Formation of large bipolarons

F. Luczak, F. Brosens, and J. T. Devreese*
Universteit Antwerpen, Departement Natuurkunde, Universiteitsplein 1, 2610 Antwerpen, Belgium
(Received 12 June 1995)

The ground-state energy of the large bipolaron is investigated by use of a variational approach and a canonical transformation, which was introduced in earlier studies of the bound polaron. For the bipolaron the transformation reproduces both the oscillator-type strong-coupling results and the weak-coupling limit. The stability region for the bipolaron is compared with existing theories. The main advantage of the present method is the transparency of the variational results. To the best of our knowledge, the present Ansatz yields the lowest bounds predicted so far for two dimensions in the case of $\alpha > 4.5$. The theory is analyzed with reference to materials with high $(\epsilon_0/\epsilon_\infty)$ ratio.

I. INTRODUCTION

An electron in a polar crystal lattice interacting with the longitudinal optical phonon modes is called a polaron. Since the effective electron-phonon interaction is attractive, it enhances the electron's effective mass. If a second electron in the phonon bath is taken into account, its interaction with the phonons might overcome the electron-electron repulsion. If so, the pair of electrons forms a stable bound state, called bipolaron. Due to the competition between the opposite forces, the bipolaron exists only in a small region of electron-phonon coupling constant α and electron-electron repulsion U. It is the aim of the present paper to contribute to the investigation of this stability region.

Our theoretical description is limited to large polarons described by Fröhlich's Hamiltonian.[1] Up to now, the model can not be treated exactly, but a large variety of approximate methods has been developed. The Feynman path integral method[2–4] is superior in the case of intermediate α. With this method the phonons can be eliminated exactly, and the remaining effective electronic system can be studied with oscillator-based variational principles. For operator methods the main problem is the exact phonon elimination while simultaneously taking an appropriate electronic behavior into account, i.e., describing the screening of the electron at short distance by the polarization cloud of the phonons. Especially the bipolaron must not collapse in one spatial point.

Many researchers propagate variational methods, wherein wave functions are simulated clearly, but in general phonons can only be eliminated approximately, except for very weak and very strong coupling. Because of their simplicity, variational procedures offer the freedom to choose wave functions nearly at will. However, a clear and appropriate bipolaron wave function, accurate for all α, has not yet been found. The price one has to pay for accurate strong-coupling results seems to be a less accurate weak-coupling description. An inadequate consideration of translational invariance or phonon-phonon correlations might result in a positive α^2 behavior of the ground-state energy for small α.

One should also remark that exact results are not known for $\alpha \to \infty$, but the actual estimates[3,5] seem to be almost rigorous.

The lowest ground-state energy bounds for the bipolaron were obtained by the variational calculation,[5] for $\alpha \gtrsim 8$, and the path integral formalism,[4] $\alpha \lesssim 8$. The lowest reliable critical $\alpha_c \approx 6.8$, i.e., the onset of the stability region, has been predicted in Ref. 4.

In the present paper we first present a transparent ansatz, which is a generalization of the work by Devreese, Evrard, Kartheuser, and Brosens[6] (hereafter referred to as DEKB), to estimate the ground-state energy of a system of N electrons interacting with a longitudinal optical phonon bath. The formalism is subsequently applied to the bipolaron. The weak- and strong-coupling limits are extracted analytically. The ground-state energy is examined numerically and compared with already existing bounds. Finally, we interpret our results also in connection with possible high-T_c superconductivity and experimental data.

II. VARIATIONAL PRINCIPLE

The present work starts from the well known shifted-harmonic-oscillator transformation

$$U = \exp\left(\sum_{\vec{k}} \left(V_{\vec{k}}\, \rho_{\vec{k}}\, a_{\vec{k}}^{\dagger} - \text{H.c.} \right) \right),$$

$$\rho_{\vec{k}} = \left\langle \phi_e \left| \sum_{j=1}^{N} e^{i\vec{k}\cdot\vec{r}_j} \right| \phi_e \right\rangle \tag{1}$$

which is here applied to the bipolaron formation. The transformed Hamiltonian $U_1^{-1} H U_1$ is investigated by use of a trial wave function of the type proposed in Ref. 6,

