{r}_1' + \mathbf{r}_2')}{2}, \tag{3}$$

in terms of which the Hamiltonian (1) reads

$$\tilde{H} = -\frac{\hbar^2}{2\mu}\nabla_{\boldsymbol{\rho}'}^2 - \frac{\hbar^2}{2M}\nabla_{\mathbf{R}'}^2 + \frac{e^2}{\epsilon_\infty \rho'} + \hbar\omega \sum_{\mathbf{q}'} b_{\mathbf{q}'}^\dagger b_{\mathbf{q}'} + \sum_{\mathbf{q}'} [\tilde{\xi}_{\mathbf{q}'}\{e^{-i\mathbf{q}'\cdot(\mathbf{R}'+\boldsymbol{\rho}'/2)} + e^{-i\mathbf{q}'\cdot(\mathbf{R}'-\boldsymbol{\rho}'/2)}\} b_{\mathbf{q}'}^\dagger + \text{H.c.}], \tag{4}$$

where μ is the reduced mass ($\mu = m/2$) and M is the total mass ($M = 2m$).

Following Huybrechts[25] we introduce creation and annhilation operators $a_j^\dagger$ and a_j by

$$-\imath\hbar\nabla_{\mathbf{R}_j'} = \left(\frac{M\hbar\lambda}{2}\right)^{1/2}(a_j^\dagger + a_j), \tag{5}$$

$$\mathbf{R}_j' = \imath\left(\frac{\hbar}{2M\lambda}\right)^{1/2}(a_j - a_j^\dagger), \tag{6}$$

where the index j refers to the x,y,z directions and λ is a parameter to be determined presently.

Then rewriting the Hamiltonian, one gets

$$\tilde{H} = -\frac{\hbar^2}{2\mu}\nabla_{\boldsymbol{\rho}'}^2 + \frac{\hbar\lambda}{2}\left(\sum_j a_j^\dagger a_j + \frac{3}{2}\right) + \frac{\hbar\lambda}{4}\sum_j (a_j^\dagger a_j^\dagger + a_j a_j) + \frac{e^2}{\epsilon_\infty \rho'} + \hbar\omega\sum_{\mathbf{q}'} b_{\mathbf{q}'}^+ b_{\mathbf{q}'} + \sum_{\mathbf{q}'}\left\{2\tilde{\xi}_{\mathbf{q}'}\cos\left(\frac{\mathbf{q}'}{2}\cdot\boldsymbol{\rho}'\right) b_{\mathbf{q}'}^\dagger \exp\left(-\frac{\hbar q'^2}{4M\lambda}\right) \times \exp\left[-\left(\frac{\hbar}{2M\lambda}\right)^{1/2}\sum_j q_j' a_j^\dagger\right]\exp\left\{\left(\frac{\hbar}{2M\lambda}\right)^{1/2}\sum_j q_j' a_j\right\} + \text{H.c.}\right\}. \tag{7}$$

Introducing Fröhlich units [energy is scaled by $\hbar\omega$ and length by $(\hbar/2m\omega)^{1/2}$], the Hamiltonian becomes

$$\bar{H} = -2\nabla_{\boldsymbol{\rho}}^2 + \frac{\lambda}{2\omega}\left(\sum_j a_j^\dagger a_j + \frac{3}{2}\right) + \frac{\lambda}{4\omega}\sum_j (a_j^\dagger a_j^\dagger + a_j a_j) + \frac{\beta}{\rho} + \sum_{\mathbf{q}} b_{\mathbf{q}}^+ b_{\mathbf{q}} + \sum_{\mathbf{q}}\left\{\xi_{\mathbf{q}} b_{\mathbf{q}}^\dagger \exp\left(-\frac{\omega q^2}{4\lambda}\right) \times \exp\left[-\left(\frac{\omega}{2\lambda}\right)^{1/2}\sum_j q_j a_j^\dagger\right]\exp\left[\left(\frac{\omega}{2\lambda}\right)^{1/2}\sum_j q_j a_j\right] + \text{H.c.}\right\}, \tag{8}$$

where $\bar{H} = \tilde{H}/\hbar\omega$, $\boldsymbol{\rho} = \boldsymbol{\rho}'(2m\omega/\hbar)^{1/2}$, $\mathbf{q} = \mathbf{q}'(\hbar/2m\omega)^{1/2}$, $\beta = (e^2/\hbar\omega\epsilon_\infty)/(\hbar/2m\omega)^{1/2}$,

$$\xi_{\mathbf{q}} = -2i\left(\frac{\Gamma\left(\frac{N-1}{2}\right)2^{N-1}\pi^{(N-1)/2}}{Vq^{N-1}}\alpha\right)^{1/2}\cos\left(\frac{\mathbf{q}}{2}\cdot\boldsymbol{\rho}\right),$$

