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Path-integral treatment of the large-bipolaron problem

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We derive analytical expressions for the upper bound of the ground-state energy E_0 and an estimate for the effective mass of a large bipolaron using path-integral methods.

I. INTRODUCTION

The possibility of formation of a bipolaron structure in some crystals or polar semiconductors was first considered by Pekar[1] and subsequently by Schultz.[2] Normally two identical electrons or holes in a solid do not form a bound state due to Coulomb repulsion between their screened charges. However, the presence of electron-phonon coupling in a lattice gives rise to additional effects. In particular, this coupling can be strong enough in an ionic crystal to overcome the Coulomb repulsion, resulting in the formation of a stable electron or hole pair, called the bipolaron. Thus the possibility of creating a bipolaron in solids depends on the competition between the Coulomb repulsion of electrons or holes and the attractive interactions due to the distortions of the lattice induced by them. This problem has been considered extensively in the literature.[3–12]

The importance of bipolarons in semiconductor technology was first pointed out by Anderson.[13] In order to explain the anomalous behavior of amorphous semiconductors, Anderson[13] introduced the idea of a negative-U center, where two electrons can bind to form a bipolaron in the singlet state. This idea was explored by many others subsequently, giving several examples of negative-U centers.[14–17] The original concept of the intersite singlet bipolaron has also been extended to the intrasite singlet bipolaron.[18] The issue of stability of such a bipolaron has also received some attention.[18–20] Alexandrov and collaborators[21–24] have also explored the possibility of superconductivity of singlet bipolarons. The current interest in bipolarons is due to the role they might play in understanding the mechanism of high-temperature superconductivity.[25] A plausible mechanism proposed[26,27] is that the bipolarons of high enough density undergo a Bose-Einstein condensation leading to the superconducting state.

The bipolaron may be "small' or "large" (Fröhlich type), depending on the details of the electron-phonon interaction. There is both theoretical[18] and experimental[19] evidence for the formation of small bipolarons in polar materials. A large number of theoretical calculations, including the recent one by Adamowski,[6] predict the stability of Fröhlich bipolarons. There seem to be no experimental observations so far supporting the theory. The issue is still open and it may be of interest to probe it further.

In the present paper we consider the problem of the binding of two electrons or two holes in an ionic crystal or a polar semiconductor. In this material the dominant coupling with the phonons is that with the longitudinal-optical (LO) phonons described by the Fröhlich interactions. We study the problem by an extension of the path-integral variational method employed by Feynman[28,29] in the polaron problem. The advantage here is that the bipolaron energy and the effective mass can be obtained for arbitrarily coupling strength of the electron-phonon interaction. We obtain analytically an estimate for the ground-state energy for the bipolaron both in the weak- as well as the strong-coupling limit. We examine the stability of the bipolaron based on these estimates. For arbitrary coupling, a numerical evaluation might be necessary. We define the bipolaron effective mass by generalizing the definition for the polaron effective mass given by Saitoh.[30] The definition is based on the response of the bipolaron when its center of mass is coupled to a small perturbative force and seems to be adequate.[31] We mention here that Hiramoto and Toyozawa[32] have also calculated the bipolaron energy with the help of the path-integral method and obtained the binding energy of the bipolaron in the strong-coupling limit. These authors have, however, used a truncated Fourier expansion of the Coulomb potential between the pair of electrons (holes). Also, their definition of effective mass is different from ours, being similar to what Feynman used in his work on polarons. The form of the Hamiltonian used in Ref. 32 also precludes the possibility of obtaining analytical results for quantities of interest.

The basic formulation of the problem is presented in Sec. II. This is used in Sec. III to obtain the ground-state energy and effective mass of the bipolaron. A discussion on the stability of the bipolaron is also included. Concluding remarks are added in Sec. IV.