$$|\Psi\rangle = \left[c + \sum_{\vec{k}} V_{\vec{k}}^{*}\, g_{\vec{k}}^{*} \left(\sum_{j=1}^{N} e^{-i\vec{k}\cdot\vec{r}_j} - f_{\vec{k}}^{*} \right) a_{\vec{k}}^{\dagger} \right] |0\rangle |\phi_e\rangle, \tag{2}$$

where $f_{\vec{k}}$ and $g_{\vec{k}}$ are variational parameters and c is a normalization constant. $|\phi_e\rangle$ represents the electronic part of the trial function. For the bound polaron[6] this ansatz can reproduce the ground-state energy both for strong and weak electron-phonon coupling limit to leading order. In the present article the method is applied to a system of N polarons, whose Hamiltonian is

$$H=H_e+\sum_{\vec{k}} a_{\vec{k}}^{\dagger}a_{\vec{k}}+\sum_{\vec{k}}\sum_{j=1}^{N}(V_{\vec{k}}\,e^{i\vec{k}\cdot\vec{r}_j}a_{\vec{k}}+\text{H.c.}), \quad (3)$$

with

$$V_{\vec{k}}=-\frac{i}{k\sqrt{V}}\sqrt{\frac{4\pi\alpha}{\sqrt{2}}}, \quad \alpha=\frac{e^2}{\sqrt{2}}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right).$$

The electronic part H_e of H includes the Coulomb repulsion between the electrons and takes the form

$$H_e=\sum_{j=1}^{N}\frac{\vec{p}_j^{\,2}}{2}+\frac{1}{2}\sum_{j,j'=1}^{N}\frac{U}{|\vec{r}_j-\vec{r}_{j'}|}, \quad U=\frac{e^2}{\epsilon_\infty}. \quad (4)$$

Minimization with respect to $f_{\vec{k}}^{*}$ and $g_{\vec{k}}^{*}$ leads to

$$E=\langle\phi_e|\tilde{H}_e|\phi_e\rangle+\frac{\chi}{2}. \quad (5)$$

The resulting energy functional thus splits into two parts. In fact, the first contribution gives the adiabatic strong-coupling limit, while χ is most important in the intermediate- and weak-coupling regimes. For the above Hamiltonian (3), χ has to be determined from a transcendental equation

$$\frac{\chi}{2}=-\sum_{\vec{k}}|V_{\vec{k}}|^2\frac{Z^2(\vec{k})}{D_1(\vec{k})-\dfrac{|F(\vec{k})|^2}{1-\dfrac{\chi}{2}}-\left(\langle\phi_e|\tilde{H}_e|\phi_e\rangle-1+\dfrac{\chi}{2}\right)Z(\vec{k})}, \quad (6)$$

with

$$\tilde{H}_e=H_e+\sum_{\vec{k}}|V_{\vec{k}}|^2|\rho_{\vec{k}}|^2-\sum_{\vec{k}}|V_{\vec{k}}|^2\left(\rho_{\vec{k}}^{*}\sum_{j=1}^{N}e^{i\vec{k}\cdot\vec{r}_j}+\text{H.c.}\right)$$

and

$$Z(\vec{k})=\left\langle\phi_e\left|\sum_{j,j'=1}^{N}e^{i\vec{k}\cdot(\vec{r}_j-\vec{r}_{j'})}\right|\phi_e\right\rangle-|\rho_{\vec{k}}|^2,$$

$$F(\vec{k})=\left\langle\phi_e\left|\left(\sum_{j=1}^{N}e^{i\vec{k}\cdot\vec{r}_j}-\rho_{\vec{k}}\right)H_e\right|\phi_e\right\rangle,$$

$$D_1(\vec{k})=\left\langle\phi_e\left|\left(\sum_{j=1}^{N}e^{i\vec{k}\cdot\vec{r}_j}-\rho_{\vec{k}}\right)H_e\left(\sum_{j=1}^{N}e^{-i\vec{k}\cdot\vec{r}_j}-\rho_{\vec{k}}^{*}\right)\right|\phi_e\right\rangle.$$

Equation (5) is the same as that derived in DEKB apart from an extra parameter $F(\vec{k})$, which yields small negative definite contributions in χ and hence lowers the energy. The present energy bound is therefore slightly more accurate than the one of DEKB.

