PHYSICAL REVIEW B VOLUME 39, NUMBER 6 15 FEBRUARY 1989-II

Formation of Fröhlich bipolarons

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(Received 16 June 1988)

The binding energy of a bipolaron is calculated by the variational method as a function of the Fröhlich coupling constant α and $\eta=\epsilon_\infty/\epsilon_0$, where ϵ_∞ (ϵ_0) is the optic (static) dielectric constant. It is found that the system of two equally charged polarons is stable in a broad region of α and η. Since α and η for strongly ionic crystals take on values close to this region, the possibility of experimental evidence for Fröhlich bipolarons is suggested. The estimated average electron-electron separation for the bound state takes on values between 0.2 and 1.0 polaron radius.

I. INTRODUCTION

Two identical charge carriers in solids, i.e., electrons or holes, repel each other via the screened Coulomb potential and, in most cases, do not form a bound state. However, the properties of the charge carriers are modified by their interaction with the vibrating lattice, i.e., by electron-phonon coupling. In some materials, e.g., in ionic crystals, this coupling can be strong enough to overcome the Coulomb repulsion and create a stable electron pair or hole pair. This pair is called a bipolaron since it consists of two equally charged polarons, i.e., the charge carriers coupled with phonons. A possibility of the bipolaron formation in solids is determined by the competition between the Coulomb repulsion of electrons or holes and their attraction to the distorted lattice. This problem was qualitatively discussed by Pekar[1] and Schultz.[2]

The recent interest in the bipolarons is caused by their role in attempts of explanation of the high-temperature superconductivity.[3] According to the proposed bipolaronic mechanism of superconductivity,[4–8] the bipolarons of high enough density undergo the Bose-Einstein condensation, which leads to a formation of the superconducting state. The bipolaron concept can as well be useful in studying the properties of negative-U centers[9,10] and D^- complexes[11] in ionic crystals. These systems consist of the defect and the two bound electrons and can be considered as extrinsic bipolarons. The problem of stability of the bipolaron is of general interest in physics, because its solution provides an answer to the question: When do two identical charge carriers form a bound state in a polarizable medium?

The bipolaron in a bound state yields an example of a real-space pairing of electrons,[12] which should be distinguished from a **k**-space pairing being characteristic of the Cooper pair. Another difference between these two types of the electron pairing relies on the position of the energy levels, which lie inside the conduction band for the Cooper pair and below the bottom of the conduction band (in the semiconductor band gap) for the bipolaron.

A quantitative treatment of the bipolaron problem was a subject of the papers.[13–18] Bishop and Overhauser[13] found that the effective phonon-mediated electron-electron interaction can be attractive in polar crystals. However, the direct calculations[14–17] of the bipolaron energy either provided no bound state in three-dimensional crystals[17] or were unreliable due to the use of the considerably underestimated free polaron dissociation energy.[14–16] Recently, Hiramoto and Toyozawa[18] calculated the bipolaron energy with the help of the path-integral method and obtained the binding of the bipolaron in the strong-coupling limit. In the present paper the problem of the bipolaron is solved by the variational method, which is a generalization of the method previously proposed for the exciton[19] and the bound polaron,[20] and yields the binding energy and the region of the bipolaron stability considerably larger than those in Ref. 18. The preliminary results of this approach have been announced in Ref. 21.

II. THEORY

The present paper deals with the problem of the binding of two electrons or two holes in an ionic crystal or a polar semiconductor. In these materials the dominant coupling with phonons is that with the longitudinal optical (LO) phonons, which can be described by the Fröhlich interaction Hamiltonian

$$H_{\text{int}}=\sum_{\mathbf{k}}[v_{\mathbf{k}}a_{\mathbf{k}}(e^{i\mathbf{k}\cdot\mathbf{r}_1}+e^{i\mathbf{k}\cdot\mathbf{r}_2})+\text{H.c.}] , \tag{1}$$

with

$$v_{\mathbf{k}}=-(i/|\mathbf{k}|)(4\pi\alpha/\Omega)^{1/2} , \tag{2}$$

where $\mathbf{r}_1$ and $\mathbf{r}_2$ are the position vectors of the electrons or holes, $a_{\mathbf{k}}$ is the annihilation operator of the LO phonon with the wave vector $\mathbf{k}$ and the frequency ω, and Ω is the quantization volume. The Fröhlich coupling constant is defined as