II. BASIC FORMULATION OF THE PROBLEM

For the three-dimensional Fröhlich bipolaron problem, the classical Lagrangian consists of a sum of the Lagrangian of the free phonons, the Lagrangian of the two electrons, and the Lagrangian corresponding to the interaction between electrons and phonons. The electronic Lagrangian consists of the sum of the kinetic energies of the two electrons and the potential energy due to their mutual Coulomb repulsion. The action integral may therefore be written in the form similar to that of the polaron problem as

$$S=\int_0^\beta[(\dot{\mathbf{x}}_1^2+\dot{\mathbf{x}}_1^2)/2+\delta/|\mathbf{x}_1-\mathbf{x}_2|]dt+\sum_k(\dot{\mathbf{q}}_k^2+\mathbf{q}_k^2)/2+(\alpha\pi\sqrt{2})^{1/2}\sum_k(\mathbf{q}_k/k)[(\exp(i\mathbf{k}\cdot\mathbf{x}_1)+\exp(i\mathbf{k}\cdot\mathbf{x}_2)] \ . \tag{2.1}$$

Here $\mathbf{x}_i$ and $\mathbf{q}_k$ are the coordinates of the electrons and the phonons, respectively; α is the coupling coefficient for the interaction between electrons and phonons, and δ measures the strength of the Coulomb repulsion between the electrons; k is the wave vector of a phonon mode. The units chosen are $m=\omega=\hbar=1$, where m is the Block effective mass of the electron and ω is the optical-phonon frequency assumed to be dispersionless. The dynamics of this system is then described by a path integral over electron and phonon coordinates. Since the Lagrangian is quadratic in phonon coordinates, the path integration over these coordinates can be performed exactly. Further, after eliminating the phonon end points, the problem reduces to the path integration of a two-time (nonlocal) effective action functional S_{eff} involving only the electron coordinates and the phonon kernel $G(t-s)$

$$S_{\text{eff}}=\int_0^\beta[(\dot{\mathbf{x}}_1^2+\dot{\mathbf{x}}_2^2)/2+\delta/|\mathbf{x}_1-\mathbf{x}_2|]dt-S_1 \ , \tag{2.2}$$

where

$$S_1=\pi\alpha\sqrt{2}\int_0^\beta dt\int_0^\beta ds\int[d^3k/(2\pi)^3]G(t-s)\{\exp[i\mathbf{k}\cdot\mathbf{x}_1(t)]+\exp[i\mathbf{k}\cdot\mathbf{x}_2(t)]\}\{\exp[-i\mathbf{k}\cdot\mathbf{x}_1(s)]+\exp[-i\mathbf{k}\cdot\mathbf{x}_2(s)]\} \ . \tag{2.3}$$

The first term in (2.2) is the action for the motion of the electron pair under their mutual repulsion. The second term S_1 defined in (2.3) is the nonlocal contribution to the effective action arising from the electron-phonon interaction. The explicit form of the kernel $G(t-s)$ depends on how the phonon end points are eliminated from the joint electron-phonon density matrix. If we perform an average by taking the traces of the total density matrix over the phonon coordinates, we obtain the so-called finite-temperature kernel:

$$G(t-s)=\cosh(\beta/2-|t-s|)/\sinh(\beta/2) \ . \tag{2.4}$$

Note that the kernel $G(t-s)$ is symmetric in t and s. It is convenient to introduce the following transformation:

$$\begin{aligned}\mathbf{x}_1+\mathbf{x}_2&=\sqrt{2}\boldsymbol{\mu} \ ,\\ \mathbf{x}_1-\mathbf{x}_2&=\sqrt{2}\eta \ ,\end{aligned} \tag{2.5}$$

so that the effective action S_{eff} takes the form

$$S_{\text{eff}}=\int_0^\beta dt[\tfrac{1}{2}(\dot{\boldsymbol{\mu}}^2+\dot{\boldsymbol{\eta}}^2)+\delta/\sqrt{2}|\boldsymbol{\eta}|]-S_1 \ , \tag{2.6}$$

with

$$\begin{aligned}S_1=\pi\alpha\sqrt{2}\int_0^\beta dt\int_0^\beta ds\int[d^3k/(2\pi)^3]G(t-s)\exp\{i\mathbf{k}\cdot[\boldsymbol{\mu}(t)-\boldsymbol{\mu}(s)]/\sqrt{2}\}\\ \times(\exp\{i\mathbf{k}\cdot[\boldsymbol{\eta}(t)-\boldsymbol{\eta}(s)]/\sqrt{2}\}+\exp\{i\mathbf{k}\cdot[\boldsymbol{\eta}(t)+\boldsymbol{\eta}(s)]/\sqrt{2}\}+\text{c.c.}) \ ,\end{aligned} \tag{2.7}$$