III. APPLICATION TO THE BIPOLARON

With the ansatz (2) the ground-state energy of the large bipolaron is evaluated. In the asymptotic limits $\alpha\to 0$ and $\alpha\to\infty$ analytical expressions are obtained.

As already known from earlier calculations[1,7,8] the oscillator wave function represents a relatively simple, but adequate description of strong-coupled polaronic problems. Furthermore, the use of center-of-mass and relative coordinates introduces substantial simplifications.[3,9] We therefore propose two types of trial functions ($D=2,3$)

$$\phi_A(\vec{R},\vec{r})=\sqrt{\frac{ab}{\pi}}^{D}\exp\left(-\frac{a^2R^2}{2}\right)\exp\left(-\frac{b^2r^2}{2}\right)\to E_A \quad (7)$$

and

$$\phi_B(\vec{R},\vec{r})=\sqrt{\frac{2}{D}}\,b\,r\sqrt{\frac{ab}{\pi}}^{D}\exp\left(-\frac{a^2R^2}{2}\right).\exp\left(-\frac{b^2r^2}{2}\right)\to E_B. \quad (8)$$

The resulting expressions can be exploited in two ways. A numerical evaluation of (5) as a function of α and U allows us to plot the energy values and to compare them with already known bounds. From the point of view of exact results, analytical limits are important, since they allow to judge the quality of the theory in the weak- and strong-coupling limits.

Before dealing with the bipolaron, the related results for a single polaron are briefly presented. Applying the described ansatz to the Fröhlich polaron an upper bound to the ground-state energy has been calculated. Both the weak- and strong-coupling limits were obtained, i.e., $E(\alpha)=-\alpha+O(\alpha^2)$ for $\alpha\to 0$ and $E(\alpha)=-(\alpha^2/3\pi)+O(1)$ for $\alpha\to\infty$, where, referring to Ref. 10, the following scaling relation holds: $E_{2D}(\alpha)=\frac{2}{3}E_{3D}[(3\pi/4)\alpha]$. The three-dimensional (3D) ground-state energy is lower than Pekar's result[8] for $\alpha\lesssim 30$. At weak coupling, it turns out that the coefficients of α^2 are positive. Improvements can be realized, e.g., by including the conservation of the total polaron linear momentum, as was done by Ercelebi and Senger.[11] Furthermore, consideration of phonon-phonon correlations (cf. also Refs. 12 and 13) in the wave function (2) would lower the bounds in this regime. However, since the onset of bipolaron stability is situated at relatively large α, the above mentioned deficiency for $\alpha\to 0$ does not affect the bipolaron stability region essentially.

By use of the bipolaron Hamiltonian we obtain the following results.

(i) For $\alpha\to 0$ the self-consistent equation (6) takes the form

$$\frac{\chi}{2}=-\frac{2\alpha}{\sqrt{1-\frac{\chi}{2}}}\Rightarrow\frac{\chi}{2}=-2\alpha+O(\alpha^2). \tag{9}$$

The interaction between the electrons does not contribute to first order in α. Two polarons with energy $-\alpha$ result. The right-hand side of (9) thus gives the standard weak coupling result.[14]

(ii) The strong-coupling case, $\alpha\to\infty$, reveals large bipolaron formation, as is analytically seen from the following considerations. Since the ground-state energy is expected to be proportional to α^2 (Ref. 15) the parameters a,b can be scaled in terms of α

$$a=\gamma\alpha,\quad b=\delta\alpha,\quad U\propto\alpha.$$

One can show that the leading contributions from $\chi/2$ are of order $O(1)$ and that the dominant contribution to the energy for strong coupling is therefore given by $\langle\,\phi\,|\,\tilde{H}_e|\,\phi\,\rangle$. This expectation value is examined here for both electronic wave functions (7) and (8). The minimization of $\langle\,\phi\,|\,\tilde{H}_e|\,\phi\,\rangle$ leads to a rather complicated set of equations, but after the transformation

$$\lambda=\cos\theta,\quad a=2b\,\frac{\cos\theta}{\sin\theta},\quad \lambda\in\,]0,1[,$$

the energy can be written in terms of b and λ for both types of wave functions. In the case of (7) one obtains (3D case)

$$E_A=\frac{3\,b^2}{2(1-\lambda^2)}+\frac{2\,U\,b}{\sqrt{\pi}}-\frac{8\alpha}{\sqrt{\pi}}b\,\lambda. \tag{10}$$