$$\alpha=(1/\epsilon_\infty-1/\epsilon_0)e^2/2\hbar\omega a_p , \tag{3}$$

where $a_p=(\hbar/2m\omega)^{1/2}$ is the free polaron radius, m is the band mass of the electron ($m=m_e$) or the hole ($m=m_h$), and ϵ_∞ and ϵ_0 are the optic and the static dielectric constants, respectively. In Eqs. (1) and (2) the polaron units of energy ($\hbar\omega$) and length (a_p) are used. In these units the Hamiltonian of the bipolaron has a form

$$H=-\nabla_1^2-\nabla_2^2+\frac{\beta}{r_{12}}+\sum_{\mathbf{k}} a_{\mathbf{k}}^{\dagger}a_{\mathbf{k}}+H_{\text{int}} , \tag{4}$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$, $\beta=2\alpha/(1-\eta)$, and $\eta=\epsilon_\infty/\epsilon_0$. The parameter β characterizes the strength of the Coulomb interaction, which expressed in the usual units is equal to e^2/ϵ_∞. The material parameters fulfill the following inequalities: $\alpha\geq 0$, $\beta\geq 0$, and $0\leq\eta\leq 1$. Throughout this paper we will express the bipolaron energy as a function of α and η.

The bipolaron is stable if its binding energy

$$W=2E_0-E \tag{5}$$

is positive. In (5) E_0 and E are the ground-state energies of the free polaron and the bipolaron, respectively, measured with respect to the bottom of the conduction band. If the bipolaron consists of the two holes, the zero of energy scale is put on at the top of the valence band.

In the present paper the following variational wave function is applied in order to calculate the bipolaron ground-state energy:

$$\Psi=\phi T\chi_0 . \tag{6}$$

In (6) ϕ depends on the electron coordinates only, T is the canonical transformation

$$T=e^{S-S^{\dagger}} , \tag{7}$$

where

$$S=\sum_{\mathbf{k}} F_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)a_{\mathbf{k}} , \tag{8}$$

and χ_0 is the phonon vacuum state defined by $a_{\mathbf{k}}\chi_0=0$ and $\langle\chi_0|\chi_0\rangle=1$. The displacement amplitude $F_{\mathbf{k}}$ in (8) is proposed in the form, which is a generalization of that applied previously by the author to the bound polaron problem[20]

$$F_{\mathbf{k}}(\mathbf{r}_1,\mathbf{r}_2)=v_{\mathbf{k}}\left[\frac{\lambda_1}{\rho_1^2k^2+1}(e^{i\mathbf{k}\cdot\mathbf{r}_1}+e^{i\mathbf{k}\cdot\mathbf{r}_2})+\frac{\lambda_2}{(\rho_2^2k^2+1)^2}\right] \tag{9}$$

with the variational parameters λ_1, λ_2, ρ_1, and ρ_2.

The present choice of $F_{\mathbf{k}}$ is motivated as follows.

(i) Canonical transformation (7) can be expressed as a product of weak- and strong-coupling variational solutions resulting from the first and the second term in (9), respectively. One can therefore expect that the transformation T provides reasonable results for arbitrary electron-phonon coupling.

(ii) An application of the corresponding trial wave function, i.e., in the form (6) but with $F_{\mathbf{k}}$ (9) without the $\mathbf{r}_2$ dependence, to the free polaron problem provides estimates of the ground-state energy, which for large α are very close to the best results.[22]

Due to the presence of the spatially independent term in $F_{\mathbf{k}}$ [the second term within the large parentheses in (9)] the proposed trial wave function is not translationally invariant although Hamiltonian (4) possesses the translational symmetry. Nevertheless, the use of such trial wave function is not in contradiction with the variational principle. Any translationally invariant trial wave function should provide better estimates for the bipolaron energy, however, one cannot expect an essential improvement of the present results. The physical consequence of this choice is a localization of the bipolaron, which corresponds to the self-trapping of polarons in the strong-coupling limit.

The ground-state energy of the bipolaron is calculated in two steps. First, we construct the effective Hamiltonian

$$H_{\text{eff}}=\langle\chi_0|T^{\dagger}HT|\chi_0\rangle , \tag{10}$$

and next we calculate an expectation value of H_{eff} with the help of the electronic wave function ϕ. The first step leads to the following form of the effective Hamiltonian for the bipolaron:

$$H_{\text{eff}}=-\nabla_1^2-\nabla_2^2+V(r_{12})+U(r_1)+U(r_2)+\Sigma \tag{11}$$

with the effective polaron-polaron interaction

$$V(r_{12})=\frac{1}{r_{12}}[\beta+2\alpha\lambda_1(\lambda_1-2)(1-e^{-r_{12}/\rho_1})] -\frac{\alpha\lambda_1^2}{\rho_1}e^{-r_{12}/\rho_1} \tag{12a}$$

and the self-energy

$$\Sigma=\alpha\left[\frac{\lambda_1}{\rho_1}[\lambda_1(1+1/\rho_1^2)-4]+\frac{5\lambda_2^2}{16\rho_2}\right] . \tag{12b}$$

