PHYSICAL REVIEW B VOLUME 26, NUMBER 3 1 AUGUST 1982

Large bipolaron in one- and two-dimensional systems

Yasutami Takada*
Department of Physics, Purdue University, West Lafayette, Indiana 47907
(Received 8 February 1982)

The bound state of two electrons in polar crystals is investigated in various dimensional systems by numerical solution of the Bethe-Salpeter equation in which the interaction is composed of the Coulomb repulsion and the attractive interaction mediated by longitudinal, polar-optic phonons. In three-dimensional (3D) systems, no bound state is found, while in both 1D and 2D systems a bound state exists. In particular, in 1D systems, the binding energy can be of the order of the energy of the longitudinal-optic phonon (although the binding radius is large compared to the lattice constant).

I. INTRODUCTION

A problem of great physical and technological interest is to obtain a superconductor with a high transition temperature T_c. Several theoretical proposals have been made,[1-4] but none of them have been realized. Recent experiments, however, in some specially prepared samples of CuCl and CdS suggested the possibility of high-T_c superconductivity, although they have not been proved convincingly to be related to high-T_c superconductivity. Large diamagnetic anomalies have been observed in CuCl samples under high pressures at temperatures as high as 200 K.[5-8] Nearly complete diamagnetism has been reported in pressure-quenched (i.e., prepared by releasing high pressures at a rapid rate) samples of CdS at 77 K.[9,10]

If we interpret these experimental results at such high temperatures as the occurrence of superconductivity, we have to ask why high-T_c superconductivity appears in these systems in which the electron density is presumably small. Since both CuCl and CdS are ionic crystals, polar-optic phonons might play an important role in superconductivity in such low electron density systems. This idea seems to be true, particularly because the coupling constant between polar phonons and electrons becomes large owing to the decrease of the screening effect of electrons themselves with the decrease of the electron density. Concerning this point, however, the present author has already made a numerical evaluation of the effect of polar-optic phonons on T_c in one of his papers.[11] According to the paper, when the conventional theory of superconductivity which is based on the BCS theory[12] is applied to superconductivity in an ionic crystal with a rather low electron density, T_c increases first and then decreases with the decrease of the electron density. The maximum T_c thus obtained depends on the effective mass of an electron m, the optic dielectric constant ϵ_∞, the static dielectric constant ϵ_0, and the frequency of the longitudinal-optic phonon ω_l, but whatever values we may take for ϵ_0 and ω_l, this maximum value of T_c is at most $5(m/\epsilon_\infty^2)$ (K) when m is measured in the unit of the mass of a free electron. Since the factor m/ϵ_∞^2 is usually smaller than unity, T_c hardly exceeds 10 K. Therefore, when we consider superconductivity on the basis of the BCS theory, polar-optic phonons do not bring about high-T_c superconductivity even if they couple strongly with electrons.

Recently, Bishop and Overhauser suggested another possibility of obtaining high-T_c superconductivity with the help of polar-optic phonons.[13] They calculated the optic-phonon-mediated electron-electron interaction in real space for electrons at the bottom of the conduction band and speculated that even if there were only two electrons in the system, they might form a bound pair. This idea opens the way to consider that in an ionic crystal with a very low electron density, the superconductivity of electron quasimolecules, proposed by Schafroth, Butler, and Blatt,[14] might occur rather than the BCS-type superconductivity. If an energy to bind two electrons is so large that these two electrons behave like a molecule even at high temperatures, and if the number of such molecules can be increased so as to give a kind of Bose-Einstein condensation at a sufficiently high temperature, we will obtain a high-T_c superconductor.

Motivated by the consideration mentioned above, this paper treats a quantitative discussion of the bound state of two electrons in an ionic crystal. At first sight, however, one might think that even if the electron-phonon interaction becomes large, these two electrons will not be bound together, since the polarization of the lattice can at most reduce the electron-electron interaction from the direct Coulomb repulsion $e^2/\epsilon_\infty r$ to $e^2/\epsilon_0 r$ which is still positive, where r is the distance between two electrons. But this discussion forgets about the point that the dynamic interaction rather than the static one is important in the formation of a bound state, because in a bound state, physically speaking, an electron goes back and forth inside the binding radius, which is just a kind of an oscillatory motion. When the interaction become attractive at the frequency ω of the oscillation, a bound state may appear, even if the static interaction is repulsive. In the case of ionic crystals, if this ω lies between the transverse-phonon frequency ω_t and the longitudinal one ω_l, the interaction does become negative, so that a bound state of two electrons can be expected. Thus, in order to discuss a bound state of this kind, it is very important to take proper account of the ω dependence of the interaction, i.e., the retardation effect.

Another important point in treating a bound state is the dimensionality of the electron motion. As is known by an elementary problem in quantum mechanics, a bound state can be formed more easily when the dimensionality is decreased. When we consider the same problem in the momentum representation, this is related to the fact that the density of states near the bottom of the band increases with the decrease of the dimensionality. The density of states near the bottom of the band enters the problem of a bound state, because in momentum space, a bound state of two electrons can be considered to be created by successive mutual scatterings, in particular, by the use of the states near the bottom of the band in order to minimize the expense of the kinetic energy in the scatterings. In such scattering problems as this, the magnitude of the density of states as well as the strength of the potential itself plays an important role in the calculation of the transition rate. Thus we need to investigate the bound state of two electrons not only in the three-dimensional (3D) character of the electron motion but also in 2D and 1D cases in which the density of states near the bottom of the band becomes large.

The bound state of two electrons in an ionic crystal is usually called the bipolaron and has already been considered by a few workers.[15–17] However, these works are insufficient in the following two respects. First, all these discussions were limited to the strong-coupling region, i.e., the case of the small bipolaron. The small bipolaron is unfavorable for the discussion of superconductivity, because it is trapped in some place of the lattice and some additional mechanism is necessary to move the small bipolaron through the whole crystal. Second, the bipolaron itself was not investigated quantitatively except by Vinetskii.[15] By applying the method of Pekar[18] which was developed for the polaron problem in the strong-coupling region, and also by employing the variational method to determine the wave function of the bipolaron, Vinetskii obtained that in 3D systems, the bipolaron existed only in a very limited region, i.e., only when $\epsilon_\infty/\epsilon_0$ was less than 0.05.