V is the volume of the ND crystal, and α is the electron phonon coupling constant that depends on the dimensionality of the system. In three dimensions (3D) α is given by

$$\alpha = \frac{e^2}{\hbar\omega}\left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_o}\right]\left(\frac{2m\omega}{\hbar}\right)^{1/2}, \tag{9}$$

while in 2D it takes the following expression:

$$\alpha = \frac{e^2}{\hbar\omega}(E_o - E_\infty)\left(\frac{2m\omega}{\hbar}\right)^{1/2}, \tag{10}$$

where $E_0 = (\epsilon_0 - 1)/(\epsilon_0 + 1)$, $E_\infty = (\epsilon_\infty - 1)/(\epsilon_\infty + 1)$, and ϵ_0 is the static dielectric constant of the medium.

Now performing the unitary transformation

$$U = \exp\sum_{\mathbf{q}} [f_{\mathbf{q}} b_{\mathbf{q}}^\dagger - \text{H.c.}] \tag{11}$$

with $f_{\mathbf{q}}$'s as variational functions, one gets

$$H = -2\nabla_{\boldsymbol{\rho}}^2 + \frac{\overline{\lambda^2}}{2}\left(\sum_j a_j^\dagger a_j + \frac{3}{2}\right) + \frac{\overline{\lambda^2}}{4}\sum_j (a_j^\dagger a_j^\dagger + a_j a_j) + \frac{\beta}{\rho} + \sum_{\mathbf{q}} (b_{\mathbf{q}}^\dagger + f_{\mathbf{q}})(b_{\mathbf{q}} + f_{\mathbf{q}}) + \sum_{\mathbf{q}}\left\{b_{\mathbf{q}}^\dagger(\overline{\xi}_{\mathbf{q}} + f_{\mathbf{q}}) \times \exp\left[-\left(\frac{1}{\sqrt{2\overline{\lambda}}}\right)\sum_j q_j a_j^\dagger\right]\exp\left[\left(\frac{1}{\sqrt{2\overline{\lambda}}}\right)\sum_j q_j a_j\right] + \text{H.c.}\right\}, \tag{12}$$

where

$$\overline{\xi}_{\mathbf{q}} = \xi_{\mathbf{q}}\exp\left(-\frac{q^2}{4\overline{\lambda^2}}\right) \tag{13}$$

and

$$\overline{\lambda} = \left(\frac{\lambda}{\omega}\right)^{1/2}. \tag{14}$$

Determining the ground state $\psi_0 = \phi_0(\boldsymbol{\rho})|0\rangle$ in the new representation[25] by

$$a_j|0\rangle = b_{\mathbf{q}}|0\rangle = 0, \tag{15}$$

one gets for the energy E_0 for the ground state

$$E_0 = -2\langle\phi_0|\nabla_{\boldsymbol{\rho}}^2|\phi_0\rangle + \left\langle\phi_0\left|\frac{\beta}{\rho}\right|\phi_0\right\rangle + 3\frac{\overline{\lambda^2}}{4} + \sum_{\mathbf{q}}|f_{\mathbf{q}}|^2 + \sum_{\mathbf{q}}(\overline{\xi}_{\mathbf{q}} f_{\mathbf{q}}^* + \text{H.c.}). \tag{16}$$

By such a choice of the averaging state, one takes account of those terms of the Hamiltonian describing the recoil energy

TABLE I. Binding energy (BE) (in units of $\alpha^2\hbar\omega$) of the bipolaron for several values of η as obtained from the present calculation compared to the variational results of Bassani *et al.* [12]

η	BE (ours)	BE (Bassani *et al.*)
0.000	0.0314	0.0314
0.035	0.0177	0.0177
0.070	0.0035	0.0035

of the bipolaron. The function $f_{\boldsymbol{q}}$ and $\overline{\lambda}$ have to be obtained by a variational calculation of the ground-state energy. The result for the ground-state energy will be compared with the existing theory in order to test the approximation made by Eq. (15).

Now from the variational principle we obtain

$$f_{\boldsymbol{q}} = -\overline{\xi_{\boldsymbol{q}}} \tag{17}$$

and the following expression for the ground-state energy:

$$E_0 = -2\langle \phi_0 | \nabla_{\boldsymbol{\rho}}^2 | \phi_0 \rangle + \left\langle \phi_0 \left| \frac{\beta}{\rho} \right| \phi_0 \right\rangle + 3\frac{\overline{\lambda}^2}{4} - \sum_{\boldsymbol{q}} |\overline{\xi_{\boldsymbol{q}}}|^2. \tag{18}$$

We choose the electron ground-state trial wave function

$$|\phi_0\rangle = \left(\frac{\kappa}{\sqrt{\pi}} \right)^{N/2} e^{-\kappa^2 \rho^2/2}, \tag{19}$$

where κ is a variational parameter.