where c.c. denotes the complex conjugate of the quantities in the curly brackets. The subsequent calculations are in the spirit of Feynman's variational formulation of the polaron problem. By using a suitable trial action, we invoke a variational principle to obtain an approximate form for the bipolaron density matrix (BPDM). We can then determine the main properties of the bipolaron, viz., its ground-state energy E_0 and its effective mass m^*. The choice of the trial action for arbitrary coupling strength α depends on two basic requirements. First, it must mimic qualitatively the nonlocal character of the effective action S_{eff}. Second, it must be easy to path integrate, yielding preferably an exact analytical form for the density matrix. In this work, we choose the following trial action:

$$S_0=\int_0^\beta dt[(\dot{\boldsymbol{\mu}}^2+\dot{\boldsymbol{\eta}}^2)/2+\omega^2\boldsymbol{\eta}^2/2]+(\Omega^2/4\beta)\int_0^\beta\int_0^\beta[\boldsymbol{\mu}(t)-\boldsymbol{\mu}(s)]^2dt\,ds \ , \tag{2.8}$$

where ω^2 and Ω^2 are variational parameters. The action S_0 is a sum of the action for a three-dimensional isotropic harmonic oscillator and a nonlocal quadratic action. The density matrix for each of these actions is known in analytical form. The density matrix for S_0 is therefore the product of the density matrices of the two individual actions.

For obtaining the effective mass m^* of the bipolaron, we need a further modification. We assume that the system is coupled to a constant force $\mathbf{f}$ so that the linear potential due to this force is simply given by $\mathbf{f}\cdot\boldsymbol{\mu}$. The effective action (2.2) is then modified to

$$\tilde{S}_{\text{eff}}=S_{\text{eff}}+i\int_0^\beta\mathbf{f}\cdot\boldsymbol{\mu}dt \ , \tag{2.9}$$

where S_{eff} is as in Eq. (2.6). A similar term must also be added to the trial action S_0.

For obtaining the estimates of the ground-state energy and the effective mass of the bipolaron, we evaluate the BPDM in the so-called first cumulant approximation. This implies that the BPDM has the form

$$\rho(\mu'',\eta'';\mu'\eta';\beta)=\rho_0(\mu'',\eta'';\mu',\eta';\beta)\times\exp(-\langle S_{\text{eff}}-S_0\rangle_{S_0}) \, . \tag{2.10}$$

Here, the symbols ρ and ρ_0 represent the density matrices corresponding to the actions S_{eff} and S_0, respectively. The expectation value $\langle\ \rangle_{S_0}$ is defined as

$$\langle(S_{\text{eff}}-S_0)\rangle_{S_0}=(1/\rho_0)\int\int D\boldsymbol{\mu}(t)D\boldsymbol{\eta}(t)\times(S_{\text{eff}}-S_0)\exp(-\beta S_0) \, , \tag{2.11}$$

where

$$\rho_0(\mu'',\eta'';\mu'\eta';\beta)=\int D\boldsymbol{\mu}(t)D\boldsymbol{\eta}(t)\exp(-\beta S_0) \, , \tag{2.12}$$

written as a path integral with $D\mu(t)D\eta(t)$ as the path differential measure.

In the subsequent calculations, we are interested only in the density matrix $\rho(0,0,\beta)$. The computation of the expectation value $\langle(S_{\text{eff}}-S_0)\rangle_{S_0}$ is facilitated by means of the following results. Consider the more general action inclusive of some force terms added to the trial action S_0:

$$\mathcal{S}_0=S_0+i\int_0^\beta \mathbf{f}_1\cdot\boldsymbol{\mu}\,dt+i\int_0^\beta \mathbf{f}_2\cdot\boldsymbol{\eta}dt \, , \tag{2.13}$$

where $\mathbf{f}_1$ and $\mathbf{f}_2$ depend on time t but are independent of the coordinates $\boldsymbol{\mu},\boldsymbol{\eta}$. One may then write

$$\mathcal{S}_0(\mathbf{f}_1,\mathbf{f}_2)=S_1(\mathbf{f}_1)+S_2(\mathbf{f}_2) \, , \tag{2.14}$$

and consequently

$$\rho_0=\rho_1\rho_2 \, . \tag{2.15}$$

Here

$$S_1=\int_0^\beta(\dot{\boldsymbol{\mu}}^2/2)dt+(\Omega^2/4\beta)\int_0^\beta dt\int_0^\beta ds[\boldsymbol{\mu}(t)-\boldsymbol{\mu}(s)]^2+i\int_0^\beta \mathbf{f}_1\cdot\boldsymbol{\mu}\,dt \tag{2.16}$$