Taking these physical and historical circumstances into account, we approach the problem of the bipolaron from the opposite direction, that is, from the weak-coupling limit and investigate the possibility of the existence of the bipolaron by the use of the lowest-order perturbation theory instead of the variational method. In Sec. II of this paper, we describe a formulation to derive an equation of motion for the bipolaron by starting from a Bethe-Salpeter equation for two electrons, in which the retardation effect is included. A method to solve the equation numerically is also shown here. Calculated results for the binding energy and the wave function are shown in Sec. III. The binding energy becomes as high as ω_l in 1D systems, although the binding radius is very large compared to the lattice constant. This indicates that the present bipolaron is not small, but large and will move rather freely in the crystal. We also discuss the criteria to choose a material which has a large binding energy. In Sec. IV, we summarize the results and discuss several problems for future research.

II. EQUATION OF MOTION FOR BIPOLARON

We consider a system composed of two electrons in a singlet spin state in an ionic crystal. Although phonons are always considered to be 3D, electrons are treated to be 1D, 2D, or 3D. In the following, we go through a formulation for a 3D system first. Some modifications which are necessary in order to discuss 1D and 2D systems are shown later.

The Hamiltonian of the system in second quantization is written as[19]

$$H=\sum_{\vec{p}\sigma}\epsilon_{\vec{p}}C^{\dagger}_{\vec{p}\sigma}C_{\vec{p}\sigma}+\sum_{\vec{q}}\omega_l a^{\dagger}_{\vec{q}}a_{\vec{q}}+\sum_{\vec{q}}\sum_{\vec{p}\sigma}V_{\vec{q}}C^{\dagger}_{\vec{p}+\vec{q}\sigma}C_{\vec{p}\sigma}(a_{\vec{q}}-a^{\dagger}_{-\vec{q}})$$
$$+\tfrac{1}{2}\sum_{\vec{q}}\sum_{\vec{p}\,\vec{p}\,'}\sum_{\sigma\sigma'}\frac{V^0(q)}{\epsilon_\infty}C^{\dagger}_{\vec{p}+\vec{q}\sigma}C^{\dagger}_{\vec{p}\,'-\vec{q}\sigma'}C_{\vec{p}\,'\sigma'}C_{\vec{p}\sigma}\;, \tag{1}$$

where $C_{\vec{p}\sigma}$ is the annihilation operator of an electron with momentum $\vec{p}$ and spin σ whose dispersion relation $\epsilon_{\vec{p}}$ is assumed to be parabolic, i.e., $\epsilon_{\vec{p}}=\vec{p}^{\,2}/2m$, $a_{\vec{q}}$ is the annihilation operator of a longitudinal-optic phonon whose energy ω_l is assumed to be dispersionless, the electron-phonon coupling constant $V_{\vec{q}}$ is given by

$$V_{\vec{q}}=-\frac{i\omega_l}{q}\left[\frac{1}{2m\omega_l}\right]^{1/4}(4\pi\alpha)^{1/2}\;, \tag{2}$$

and $V^0(q)$ is the Fourier transform of the Coulomb repulsion, given by

$$V^0(q)=4\pi e^2/q^2\;. \tag{3}$$

The total volume of the system is taken to be unity and the parameter α in Eq. (2) is usually called the dimensionless coupling constant in the polaron problem, defined by

$$\alpha=e^2\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right](m/2\omega_l)^{1/2}\;. \tag{4}$$

The origin of energy is defined as to give the energy of an electron when it is placed at an infinitely separated site from another electron. Therefore, the energy of the bound state of two electrons is negative.

In the language of thermal Green's functions, the binding energy of two electrons appears at the pole of the two-particle vertex part $\Gamma(\vec{p},\vec{p}\,';i\omega_p,i\omega_{p'};i\omega_k)$ in the space of the total-energy variable $i\omega_k$. This vertex part Γ represents the multiple-scattering process in which one electron with momentum $\vec{p}$ and energy $i\omega_p+i\omega_k/2$ collides with another electron with momentum $-\vec{p}$ and energy $-i\omega_p+i\omega_k/2$, and is scattered into the state with momentum $\vec{p}\,'$ and energy $i\omega_{p'}+i\omega_k/2$, where $\omega_p=\pi T(2p+1)$ and $\omega_k=2\pi Tk$ with the temperature T and integers p and k. In the lowest order of the interaction, the equation for this vertex part can be written as

$$\Gamma(\vec{p},\vec{p}\,';i\omega_p,i\omega_{p'};i\omega_k)$$
$$=V(\vec{p}-\vec{p}\,',i\omega_p-i\omega_{p'})-T\sum_{\omega_{p''}}\sum_{\vec{p}\,''}V(\vec{p}-\vec{p}\,'',i\omega_p-i\omega_{p''})\frac{1}{i\omega_{p''}+i\omega_k/2-\epsilon_{\vec{p}\,''}}\,\frac{1}{-i\omega_{p''}+i\omega_k/2-\epsilon_{-\vec{p}\,''}}$$
$$\times\Gamma(\vec{p}\,'',\vec{p}\,';i\omega_{p''},i\omega_{p'};i\omega_k)\;, \tag{5}$$

where the total effective interaction between electrons $V(\vec{q},i\omega_q)$ is given by

$$V(\vec{q},i\omega_q)=\frac{V^0(q)}{\epsilon_\infty}+V_{\vec{p}}V^*_{-\vec{q}}\frac{2\omega_l}{(i\omega_q)^2-\omega_l^2}\;. \tag{6}$$

The first term is the Coulomb repulsion and the second one is the phonon mediated interaction. With the use of the dielectric function $\epsilon(i\omega_q)$, defined by

$$\epsilon(i\omega_q)=\epsilon_\infty+(\epsilon_0-\epsilon_\infty)\frac{\omega_t^2}{\omega_t^2-(i\omega_q)^2}\;, \tag{7}$$