Assuming $\rho_1\neq\rho_2$ and introducing $\delta_{12}=1/(\rho_1^2-\rho_2^2)$ we obtain

$$\begin{aligned}U(r_j)=\frac{1}{r_j}(2\alpha\lambda_2\{\lambda_1-1-\lambda_1\rho_1^4\delta_{12}^2e^{-r_j/\rho_1}\\ +[1+\lambda_1\rho_2^2\delta_{12}(1+\rho_1^2\delta_{12})]e^{-r_j/\rho_2}\})\\ +\alpha\lambda_2(\lambda_1\rho_2\delta_{12}+1/\rho_2)e^{-r_j/\rho_2} ,\end{aligned} \tag{12c}$$

where $r_j=|\mathbf{r}_j|$ and $j=1,2$. The terms $U(r_1)$ and $U(r_2)$, which result from the breaking of the translational symmetry, can be interpreted as self-energies of the polarons. Similar terms appear when calculating the ground-state energy of the free polaron by the present approach.

The ground state of the bipolaron is the spin singlet, accordingly, the function ϕ in (6) is proposed in the symmetric form

$$\sum_{n=1}^{N} d_n(1+P_{12})e^{-a_nr_1-b_nr_2-c_nr_{12}} , \tag{13}$$

which is properly normalized. In (13) P_{12} is the permutation operator interchanging the indices 1 and 2; a_n, b_n, and c_n are the nonlinear variational parameters chosen similarly as in Ref. 23, and d_n are the linear variational parameters obtained from the diagonalization procedure. The calculations have been performed with the use of an $N=16$-element basis (13), which consists of four terms with $a_n\neq b_n$ and twelve with $a_n=b_n$. Form (13) of the electronic wave function has been chosen as the optimum trial function after experimentation with several other functions.

III. RESULTS AND DISCUSSION

The results are shown in Fig. 1. The two polarons can form a bound state if $\alpha \geq \alpha_c$ and $\eta \leq \eta_c$, and are free otherwise. The estimated values of α_c are given in Fig. 1 by the crossing points of the dashed curves with the abscissa and the solid curve shows the dependence of η_c on α. The minimum value of α_c obtained by the present method is 7.3. Due to the variational character of this approach, the estimated values of α_c provide upper bounds whereas those of η_c provide lower bounds for the corresponding limits of the bipolaron stability. The binding energy W of the bipolaron (the dashed curves in Fig. 1) is an increasing function of α and a decreasing function of η. It can take on rather large values reaching 50% of the free polaron dissociation energy D_0, where $D_0 = -E_0$. In energy units of $\hbar\omega$ the estimated maximum values of W are 25.8, 56.8, 80.7, and 86.3 for $\eta = 0.1$, 0.05, 0.01, and 0, respectively.

The present approach allows us to understand a physical nature of the binding of the two identical polarons. For this purpose let us consider the effective Hamiltonian (11). It appears that in the bound state the effective polaron-polaron interaction $V(r_{12})$ is repulsive, however, the self-energy given by the sum $U(r_1) + U(r_2) + \Sigma$ is much lower than the self-energy of the two free polarons. Therefore, the binding results from the lowering of the self-energy, but not from the attractive interaction between the polarons. Nevertheless, the strength of the Coulomb potential, which dominates in $V(r_{12})$, decreases taking on the values smaller than e^2/ϵ_∞, but larger than e^2/ϵ_0. The lowering of the bipolaron energy which results from the terms $U(r_j)$ means that the bipolaron is (nearly) self-localized similarly as the polaron in the strong-coupling region.

In the present calculations the polaron dissociation energy D_0 is taken from Ref. 22, which provides the best estimates of D_0 for $3.5 \leq \alpha \leq 35$, i.e., for the coupling range of special importance in the bipolaron problem. The authors of papers[14-16] have applied the Pekar strong-coupling method[1] to estimate both the polaron and bipolaron energy. It means, however, that the values used[14-16] for D_0 were much too low (cf. Ref. 22). After recalculating the results[14-16] with the use of the values for D_0 taken from Ref. 22, one obtains no binding of two polarons, with an exception of very large α. Moreover, the calculated energies[14,15] exhibit the dependence on α^2 only, which is generally not true. The correct dependence on α is shown in Fig. 1. The ratios W/D_0 grow with α and approach their constant asymptotic values for very large α. Then, η_c becomes independent of α as well and is equal to 0.14. This value can be compared with $\eta_c = 0.079$ quoted by Hiramoto and Toyozawa[18] for the strong-coupling limit. It is seen that the region of the bipolaron stability obtained by the present method is much broader than that in Ref. 18.