Minimization with respect to b yields

$$E_A=-\frac{2}{3\pi}(1-\lambda^2)(4\alpha\lambda-U)^2. \tag{11}$$

Further minimization results in a factorizable cubic equation for λ from which the optimal $\lambda_{\min}$ can be extracted.

$$\lambda_{\min}=\frac{V+\sqrt{V^2+128}}{16},\quad V=\frac{U}{\alpha}, \tag{12}$$

$$E_A=\frac{(3\,V-\sqrt{V^2+128})^2(64-V^2-V\,\sqrt{V^2+128})}{3072\,\pi}\,\alpha^2. \tag{13}$$

For the trial wave function ϕ_B, the minimization of $\langle\phi_e|\tilde{H}_e|\phi_e\rangle$ with respect to λ involves the roots of a polynomial of degree 8. An accurate approximation in closed form can be obtained as follows. Numerical examinations of this polynomial yields $\lambda_{\min}\approx 0.7$. Improvements are obtained by introducing a new parameter u, with $\lambda=u+0.7$. The corresponding algebraic equation is then considered to first order in u, leading (in 3D) to

$$\lambda_{\min}=\frac{7}{10}+\frac{12.6\,V-15.542\,27}{222.669-18\,V},\quad V=\frac{U}{\alpha}, \tag{14}$$

TABLE I. Comparison of some characteristic values for the bipolaron stability region.

		Present	Ref. 4	Ref. 5
3D	α_c	8.1	6.8	7.3
	η_c	0.131	0.079	0.14
2D	α_c	3.5	2.9	–
	η_c	0.158	0.079	–

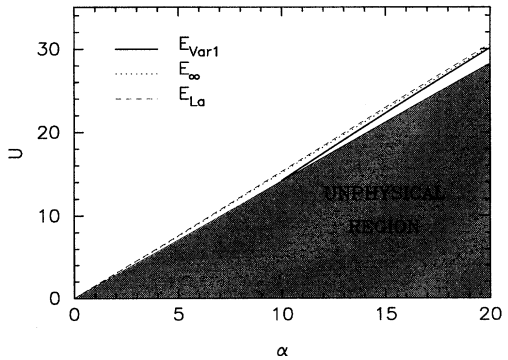

FIG. 1. Boundaries of the three-dimensional bipolaron stability region (compared with Feynman's polaron energies) from (7) ($E_{\rm var1}$) as compared with the high coupling limit E_∞ and the parameter values of La_2CuO_4, E_{La}.

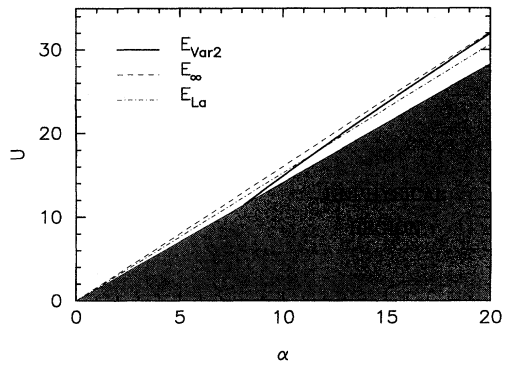

FIG. 2. Boundaries of the three-dimensional bipolaron stability region (compared with Feynman's polaron energies) from (8) (E_{var2}) as compared with the high coupling limit E_∞ and the parameter values of La_2CuO_4, E_{La}.

$$E_B=-\frac{2}{3\pi}\frac{1-\lambda^2}{7+2\lambda^2}[2U-\alpha\lambda(12-4\lambda^2+\lambda^4)]^2. \quad (15)$$

The error corresponding to our last approximation is about 10^{-5} in λ and much smaller for the ground-state energy.