It then follows

$$E_0 = N\kappa^2 + \kappa\beta \frac{\Gamma\left(\frac{N-1}{2}\right)}{\Gamma\left(\frac{N}{2}\right)} - 4\sqrt{2}\alpha\kappa \frac{t}{\sqrt{1+t^2}} \frac{\Gamma\left(\frac{N-1}{2}\right)}{\Gamma\left(\frac{N}{2}\right)} + N\kappa^2 t^2, \tag{20}$$

where

$$t = \frac{\overline{\lambda}}{2\kappa}. \tag{21}$$

Now the minimum of E_0 with respect to the appropriate variational parameters κ and t would give the ground-state energy. In order to test the validity of the model developed above we compare our result for the ground-state energy with that of Bassani *et al.* (Table I). We can say that the model that is presented here provides a good approximation for the calculation of the binding energy of the bipolaron. Compared to Adamowskii[10] and others[26] the binding energy of the bipolaron turns out to be of smaller magnitude in our approach. This is because, apart from the difference in approximation, we have considered the free motion of the center of mass, while in the case of Adamowskii and others the bipolaron is intrinsically immobile. Therefore a large part of the binding energy in their case comes from the localization energy. Since we are interested only in mobile bipolarons with their possible connection in high T_c superconductivity, we have not considered this possible source of binding energy. In Table II we give the binding energy of 2D bipolarons in the present approach. It can be observed that the results are consistent with the others.[11,12] The change in dimensionality increases the binding energy of the bipolaron, thus making the pair formation a much more realistic process. Furthermore, the simple structure of the Hamiltonian and the ground state makes it possible to elaborate the energy of the excited states of the bipolaron where the electrons are assumed to be excited into higher levels in the potential well together with the readaptation of the ionic polarization to the new electronic configuration. This means that the potential used to describe the excited state is relaxed with respect to the initial potential built by the phonon field. These types of excited states can be treated by the Landau-Pekar wave function.

TABLE II. Excitation energy (Δ) and binding energy (BE) (in units of $\alpha^2\hbar\omega$) of the 3D bipolaron for several values of η as obtained from the present calculation.

η	Δ	BE
0.00	0.0615	0.0314
0.02	0.0640	0.0236
0.04	0.0665	0.0157
0.06	0.0690	0.0076

In order to get a first approximation to the energy of the first internal excited state we choose the first excited state

$$\psi_1 = \phi_0(\boldsymbol{\rho})|1\rangle, \tag{22}$$

where

$$|1\rangle = a_j^\dagger |0\rangle \tag{23}$$

and the energy of the first excited state becomes

$$E_1 = N\kappa^2 + \kappa\beta \frac{\Gamma\left(\frac{N-1}{2}\right)}{\Gamma\left(\frac{N}{2}\right)} - 4\sqrt{2}\alpha\kappa \frac{t}{\sqrt{1+t^2}} \frac{\Gamma\left(\frac{N-1}{2}\right)}{\Gamma\left(\frac{N}{2}\right)} \times \left\{ 1 - \frac{1}{N(1+t^2)} + \frac{3}{4N^2(1+t^2)^2} \right\} + (N+2)\kappa^2 t^2. \tag{24}$$

Thus we calculate the energy of the first excited state E_1 in the same model potential we used in determining the self-energy of the bipolaron. Using the same idea as that developed in the study of the absorption coefficient of continuum polarons,[27] that the polaron absorption spectrum is dominated by a sharp peak from the ground state to the first internal excited state, one can also understand and characterize the peaks observed in high T_c materials, and from this work on the optical properties one can estimate the difference in energy between the first excited state and the ground state.

In Tables II and III we collect our result for the excitation energy ($\Delta = E_1 - E_0$) along with the binding energy ($E_B = 2E_p - E_0$; E_p is the ground-state energy of the single polaron) of the bipolaron. We find that the excitation energy is smaller than the self-energy of the bipolaron. Thus we can

TABLE III. Excitation energy (Δ) and binding energy (BE) (in units of $\alpha^2\hbar\omega$) of the 2D bipolaron for several values of η as obtained from the present calculation.

η	Δ	BE
0.00	0.5703	0.1163
0.02	0.5706	0.0875
0.04	0.5707	0.0582
0.06	0.5705	0.0282

conclude that this type of excited state may occur for the Fröhlich bipolaron, and the mid-ir feature in the high T_c superconductors can be tentatively ascribed to the photoinduced electronic transition from biploarons. As can be seen, there is good agreement between the excitation energy calculated in our model and the result estimated from the calculation of the mid-ir peak obtained in the high T_c superconductors. For a two-dimensional polar crystal with $\alpha=5$, $\beta=3.5$, and $\hbar\omega=60$ meV, we find that the excitation energy turns out to be 0.584 eV in our calculation, where in the experiments of Kim *et al.*[18] and others a broad photoinduced electronic absorption is found to be peaked around 0.5 eV in La_2CuO_4. Thus the existence of large bipolarons is not unrealistic in the copper oxides.The present paper supplies theoretical support for the fact that the Fröhlich bipolaron may exist in the high T_c superconductor as well.