$V(\vec{q},i\omega_q)$ is rewritten as

$$V(\vec{q},i\omega_q)=V^0(q)/\epsilon(i\omega_q)\;. \tag{8}$$

The energy of the transverse-optic phonon ω_t is related to ω_l through

$$\omega_t=\sqrt{\beta}\omega_l\;, \tag{9}$$

where the ionicity of the crystal β is defined by

$$\beta=\epsilon_\infty/\epsilon_0\;. \tag{10}$$

As $i\omega_k$ in Eq. (5) approaches the binding energy E_0, the vertex part tends to infinity by taking the following form:

$$\Gamma(\vec{p},\vec{p}\,';i\omega_p,i\omega_{p'};i\omega_k) \to \frac{\tilde{\Gamma}(\vec{p},i\omega_p)\tilde{\Gamma}(\vec{p}\,',i\omega_{p'})^*}{i\omega_k - E_0}\,, \qquad (11)$$

while the first term in the right-hand side of Eq. (5) gives only a finite contribution and can be neglected compared with other terms in Eq. (5). Then, putting Eq. (11) into Eq. (5) and dividing both sides of the equation by the common factor, we obtain the following equation:

$$F(\vec{p},i\omega_p) = -G_0(\vec{p},i\omega_p)G_0(-\vec{p},-i\omega_p) \times T\sum_{\omega_p}\sum_{\vec{p}\,'} V(\vec{p}-\vec{p}\,',i\omega_p - i\omega_{p'}) \times F(\vec{p}\,',i\omega_{p'})\,, \qquad (12)$$

where $G_0(\vec{p},i\omega_p)$ and $F(\vec{p},i\omega_p)$ are, respectively, defined as

$$G_0(\vec{p},i\omega_p) = \frac{1}{i\omega_p - \epsilon_{\vec{p}} + E_0/2}\,, \qquad (13)$$

and

$$F(\vec{p},i\omega_p) = \tilde{\Gamma}(\vec{p},i\omega_p)G_0(\vec{p},i\omega_p) \times G_0(-\vec{p},-i\omega_p)\,. \qquad (14)$$

Equation (12) is just the same equation as the gap equation for the Cooper pair at $T = T_c$ in the weak-coupling superconductivity.[20] The only difference between Eq. (12) and the gap equation is in $G_0(\vec{p},i\omega_p)$. In the usual theory of superconductivity, the Fermi energy ϵ_F appears in Eq. (13) instead of $E_0/2$. Since ϵ_F is positive and very large compared to the binding energy of the Cooper pair, the bound state of the Cooper pair is in the continuum of the single-particle states. On the other hand, we consider $E_0/2$ to be negative and thus treat a bound state below the continuum of the single-particle states. Except for such a difference in the Fermi level, Eq. (12) is the same as the gap equation mathematically. Thus we can apply the same analytical method to the solution of this equation as developed in the theory of superconductivity.[21] Performing the frequency sum in Eq. (12) and making an analytical continuation from $i\omega_p$ to $\omega + i0^+$ to use the retarded Green's function which will be denoted by the superscript R, Eq. (12) leads to the following equation at $T = 0$:

$$(2\epsilon_{\vec{p}} - E_0)\phi_{\vec{p}} = -\sum_{\vec{p}\,'}\int_0^\infty \frac{d\omega'}{\pi}\,\mathrm{Im}F^R(\vec{p}\,',\omega')V_{\vec{p}\vec{p}\,'}(E_0)\,, \qquad (15)$$

where the function $\phi_{\vec{p}}$ is defined by

$$\phi_{\vec{p}} = \int_0^\infty \frac{d\omega}{\pi}\,\mathrm{Im}F^R(\vec{p},\omega)\,, \qquad (16)$$

and the interaction $V_{\vec{p}\vec{p}\,'}(E_0)$, which takes account of the retardation effect, is given by

$$V_{\vec{p}\vec{p}\,'}(E_0) = \int_0^\infty \frac{2}{\pi}d\Omega\,\frac{\epsilon_{\vec{p}} + \epsilon_{\vec{p}\,'} - E_0}{\Omega^2 + (\epsilon_{\vec{p}} + \epsilon_{\vec{p}\,'} - E_0)^2} \times V(\vec{p}-\vec{p}\,',i\Omega)\,. \qquad (17)$$

In the case of ionic crystals, the effective interaction is given by Eq. (8). Therefore, $V_{\vec{p}\vec{p}\,'}(E_0)$ is easily calculated as

$$V_{\vec{p}\vec{p}\,'}(E_0) = \frac{V^0(\vec{p}-\vec{p}\,')}{\epsilon_\infty}\cdot\frac{\epsilon_{\vec{p}} + \epsilon_{\vec{p}\,'} - E_0 + \beta\omega_l}{\epsilon_{\vec{p}} + \epsilon_{\vec{p}\,'} - E_0 + \omega_l}\,. \qquad (18)$$

In the lowest-order of the interaction, the pole of $F^R(\vec{p},\omega)$ for $\omega > 0$ comes from $G_0^R(p,\omega)$. Thus $\mathrm{Im}F^R(\vec{p},\omega)$ in Eq. (15) can be approximated well by a single delta function, namely,

$$\mathrm{Im}F^R(\vec{p},\omega) = \pi\phi_{\vec{p}}\,\delta(\omega - \epsilon_{\vec{p}} + \tfrac{1}{2}E_0)\,. \qquad (19)$$

Substituting Eq. (19) into Eq. (15), we finally obtain the equation of motion for the bipolaron as

$$\frac{\vec{p}^{\,2}}{m}\phi_{\vec{p}} + \sum_{\vec{p}\,'} V_{\vec{p}\vec{p}\,'}(E_0)\phi_{\vec{p}\,'} = E_0\phi_{\vec{p}}\,. \qquad (20)$$

In order to see the meaning of $\phi_{\vec{p}}$, let us consider the case in which there is no retardation effect, that is, $V(\vec{p}-\vec{p}\,',i\Omega)$ is independent of the frequency variable $i\Omega$ and can be simply written as $V(\vec{p}-\vec{p}\,')$. In such a case, $V_{\vec{p}\vec{p}\,'}(E_0)$ is reduced to the interaction $V(\vec{p}-\vec{p}\,')$ itself. Then Eq. (20) is just the Schrödinger equation in the momentum representation for the relative motion of two electrons in the potential of

$$V(\vec{r}) = \sum_{\vec{q}} \exp(i\vec{q}\cdot\vec{r})\cdot V(\vec{q})\,.$$

From this observation, $\phi_{\vec{p}}$ is known to play a role of the wave function for the relative motion in the momentum representation.