For the 2D case the procedure explained above leads to the following results:

$$\text{(A)}\quad \lambda_{\min}=\frac{V}{16}\left(1+\sqrt{1+\frac{128}{V^2}}\right), \quad (16)$$

$$E_B=\frac{\pi\alpha^2}{2048}(V^4-320V^2+V\sqrt{V^2+128}^3-2048); \quad (17)$$

$$\text{(B)}\quad \lambda_{\min}=\tfrac{7}{10}+0.924-0.058V-0.996\sqrt{1-0.194V+3.348\times10^{-3}V^2}, \quad (18)$$

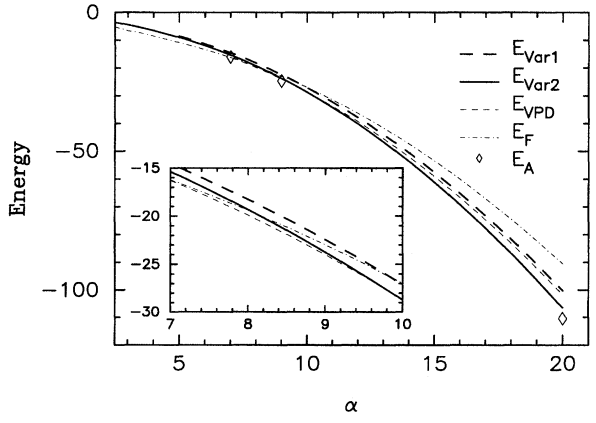

FIG. 3. Our results E_{var1} and E_{var2} as derived from (7) and (8), respectively, compared with other three-dimensional ground-state energy bounds: twice Feynman's polaron energy E_{F}, (Ref. 17), path-integral calculation by Verbist, Peeters, and Devreese E_{VPD} (Ref. 4), variational calculation by Adamowski and Bednarek E_{A} (Ref. 5).

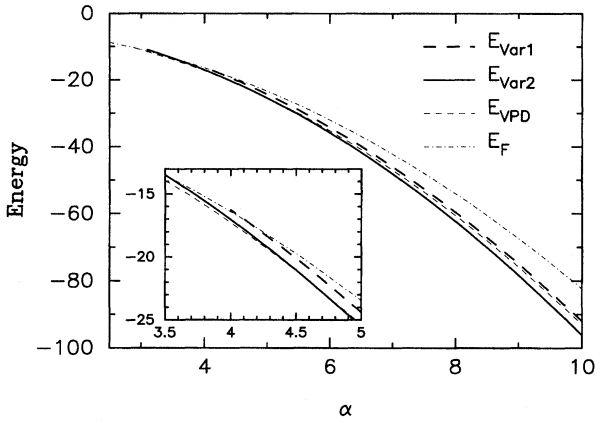

FIG. 4. The two-dimensional bipolaron ground-state energy: E_{var1}[by use of (7)], E_{var2}[by use of (8)], compared with: twice Feynman's polaron energy E_{F} (Ref. 17), path-integral calculation by Verbist, Peeters, and Devreese E_{VPD} (Ref. 4).

$$E_B=2\sqrt{2}\,\pi\alpha^2\lambda(1-\lambda^2)\left(1-\frac{\lambda^2}{2}+\frac{3\lambda^4}{16}\right)\times\left[\frac{V}{2\sqrt{2}}-\sqrt{2}\left(1-\frac{\lambda^2}{2}+\frac{3\lambda^4}{16}\right)\right], \quad (19)$$

with relative errors of order 10^{-5} in the energy.