The present approach enables us to estimate the average electron-electron separation in the bipolaron, but not the bipolaron mass. The calculated electron-electron separation (Fig. 2) varies from $0.2a_p$ ($\alpha = 40$) to $1.0a_p$ ($\alpha = 7.3$) for $\eta = 0$ and rather slowly increases with η. These numbers would suggest that the Fröhlich bipola-

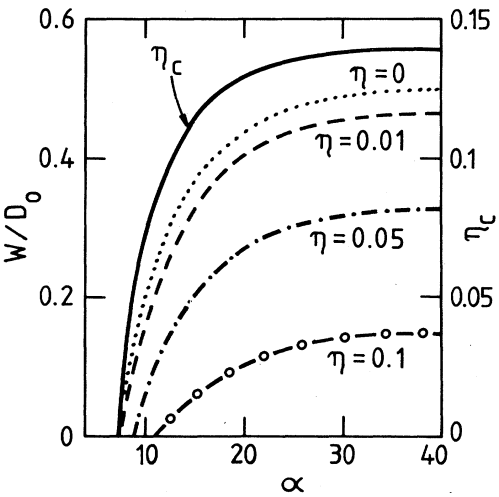

FIG. 1. Calculated binding energy W of the bipolaron as a function of the Fröhlich coupling constant α for several values of $\eta = \epsilon_\infty/\epsilon_0$ (dashed curves). The solid curve shows the estimated limit η_c of the bipolaron stability, i.e., the bipolaron is stable if $\eta \leq \eta_c$. D_0 is the dissociation energy of the free polaron.

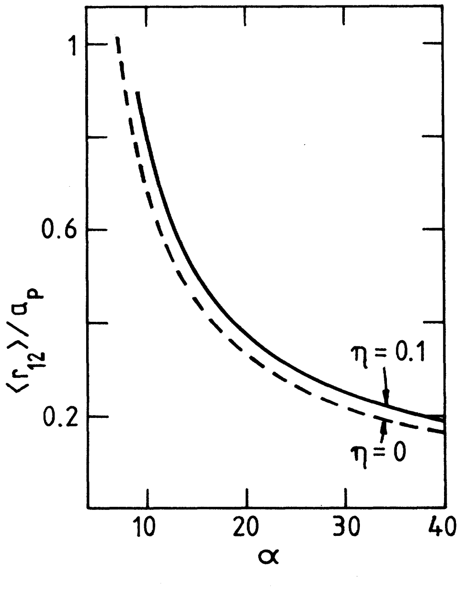

FIG. 2. Calculated average electron-electron separation $\langle r_{12} \rangle$ in the bipolaron vs electron-phonon coupling constant α. The solid curve shows the results for $\eta = 0.1$; the dashed curve for $\eta = 0$. The unit of length is the free polaron radius a_p.

ron is small (cf. Ref. 18). However, our unit of length, the polaron radius a_p for the electron, has the following dependence on the material parameters:

$$a_p/a_B=\epsilon_0\alpha\eta(m_{e0}/m_e)/(1-\eta)\ , \tag{14}$$

where a_B is the Bohr radius and m_{e0} is the electron rest mass, which means that this ratio takes on rather large values in the region of the bipolaron stability, e.g., $a_p/a_B\cong 100$ for $\alpha=10$, $\eta=0.01$, $m_e/m_{e0}=0.1$, and $\epsilon_0=100$. Therefore, the size of the bipolaron can be much larger than the typical interatomic distance in solids.

The limits of the bipolaron stability estimated in the present paper are close to the values of α and η, which correspond to real substances. Using these results to the charge carriers in crystals, we should remember the approximations of the present treatment (e.g., the assumption of the isotropic parabolic bands and neglecting the details of the band structure). An incorporation of the neglected effects will move the limits of the bipolaron stability. Therefore, we can expect the formation of bipolarons for the crystals with α and η taking on the values from the stability region, but we cannot exclude a possibility of stable bipolarons even if α and η lie somewhat outside this region. The best materials for a search of the Fröhlich bipolarons are the strongly ionic crystals of alkali halides, e.g., LiF, RbBr, and CsCl. The stability can more easily be achieved if another factor makes the binding stronger, e.g., an anisotropy of the crystal. The special case of the anisotropic crystals are the one- and two-dimensional crystals, for which the low dimensionality stabilizes the bound state of two electrons.[17] Moreover, the large mass of the charge carriers also favors the binding. It leads to the possibility of the two-hole bound states (biholes) in polar crystals. The hole-phonon coupling is larger than that for the electron by the factor of $(m_h/m_e)^{1/2}$, which is usually larger than 1 and can take on the values of the order of 10, e.g., in CuCl and CuBr. Therefore, the limit of the bihole stability is shifted towards weak electron-phonon coupling.