Since the system is isotropic, the s-wave state will be the lowest one for $\phi_{\vec{p}}$. In the s-wave state, $\phi_{\vec{p}}$ depends only on the magnitude of $\vec{p}$. By introducing the nondimensional variable t, defined by

$$t = \epsilon_{\vec{p}}/\omega_l \qquad (21)$$

we can transform Eq. (20) as

$$(t+\tilde{t})\phi(t)=-\frac{\alpha}{2\pi(1-\beta)}\times\int_0^{\infty}dt'K(t,t';\tilde{t})\phi(t')\ , \tag{22}$$

where $\phi(t)=\phi_{\vec{p}}$, $\tilde{t}=-E_0/2\omega_l$, and the kernel of the integral equation is given by

$$K(t,t';\tilde{t})=\frac{1}{\sqrt{t}}\ln\left|\frac{\sqrt{t}+\sqrt{t'}}{\sqrt{t}-\sqrt{t'}}\right|\frac{t+t'+2\tilde{t}+\beta}{t+t'+2\tilde{t}+1}\ . \tag{23}$$

Equation (22) can be solved numerically by dividing the interval $(0,\infty)$ in the t space into small ones, (t_i,t_{i+1}). In each small interval (t_i,t_{i+1}), $\phi(t)$ is assumed to be constant ϕ_i. Then Eq. (22) is equivalent to the following matrix equation:

$$(\bar{t}_i+\tilde{t})\phi_i=-\sum_j J_{ij}(\tilde{t})\phi_j\ , \tag{24}$$

with $\bar{t}_i=(t_i+t_{i+1})/2$ and

$$J_{ij}(\tilde{t})=\frac{\alpha}{2\pi(1-\beta)}\int_{t_j}^{t_{j+1}}dt'K(\bar{t}_i,t';\tilde{t})\ . \tag{25}$$

The binding energy in the nondimensional form $\tilde{t}$ is obtained by the calculation of the zero point of the determinant of the matrix $(\bar{t}_i+\tilde{t})\delta_{ij}+J_{ij}(\tilde{t})$. With the use of $\tilde{t}$ thus obtained, ϕ_i normalized by ϕ_0 which is the value of $\phi(t)$ at $t=\bar{t}_0$ is given by the solution of the following matrix equation:

$$\sum_j[(\bar{t}_i+\tilde{t})\delta_{ij}+J_{ij}(\tilde{t})-J_{0j}(\tilde{t})]\phi_j=(\bar{t}_0+\tilde{t})\phi_0\ . \tag{26}$$

As for the partition points, $|t_{i+1}-t_i|\sim10^{-8}$ is chosen for small t_i and then is increased logarithmically. The maximum value for t_i is chosen to be 500; it was checked that this cutoff value does not give any significant changes in the obtained results.

Even when we treat a 1D, or a 2D system, we obtain the same equation of motion as in Eq. (20). The only modification appears in the calculation of the interaction $V_{\vec{p}\vec{p}'}(E_0)$, in particular, $V^0(\vec{p}-\vec{p}')$ in Eq. (18). Once $V^0(\vec{q})$ is changed with the change of the dimensionality, the kernel $K(t,t';\tilde{t})$ in Eq. (22) should be changed. In a 2D case, the momentum $\vec{p}$ in Eq. (20) should be understood as a 2D vector in the x-y plane. When electrons can be assumed to be localized well around $z=0$ and thus the square of the wave function in the z direction may be taken as a delta function $\delta(z)$, $V^0(\vec{q})$ is calculated as

$$V^0(\vec{q})=2\pi e^2\Big/\left[q_x^2+q_y^2\right]^{1/2}\ , \tag{27}$$

and the kernel in Eq. (22) is changed into

$$K(t,t';\tilde{t})=\frac{1}{\sqrt{t}+\sqrt{t'}}K\left[\frac{2(tt')^{1/4}}{\sqrt{t}+\sqrt{t'}}\right]\times\frac{t+t'+2\tilde{t}+\beta}{t+t'+2\tilde{t}+1}\ , \tag{28}$$

with the use of the elliptic integral of the first kind $K(k)$. For a 1D system, $\vec{p}$ in Eq. (20) is now a 1D vector in the x direction. Assuming the azimuthal symmetry around the x axis and writing the wave function of the electron in the y-z plane as $\chi((y^2+z^2)^{1/2})$, we can obtain $V^0(\vec{q})$ as

$$V^0(q_x)=\int dq_z dq_z\frac{4\pi e^2}{q_x^2+q_y^2+q_z^2}\times\left[\int_0^{\infty}r\,dr\,|\chi(r)|^2J_0(q_xr)\right]^2 \tag{29}$$

with the Bessel function of the zeroth order $J_0(z)$. When we take $\chi(r)$ as

$$\chi(r)=\left[\frac{2}{\pi}\right]^{1/2}\frac{1}{\langle r\rangle}\exp(-r/\langle r\rangle)\ , \tag{30}$$

$V^0(q_x)$ can be calculated analytically as

$$V^0(q_x)=e^2F(\langle r\rangle q_x/2\gamma)\ , \tag{31}$$

where $F(z)$ is given by

$$F(z)=\frac{[-\ln\gamma^2z^2-(1-\gamma^2z^2)(3-\gamma^2z^2)/2]}{(1-\gamma^2z^2)^3}\ , \tag{32}$$

and the parameter γ is defined as

$$\gamma=\frac{1-\beta}{2\alpha}\frac{\langle r\rangle}{a^*}\ , \tag{33}$$

with the effective Bohr radius $a^*=\epsilon_\infty/me^2$. With the use of $F(z)$, the kernel in the 1D case is obtained as

$$K(t,t';\tilde{t})=\frac{1}{\sqrt{t'}}\frac{1}{2}[F(\sqrt{t}-\sqrt{t'})+F(\sqrt{t}+\sqrt{t'})]\times\frac{t+t'+2\tilde{t}+\beta}{t+t'+\tilde{2}t+1}\ . \tag{34}$$