Another important aspect related to the stability region of the bipolaron is the existence of a critical Coulomb strength U_c. The bipolaron can only exist for values of $U\in[\sqrt{2}\alpha,U_c]$, while $U>U_c$ causes the decay into two single polarons. The system is therefore characterized by a parameter η:

$$\frac{U}{\alpha}=\frac{\sqrt{2}}{1-\eta}, \quad \eta=\frac{\epsilon_\infty}{\epsilon_0}$$

We denote by η_l the critical values of η as compared to the Miyake energies,[16] and by η_c those obtained from a com-

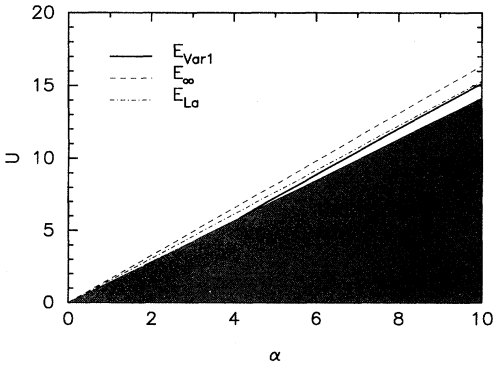

FIG. 5. Boundaries of the two-dimensional bipolaron stability region (compared with Feynman's polaron energies) from (7) (E_{var1}) as compared with the high coupling limit E_∞ and the parameter values of La_2CuO_4, E_{La}.

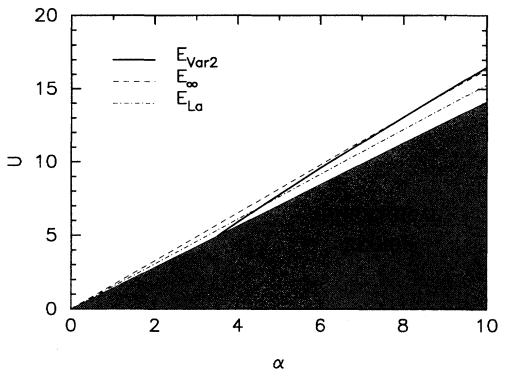

FIG. 6. Boundaries of the two-dimensional bipolaron stability region (compared with Feynman's polaron energies) from (8) (E_{var2}) as compared with the high coupling limit E_∞ and the parameter values of La_2CuO_4, E_{La}.

parison with Feynman's result[17] for two single polarons. For $\alpha \rightarrow \infty$ we obtain the same results as in Ref. 3 (see Table I) but by analytical methods.

In the intermediate-coupling regime, (5) has to be evaluated numerically. The results are shown in Fig. 3 and Fig. 4. The ground-state energies according to both types of trial wave functions (7) and (8) are shown and compared with the energy for two polarons from Feynman's approach, and with the results of Ref. 4. The second wave function (8) provides a lower upper bound than the simpler choice (7). The implied stability regions are shown in Figs. 1, 2, 5, and 6 for the trial wave functions (7), (8) in 3D and 2D, respectively. A comparison with already predicted bipolaron ground-state energies illustrates the quality of our method.

The path integral formalism as used in Ref. 4 yields the lowest-energy bounds in the intermediate-coupling region and hence the lowest α_c. For large α the variational ansatz[5] results in the lowest bounds (based on a trial wave function with 55 variational parameters) and therefore predicts the widest stability area. Our approach turns out to be quite accurate in both regimes, and it improves the path integral formalism in a wide range of $\alpha[\alpha > 10(3D), \alpha > 4.5(2D)]$.

An alternative variational approach has been investigated in Ref. 18. It is based on a LLP transformation with space-dependent displacement amplitudes $f_{\vec{k}}(\vec{r})$, which have been expanded in partial waves and applied to a wave function of Coulomb type. However, the extracted values are obtained by a comparison with polaron energies that are calculated within the same method. Because of the less accurate description of the weak coupling behavior of these consistent polaron self-energies, the results for α_c must be handled with care. Moreover, in Ref. 4 it has been shown that the path-integral formalism leads to lower upper bounds on the bipolaron ground-state energy. As far as we know, the only two-dimensional predictions for intermediate α are given in Refs. 4 and 18. To the best of our knowledge the present ansatz yields the lowest bipolaron ground-state energy bounds for $\alpha > 4.5$.

It might be relevant to interpret the present stability regions in connection with experimental data. For the copper oxide La_2CuO_4, measurements[19] of the normal plane predict $\epsilon_\infty = 4$ and $\epsilon_0 = 50$. Replacing these parameters in α and U yields $U = 1.53\alpha$. The present ansatz then shows critical α of 11.6 and 4.5 in three and two dimensions, respectively. In fact, experimental measurements do not allow to determine the bare band mass, so that α is not accurately known in this system. However, bipolaron formation in La_2CuO_4 might be due to LO-phonon effects. The inclusion of acoustical branches will furthermore decrease the onset of the stability region.