The bipolarons can also be observed indirectly in transport phenomena, e.g., in superconductors. It seems, however, that the bipolaronic mechanism of superconductivity is of minor importance, especially in the high-T_c superconductors, due to the large mass[18] and small mobility of the bipolaron (self-localization). Recently, Chakraverty *et al.*[7] have proposed a new kind of the bipolarons with low effective mass which may be responsible for the high-temperature superconductivity.

Until now, the stability has been demonstrated both experimentally[24] and theoretically[25] for the so-called "small bipolarons," in which the electrons interact with the acoustic phonons through the short-range deformation potential. Yet, no experimental evidence of the Fröhlich bipolarons has been found. The present paper supplies the theoretical support of the statement that these bipolarons can as well exist in the crystals.

ACKNOWLEDGMENTS

I am grateful to Stanisław Bednarek for fruitful discussions. This work was supported by the Institute of Physics of the Polish Academy of Sciences under Contract No. CPBP-01.04.

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[1] S. I. Pekar, *Research on Electron Theory of Crystals* (U.S. AEC, Washington, D.C., 1963) [Original (in Russian): S. I. Pekar, *Issledovaniya po Elektronnoy Teorii Kristallov* (Gosud. Izd. Techn.—Teor. Literatury, Moscow, 1951)].

[2] T. D. Schultz, in *Polarons and Excitons,* edited by C. G. Kuper and G. D. Whitfield (Oliver and Boyd, Edinburgh, 1963), p. 71.

[3] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[4] A. Alexandrov and J. Ranninger, Phys. Rev. B **23**, 1796 (1981); **24**, 1164 (1981).

[5] B. K. Chakraverty, Ferroelectrics **53**, 59 (1984).

[6] A. Alexandrov, J. Ranninger, and S. Robaszkiewicz, Phys. Rev. B **33**, 4526 (1986).

[7] B. K. Chakraverty, D. Feinberg, H. Zheng, and M. Avignon, Solid State Commun. **64**, 1147 (1987).

[8] P. Prelovsek, T. M. Rice, and F. C. Zhang, J. Phys. C **20**, L229 (1987).

[9] G. D. Watkins, in *Festkörperprobleme (Advances in Solid State Physics),* edited by P. Grosse (Vieweg, Braunschweig, 1984), Vol. 24, p. 163.

[10] K. Weiser, Phys. Rev. B **25**, 1408 (1982).

[11] D. M. Larsen, Phys. Rev. B **23**, 628 (1981).

[12] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975); T. M. Rice and L. Sneddon, *ibid.* **47**, 689 (1981).

[13] M. F. Bishop and A. W. Overhauser, Phys. Rev. B **23**, 3627 (1981).

[14] V. L. Vinetskii, Zh. Eksp. Teor. Fiz. **40**, 1459 (1961) [Sov. Phys.—JETP **13**, 1023 (1961)].

[15] S. G. Suprun and B. Ya. Moizhes, Fiz. Tverd. Tela **24**, 1571 (1982) [Sov. Phys.—Solid State **24**, 903 (1982)].

[16] V. K. Mukhomorov, Fiz. Tekh. Poluprovodn. **16**, 1095 (1982) [Sov. Phys.—Semicond. **16**, 700 (1982)].

[17] Y. Takada, Phys. Rev. B **26**, 1223 (1982).

[18] H. Hiramoto and Y. Toyozawa, J. Phys. Soc. Jpn. **54**, 245 (1985).

[19] S. Bednarek, J. Adamowski, and M. Suffczyński, Solid State Commun. **21**, 1 (1977).

[20] J. Adamowski, Phys. Rev. B **32**, 2588 (1985).

[21] J. Adamowski, Acta Phys. Pol. A **73**, 345 (1988).

[22] J. Adamowski, B. Gerlach, and H. Leschke, in *Functional Integration—Theory and Applications,* edited by J. P. Antoine and E. Tirapegui (Plenum, New York, 1980), p. 291.

[23] A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **15**, 1 (1977).

[24] S. Lakkis, C. Schlenker, B. K. Chakraverty, R. Buder, and M. Marezio, Phys. Rev. B **14**, 1429 (1976).

[25] M. H. Cohen, E. N. Economou, and C. M. Soukoulis, Phys. Rev. B **29**, 4496 (1984).