The parameter $\langle r\rangle$ represents the spread of the electron in the y-z plane around the x axis. However, unlike the 2D case, this parameter cannot be set equal to zero, because $V^0(q_x)$ becomes infinite

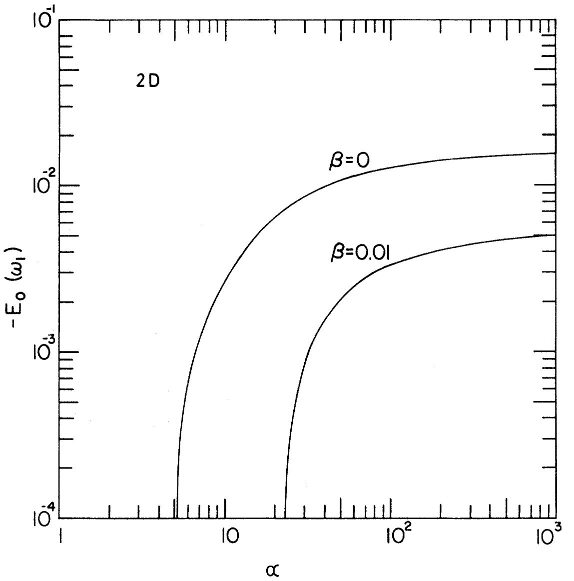

FIG. 1. Calculated binding energy $-E_0$ in units of ω_l as a function of α for two values of β in 2D systems at $T=0$.

at $\langle r \rangle=0$. Therefore, in 1D systems, calculations will be done for several nonzero values of $\langle r \rangle$.

III. RESULTS OF CALCULATION

When the electron motion is 3D, no bound state is found in the present weak-coupling approximation, even though the attractive interaction mediated by phonons is large enough to produce deep attractive potential wells in real space, as pointed out by Bishop and Overhauser.[13] This result indicates that the kinetic-energy term of each electron resists the formation of the bound state so strongly that no bound states can be created. In the strong-coupling approximation, however, we can imagine a different situation by considering the fact that even when there is only one electron in the system, the electron is trapped by the lattice to produce a small polaron. Namely in the strong-coupling limit, the effect of the kinetic energy of each electron is weakened before we treat two electrons (to be precise, two small polarons in this case). Thus we can expect the existence of the bound state in the strong-coupling limit, just as predicted by Vinetskii.[15]

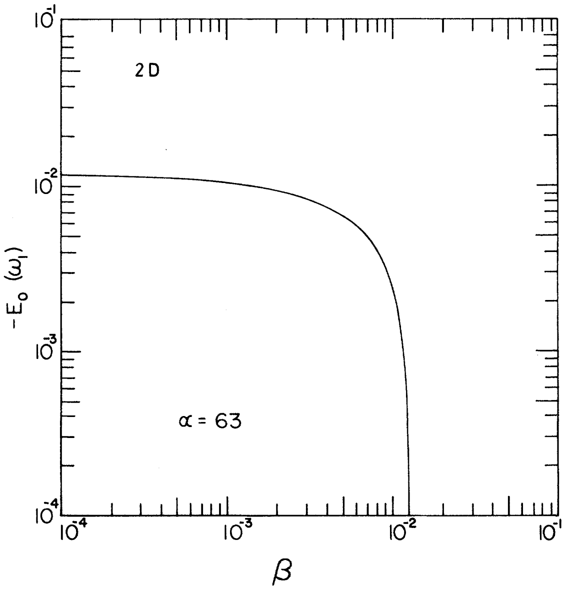

FIG. 2. Binding energy $-E_0$ in units of ω_l as a function of β in 2D systems at $T=0$. The parameter α is taken to be 63.

When we consider the problem not in real space but in momentum space, we can understand probably more easily the reason for the absence of the bound state in 3D systems in the weak-coupling approximation. Since the state of the large bipolaron (the bipolaron in the weak-coupling limit) is created by the use of the states with small momentum, the density of states of such states, in particular, near the bottom of the band should be large. In a 3D system, however, the density of states vanishes at the bottom of the band and thus the bound pair cannnot be formed. In the strong-coupling theory, on the other hand, the states with large momentum become more important than those with small momentum. In such a case, there is no difficulty in creating the bound pair, even when the density of states at the bottom of the band vanishes.

Compared with a 3D system, a 2D one has a better chance to provide the bound state, because in a 2D system, the density of states is constant and is finite even at the bottom of the band. According to expectation, the bound state is found and the calculated binding energy $-E_0$ in the unit of the energy ω_l is plotted in Fig. 1 as a function of α for two values of β. Since only one parameter α appears in the polaron problem, one might think that $-E_0$ depends only on α, but actually $-E_0$ also depends on β in a rather interesting way, as illustrated in Fig. 2. As long as β is smaller than some critical value (0.01 in the case of Fig. 2), $-E_0$ does not change so much with the increase of β. However, once β exceeds this critical value, $-E_0$ decreases very rapidly and the bound state itself disappears at the value of β slightly larger than this critical value. The reason why $-E_0$ behaves in this way is simple. As mentioned in

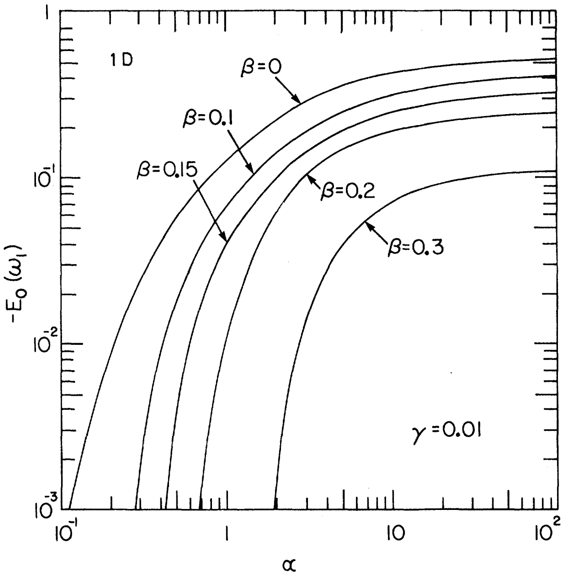

FIG. 3. Calculated binding energy $-E_0$ in units of ω_l as a function of α in 1D (chainlike) systems at $T=0$. Calculations are done for several values of β. The parameter γ which describes the size of the chain is taken to be 0.01.