IV. CONCLUSIONS

We presented a transparent variational ansatz, which is a generalization of the one introduced by Devreese, Evrard, Kartheuser, und Brosens.[6] The application to the bipolaron system led to upper bounds for the ground-state energy. In comparison with Feynman's polaron self-energies[17] the binding energy has been calculated. The implied stability regions has been compared with earlier predictions (cf. Table I). With a Gaussian type of electronic trial function (8) we obtained the following critical parameters:

$$\alpha_c^{(3D)} = 8.1, \quad \eta_c^{(3D)} = 0.131, \quad \alpha_c^{(2D)} = 3.5, \quad \alpha_c^{(2D)} = 0.158.$$

In summary, our method succeeds in deriving suitable bipolaron ground-state energies and analytical limits for weak and strong coupling. Furthermore, it opens the possibility to examine different electronic trial wave functions clearly.

ACKNOWLEDGMENTS

The authors acknowledge the support by the Human Capital and Mobility Programme of the E.C. The presented work was performed in the project "Polarons, Bipolarons and Excitons. Properties and Occurrence in New Materials," No. CHRX-CT93-0124. This work was also supported by the Belgian National Fund for Scientific Research (NFWO); research programme No. G. 0287.95.

*Also at Technische Universiteit Eindhoven, Departement Natuurkunde, Postbus 513, 5600 MB Eindhoven, The Netherlands.

[1] H. Fröhlich, H. Pelzer, and S. Zienau, Philos. Mag. **41**, 221 (1950); H. Fröhlich, Adv. Phys. **3**, 325 (1954).

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

[3] G. Verbist, M.A. Smondyrev, F.M. Peeters, and J.T. Devreese, Phys. Rev. B **45**, 5262 (1992).

[4] G. Verbist, F.M. Peeters, and J.T. Devreese, Solid State Commun. **76**, 1005 (1990); Phys. Rev. B **43**, 2712 (1991).

[5] J. Adamowski, Phys. Rev. B **39**, 3649 (1989); J. Adamowski and S. Bednarek, J. Phys. **4**, 2845 (1992).

[6] J. Devreese, R. Evrard, E. Kartheuser, and F. Brosens, Solid State Commmun. **44**, 1435 (1982).

[7] S.I. Pekar and M.F. Deigen, J. Exp. Theor. Phys. USSR **18**, 481 (1948).

[8] S.I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akademie Verlag, Berlin, 1954).

[9] M.A. Smondyrev and V.M. Fomin, in *Polarons & Applications*, edited by V.D. Lakhno (Wiley, New York, 1994), pp. 13–71.

[10] X. Wu, F.M. Peeters, and J.T. Devreese, Phys. Rev. B **31**, 3420

(1985); F.M. Peeters and J.T. Devreese, *ibid.* **36**, 4442 (1987).
[11] A. Ercelebi and R.T. Senger, J. Phys. Condens. Matter **6**, 5455 (1994).
[12] J. Röseler, Phys. Status Solidi **25**, 311 (1968).
[13] W. Huybrechts and J. Devreese, Phys. Rev. B **8**, 5754 (1973).
[14] T.D. Lee, F.E. Low, and D. Pines, Phys. Rev **90**, 297 (1953).
[15] J. Adamowski, B. Gerlach, and H. Leschke, Phys. Lett. **79A**, 249 (1980).
[16] S. Miyake, J. Phys. Soc. Jpn. **38**, 181 (1975); **41**, 747 (1976).
[17] R.P. Feynman, Phys. Rev. **97**, 660 (1955).
[18] F. Bassani, M. Geddo, G. Iadonisi, and D. Ninno, Phys. Rev. B **43**, 5296 (1991); V. Cataudella, G. Iadonisi, and D. Ninno, Phys. Scr. T **39**, 71 (1991).
[19] D. Reagor, E. Ahrens, S.W. Cheong, A. Migliori, and Z. Fisk, Phys. Rev. Lett. **62**, 2048 (1989).