The author is grateful to Dr. J. Chakrabarti, Department of Theoretical Physics, IACS, Calcutta, India, for the hospitality shown by his department.

*Electronic address: satyabrata30@hotmail.com

[1] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).
[2] S. Lakkis, C. Schlenker, B. K. Chakraverty, R. Budder, and M. Marizio, Phys. Rev. B **14**, 1429 (1976).
[3] A. Alexandrov and J. Ranninger, Phys. Rev. B **23**, 1796 (1981); A. Alexandrov, J. Ranninger, and S. Robaszkiewich, *ibid.* **33**, 4526 (1986).
[4] B. K. Chakraverty, D. Feinberg, H. Zhengand, and M. Avignin, Solid State Commun. **64**, 1147 (1987).
[5] P. Prelovsek, T. M. Rice, and F. C. Zhang, J. Phys. C **20**, L229 (1987).
[6] D. Emin, Phys. Rev. Lett. **62**, 1544 (1989); D. Emin and M. S. Hillery, Phys. Rev. B **39**, 6575 (1989).
[7] V. L. Vinetskii and M. Sh. Gitterman, Zh. Éksp. Teor. Fiz. **40**, 1459 (1961) [Sov. Phys. JETP **13**, 1023 (1961)].
[8] S. G. Suprun and B. Ya. Moizhes, Fiz. Tverd. Tela (Leningrad) **24**, 1571 (1982) [Sov. Phys. Solid State **24**, 903 (1982)].
[9] H. Hiramoto and Y. Toyozawa, J. Phys. Soc. Jpn. **54**, 245 (1985).
[10] J. Adamowski, Phys. Rev. B **39**, 3649 (1989); J. Adamowskii and S. Bednarek, J. Phys. C **4**, 2845 (1992).
[11] G. Verbist, F. M. Peeters, and J. T. Devreese, Phys. Rev. B **43**, 2712 (1991); G. Verbist, M. A. Smondyrev, F. M. Peeters, and J. T. Devreese, *ibid.* **45**, 5262 (1992).
[12] F. Bassani, M. Geddo, G. Iadonisi, and D. Ninno, Phys. Rev. B **43**, 5296 (1991).
[13] S. Sil, A. K. Giri, and A. Chatterjee, Phys. Rev. B **43**, 12 642 (1991).
[14] V. M. Fomin and M. A. Smondyrev, Phys. Rev. B **49**, 12 748 (1994).
[15] A. S. Alexandrov and N. F. Mott, Rep. Prog. Phys. **57**, 1197 (1994).
[16] S. Sahoo, Phys. Lett. A **195**, 105 (1995); J. Phys.: Condens. Matter **7**, 4457 (1995).
[17] S. L. Herr, K. Kamaras, C. D. Porter, M. G. Doss, D. B. Tanner, D. A. Bonn, J. E. Greedan, C. V. Stager, and T. Timsuk, Phys. Rev. B **36**, 733 (1987).
[18] Y. H. Kim, C. M. Foster, A. J. Heeger, S. Cox, and G. Stuky, Phys. Rev. B **38**, 6478 (1988).
[19] D. Mihailovic, C. M. Foster, K. Voss, and A. J. Heeger, Phys. Rev. B **42**, 7989 (1990).
[20] Xiang-Xin Bi, C. Peeters, and C. Ekland, Phys. Rev. Lett. **70**, 2625 (1993).
[21] J. T. Devreese and V. M. Fomin, Phys. Rev. B **54**, 3959 (1996), and references therein.
[22] V. M. Fomin and J. T. Devreese, Solid State Commun. **96**, 79 (1995).
[23] P. Vansant, F. M. Peeters, M. A. Smodyrev, and J. T. Devreese, Phys. Rev. B **50**, 12 524 (1994).
[24] F. M. Peeters, Wu Xiaoguang, and J. T. Devreese, Phys. Rev. B **33**, 3926 (1986).
[25] W. J. Huybrechts, J. Phys. C **9**, L211 (1976); **10**, 3761 (1977).
[26] V. L. Vinetskii, O. Meredov, and V. Yanchuk, Teor. Eksp. Khim. **25**, 641 (1989).
[27] J. Devreese, J. De Sitter, and M. Goovaerts, Phys. Rev. B **5**, 2367 (1972).