Sec. I, each electron oscillates inside the binding radius in the bound state with the frequency of the order of $-E_0$. In order for the interaction between electrons to be attractive, this frequency should be within the range from $\omega_t=\sqrt{\beta}\omega_l$ to ω_l. Even though β is increased from zero and thus ω_t is increased, there is no essential change in the interaction, that is, the interaction is still attractive, as long as ω_t is less than the value of the order of $-E_0$ given at $\beta=0$. Therefore, $-E_0$ is nearly independent of β in this region. However, once ω_t exceeds some critical value which is about $-E_0$ at $\beta=0$, the interaction between electrons is no longer attractive and does not provide the bound state.

In any case, the bound state appears in a 2D system, but the region in the (α,β) plane in which the bound pair is formed is very limited. The parameter α should be larger than about 5 and another parameter β should be smaller than about 0.01. As a result, it is very difficult to find materials which meet this condition. In addition, even if we obtain some material which satisfies this condition, $-E_0$ becomes at most as large as one hundredth of ω_l. Namely, we can never expect $-E_0$ larger than about 10 K. This indicates that a high-T_c superconductor will not be obtained with the use of this kind of system.

In a 1D system, we can expect an even larger binding energy, because the density of states at the bottom of the band is infinite in this case. In Fig. 3, $-E_0$ is drawn as a function of α for several values of β. The parameter γ which describes the spread of the system in the direction perpendicular to that of the electron conduction, as defined in Eq. (33), is taken to be 0.01. The qualitative behavior of the curves in this figure is just the same as in Fig. 1 for 2D systems, but there is a great quantitative difference. The bound state appears even when α is very small, i.e., as large as 0.1. The binding energy can be as large as one half of ω_l, which means that $-E_0$ becomes larger than 100 K. The dependence of $-E_0$ on β is shown in Fig. 4 for three values of α. The bound state is formed even if β is larger than 0.3 for $\alpha=5$.

In order to show that the present bipolaron is not small but large, an example of the wave function is given in real space in Fig. 5. The case of LiF is treated here, so that $\alpha=5.13$, $\beta=0.227$, $\omega_l=960$ K, and $a^*=1.02$ Å.[22] Instead of the parameter γ, the spread factor $\langle r\rangle/a^*$ is specified to be 0.2. The wave function $\phi(x)$, which is the Fourier transform of $\phi_{\vec{p}}$, is small when x is very small, because for small x, the Coulomb repulsion dominates to keep away an electron from another one. When x is increased, $\phi(x)$ has a peak at $x\approx 12a^*$ and a tail which spreads out more than $100a^*$. For x larger than $150a^*$, $\phi(x)$ shows an oscillatory behavior, but its magnitude is so small

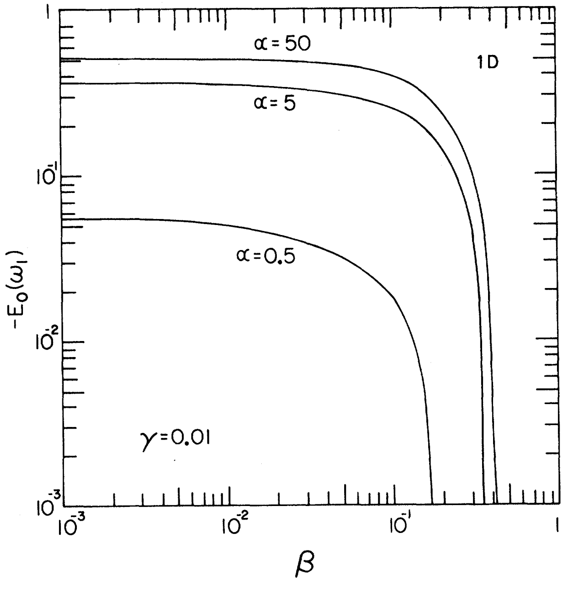

FIG. 4. Binding energy $-E_0$ as a function of β for three values of α in 1D systems at $T=0$. The parameter γ is taken to be 0.01.

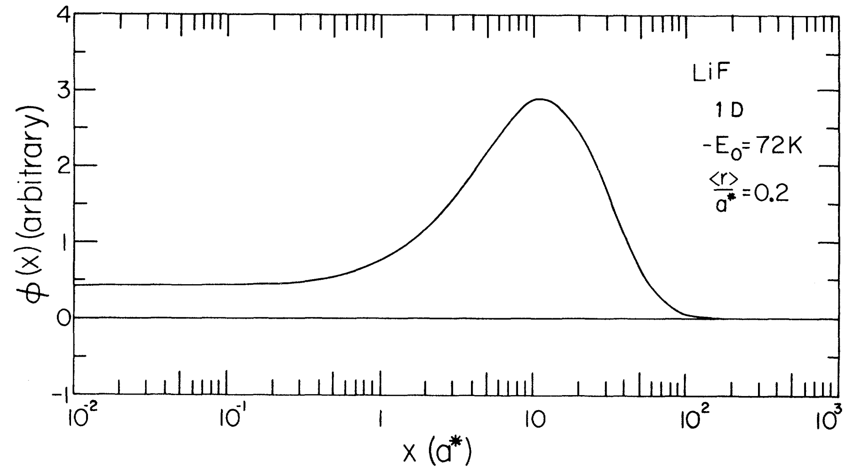

FIG. 5. Wave function $\phi(x)$ in real space for the case of LiF in which a 1D (chainlike) structure is assumed to exist. This wave function is the Fourier transform of $\phi_{\vec{p}}$. The size of the chain $\langle r \rangle$ is taken to be $0.2a^*$, where a^* is the effective Bohr radius. The calculated binding energy for this case is 72 K at $T=0$.

that we cannot recognize it in the figure. In this way, the binding radius is very large and this is the reason why the bipolaron in the present case is called the "large" bipolaron.

Since the bound state appears in a very wide region in the (α,β) space in 1D systems, we can give several materials which will give a large binding energy. The criteria to look for appropriate materials are: (i) α should be rather larger, (ii) β should be small, and (iii) ω_l should be large. Guided by these criteria, lithic halides, in particular, LiF can be pointed out. Thallous halides like TlCl can also meet these conditions, although ω_l is rather small. In TlCl, the parameters α, β, ω_l, and a^* are, 2.56, 0.133, 238 K, and 8.02 Å, respectively.[22] Calculated results of the binding energy for TlCl and LiF are shown in Fig. 6 as a function of $\langle r \rangle / a^*$. Since the interaction $V^0(q_x)$ in Eq. (31) decreases and consequently the electron-phonon interaction becomes small with the increase of $\langle r \rangle / a^*$, $-E_0$ decreases with the increase of $\langle r \rangle / a^*$. However, the rate of this decrease depends on the material, in particular, on the parameter β. In TlCl which has a smaller β than LiF, $-E_0$ decreases more slowly than that in LiF, as $\langle r \rangle / a^*$ is increased. Although no information is available for this parameter $\langle r \rangle / a^*$ at present, $\langle r \rangle$ is probably of the order of a^*. Therefore, it is desirable to find a material having very small β, because in such a material, $-E_0$ is still very large at $\langle r \rangle / a^* = 1$. In order to show that this is true, the case of $SrTiO_3$ is also plotted in Fig. 6. In $SrTiO_3$, we take $\alpha=4.04$, $\beta=2.3\times10^{-4}$, $\omega_l=607$ K, and $a^*=1.62$ Å, but there are two problems in the application of the present theory to $SrTiO_3$. First, the smallness of β stems from the presence of a ferroelectric soft-phonon mode, but the transverse-phonon mode which gives the soft mode at low temperatures is no longer soft at high temperatures. Therefore, even though $-E_0$ at $T=0$ is very large, the bipolaron state will not exist at high temperatures. Second, we have calculated $-E_0$ by assuming that there is no $\vec{q}$ dependence in ϵ_0, ϵ_∞, and ω_l, but in fact, there is a strong $\vec{q}$ dependence

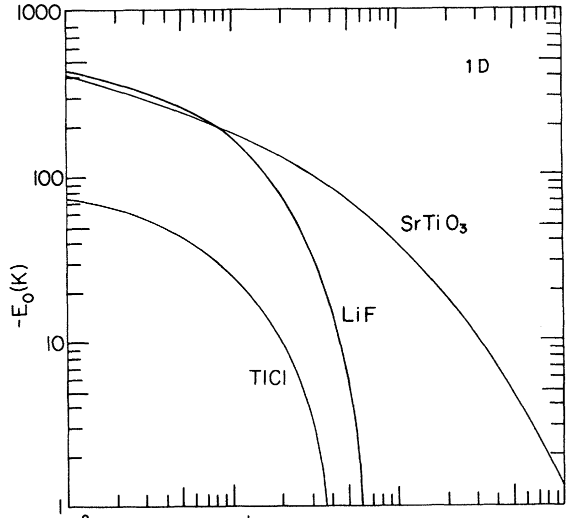

FIG. 6. Predicted binding energy $-E_0$ in K in 1D (chainlike) systems for TlCl, LiF, and $SrTiO_3$ as a function of the size of the chain $\langle r \rangle$ normalized by the effective Bohr radius a^*. Calculations are done at $T=0$.

in ϵ_0 in the case of SrTiO$_3$, though other parameters, i.e., ϵ_∞ and ω_l are nearly independent of $\vec{q}$. In spite of such problems, we present the result of SrTiO$_3$, mainly because we can point out that any material having a ferroelectric soft-phonon mode is a very good candidate for a system having a very large binding energy, even though the parameter α is not so large.

IV. DISCUSSIONS

We have found results about the bound state of two electrons in an ionic crystal which are interesting from the viewpoint of optic properties of such a system as well as high-T_c superconductivity. The large bipolaron state exists in 1D and 2D systems. In the case of 1D systems, the binding energy can be larger than 100 K. These conclusions are based on calculations in the weak-coupling approximation, but they are probably true even after strong-coupling effects are included. Since in 3D systems, the bipolaron state exists in the strong-coupling limit[15] in contrast with our result in the weak-coupling approximation, strong-coupling effects do not destroy the bipolaron state but stabilize it.

As mentioned in Sec. II, the main difference between the BCS-type superconductivity[12] and that of electron quasimolecules[14] is in the position of the Fermi level. In the former case, it is within the conduction band, while in the latter case, it is below the bottom of the band. One important consequence coming from this difference of the Fermi level is that in the formation of the bound pair in a 1D system, the latter takes a full advantage of the large density of states near the bottom of the band, while the former does not use the states near the bottom of the band because they are already occupied and cannot be used for the scatterings of the formation of the pair.

In order to obtain the superconductivity of electron quasimolecules[14] in a 1D (i.e., chainlike) system, however, there are two problems to be solved. First, Bose-Einstein condensation does not occur in a 1D, noninteracting boson system.[23] Second, there is an argument that carriers in a 1D system are localized even by the existence of very weak charged centers or disorders.[24] We might be able to solve these two problems by considering either the intra- and/or the interchain interactions between the bipolarons, or the possibility of the hopping of the bipolarons between chains, but the study on these problems is left in the future.

Our calculations were initiated to explain the anomalous experimental results in CuCl and CdS.[5-10] When we use the usually accepted parameters of α, β, and ω_l for CuCl and CdS, we cannot obtain large binding energies of the bipolaron for these materials, even if we assume that some 1D (chainlike) system is created in these materials. Therefore, we cannot give any explanation about these experiments at present. However, there is a possibility that the parameters α, β, and ω_l are different from the usually accepted values in the specially prepared samples of CuCl and CdS. In fact, Leftkowitz suggested the existence of the ferroelectric soft-phonon mode in the sample of CuCl which showed the diamagnetic anomalies.[25] If such a soft mode really exists, the parameter β becomes nearly equal to zero, which gives a large binding energy of the bipolaron, provided that a chainlike structure is created in the sample. A precise knowledge of these parameters α, β, and ω_l in these specially prepared samples is indispensable for further study on the anomalous phenomena found in these materials.

So far, we have discussed the effect of the polar-optic phonon on the bound state of two electrons, but just the same argument can be applied to the electron system in contact with the highly polarizable material which is the system usually treated in the discusssion of the exciton mechanism of superconductivity.[1,2,4] For example, when we consider a narrow-gap semiconductor as a polarized material, the dielectric function $\epsilon(i\omega_q)$ may be given by

$$\epsilon(i\omega_q)=\epsilon_\infty+\frac{\omega_p^2}{E_g^2-(i\omega_q)^2}\ , \tag{35}$$

where E_g is the band gap averaged over the Brillouin zone of the narrow-gap semiconductor and ω_p is the plasmon energy of the valence electrons in the semiconductor. By using Eq. (35) in the calculation of the interaction $V(\vec{q},i\omega_q)$ instead of Eq. (7) and then by redefining the parameters α, β, and ω_l as

$$\alpha=e^2\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_\infty+\omega_p^2/E_g^2}\right]\times[m/2(E_g^2+\omega_p^2/\epsilon_\infty)^{1/2}]^{1/2}\ , \tag{36}$$

$$\beta=E_g^2/(E_g^2+\omega_p^2/\epsilon_\infty)\ , \tag{37}$$

and

$$\omega_l=(E_g^2+\omega_p^2/\epsilon_\infty)^{1/2}\ , \tag{38}$$

respectively, we can obtain the binding energy of the bound state mediated by the polarization of the narrow-gap semiconductor. If E_g can be taken much smaller than ω_p which is supposed to be of the order of 10^5 K, and if α can still be taken not too small, we will obtain a very large binding energy even in a 2D system. Thus, by the use of this kind of system, we might be able to realize an excitonic superconductor not in the BCS-type but in the type of electron quasimolecules.

ACKNOWLEDGMENTS

The author would like to thank Professor A. W. Overhauser for stimulating discussions and the critical reading of the manuscript. He also wishes to thank Professor M. F. Bishop and Dr. M. Huberman for useful discussions. He is grateful to the National Science Foundation and the NSF-MRL program for support.

---

[*] On leave of absence from Department of Physics, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan.

[1] W. A. Little, Phys. Rev. 134, A1416 (1964); D. Davis, H. Gutfreund, and W. A. Little, Phys. Rev. B 13, 4766 (1976).

[2] V. L. Ginzburg, Contemp. Phys. 9, 355 (1968); Usp. Fiz. Nauk 101, 185 (1970) [Sov. Phys.—Usp. 13, 335 (1970)].

[3] E. A. Pashitskii, Zh. Eksp. Teor. Fiz. 55, 2387 (1968) [Sov. Phys.—JETP 28, 1267 (1969)]; E. A. Pashitskii and V. M. Chernousenko, *ibid.* 60, 1483 (1971) [*ibid.* 33, 802 (1971)].

[4] D. Allender, J. Bray, and J. Bardeen, Phys. Rev. B 7, 1020 (1973).

[5] N. B. Brandt, S. V. Kuvshinnikov, A. P. Rusakov, and M. Semyonov, Zh. Eksp. Teor. Fiz. Pis'ma Red. 27, 37 (1978) [JETP Lett. 27, 33 (1978)].

[6] C. W. Chu, A. P. Rusakov, S. Huang, S. Early, T. H. Geballe, and C. Y. Huang, Phys. Rev. B 18, 2116 (1978).

[7] I. Lefkowitz, J. S. Manning, and P. E. Bloomfield, Phys. Rev. B 20, 4506 (1979).

[8] T. H. Geballe and C. W. Chu, Comments Solid State Phys. 9, 115 (1979).

[9] C. G. Homan, D. P. Kendall, and R. K. MacCrone, Solid State Commun. 32, 521 (1979); E. Brown, C. G. Homan, and R. K. MacCrone, Phys. Rev. Lett. 45, 478 (1980); C. G. Homan, K. Laojindapun, and R. K. MacCrone, *ibid.* (in press).

[10] R. K. MacCrone and C. G. Homan, Solid State Commun. 35, 615 (1980); C. G. Homan and R. K. MacCrone, J. Non-Cryst. Solids 40, 369 (1980).

[11] Y. Takada, J. Phys. Soc. Jpn. 49, 1267 (1980).

[12] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

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

[14] M. R. Schafroth, S. T. Butler, and J. M. Blatt, Helv. Phys. Acta 30, 93 (1957).

[15] V. L. Vinetskii and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. 33, 730 (1957) [Sov. Phys.—JETP 6, 560 (1958)]; V. L. Vinetskii, *ibid.* 40, 1459 (1961) [*ibid.* 13, 1023 (1961)].

[16] P. W. Anderson, Phys. Rev. Lett. 34, 953 (1975).

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

[18] S. I. Pekar, *Untersuchungen uber die Elekronen Theorie der Kristalle* (Akademie, Berlin, 1954); See also G. R. Allcock, in *Polarons and Excitons,* edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1962), p. 45.

[19] In this paper, we employ units in which $c=\hbar=k_B=1$.

[20] See, for example, L. P. Gor'kov Zh. Eksp. Teor. Fiz. 34, 735 (1958) [Sov. Phys.—JETP 7, 505 (1958)], and also see Eq. (2.3) in Ref. 21.

[21] See, for example, Y. Takada, J. Phys. Soc. Jpn. 45, 786 (1978).

[22] E. Kartheuser, in *Polarons in Ionic Crystals and Polar Semiconductors,* edited by J. T. Devreese (North-Holland, Amsterdam, 1972), p. 717.

[23] See, for example, J. M. Blatt, *Theory of Superconductivity* (Academic, New York, 1964), p. 57.

[24] N. F. Mott and W. D. Twose, Adv. Phys. 10, 107 (1961); R. Landauer, Philos. Mag. 21, 863 (1970); See also D. J. Thouless, in *Physics in One Dimension,* edited by J. Bernasconi and T. Schneider (Springer, Berlin, 1981), p. 306.

[25] I. Lefkowitz (private communication).