is a general quadratic nonlocal action, while

$$S_2=\int_0^\beta(\dot{\boldsymbol{\eta}}^2+\omega^2\eta^2)dt+i\int_0^\beta \mathbf{f}_2\cdot\boldsymbol{\eta}dt \tag{2.17}$$

is the action of a three-dimensional isotropic forced harmonic oscillator. Analytical expressions for the density matrices ρ_1 and ρ_2 are available in the literature.[33] In particular, we have for the diagonal density matrices

$$\rho_1(0,0;\beta|\mathbf{f}_1)=(\tfrac{1}{2}\pi\beta)[\Omega\beta/2\sinh(\Omega\beta/2)]^3\times\exp\left[-\frac{1}{2}\left[\int_0^\beta dt\int_0^\beta ds\ \mathbf{f}_1(t)\mathbf{f}_1(s)C(t,s)\right]\right] , \tag{2.18}$$

$$\rho_2(0,0;\beta|\mathbf{f}_2)=[\omega/2\pi\sinh(\omega\beta/2)]^{3/2}\times\exp\left[-\frac{1}{2}\left[\int_0^\beta dt\int_0^\beta ds\ \mathbf{f}_2(t)\mathbf{f}_2(s)H(t,s)\right]\right] , \tag{2.19}$$

where

$$C(t,s)=2\cosh[\Omega(t-s)/2]\sinh(\Omega t_-/2)\sinh[\Omega(\beta-t_+)/2]/\Omega\sinh(\Omega\beta/2) \, , \tag{2.20}$$

$$H(t,s)=\sinh(\omega t_-)\sinh[\omega(\beta-t_+)]/\omega\sinh(\omega\beta) \, , \tag{2.21}$$

$$t_-=\min(t,s), \quad t_+=\max(t,s) \, . \tag{2.22}$$

We use these results for obtaining the various terms in the expectation value $\langle(S_{\text{eff}}-S_0)\rangle_{S_0}$ in the following section. Also, we shall hereafter shorten the notation by writing $\rho_1=\rho_1(0,0;\beta|\mathbf{f}_i)$, suppressing the arguments other than the parameter f_i of the forces. Note also that $\rho_0=\rho_0(\mathbf{f}_1=\mathbf{f}_2=0)$ and that $\rho_0=\rho_1(\mathbf{f}_1=0)\rho_2(\mathbf{f}_2=0)$ by Eq. (2.15).

III. GROUND-STATE ENERGY AND EFFECTIVE MASS

A. Ground-state energy

It is well known that in Feynman's prescription, the variational estimate of the ground-state energy is given by

$$E\le[E_0+\lim_{\beta\to\infty}(1/\beta\langle S_{\text{eff}}-S_0\rangle_{s_0}]\mu=\eta=0 \, , \tag{3.1}$$

where E_0 is the contribution to the ground-state energy from the density matrix ρ_0 corresponding to the trial action S_0:

$$E_0=\lim_{\beta\to\infty}(-1/\beta\ln\rho_0)=\lim_{\beta\to\infty}-1/\beta\{\ln[\rho_1(f_1=0)]+\ln[\rho_2(f_2=0)]\}=3(\Omega+\omega)/2 \, , \tag{3.2}$$

where we have used Eqs. (2.18) and (2.19). Next consider the expression

$$S_{\text{eff}}-S_0=-\Omega^2/4\beta\int_0^\beta dt\int_0^\beta ds[\boldsymbol{\mu}(t)-\boldsymbol{\mu}(s)]^2-\omega^2/2\int_0^\beta dt\ \boldsymbol{\eta}^2+\int_0^\beta\delta dt/\sqrt{2}|\eta|-S_1 \, . \tag{3.3}$$

We have to evaluate the various expectation values over the trial action S_0. It is easy to verify that

$$\left\langle-\omega^2/2\int dt\ \eta^2\right\rangle s_0=(\omega/2)\frac{\partial}{\partial\omega}\ln\rho_2(f_2=0)=\tfrac{3}{4}-(3\omega\beta/4)\coth(\omega\beta) \, . \tag{3.4}$$

In a similar manner,

$$\left\langle -\Omega^2/4\beta \int_0^\beta dt \int_0^\beta ds[\boldsymbol{\mu}(t)-\boldsymbol{\mu}(s)]^2 \right\rangle = (\Omega/2)(\delta/\delta\Omega)\ln\rho_1\ (\mathbf{f}_1=0)$$
$$= \tfrac{3}{2} - 3\Omega\beta/4\coth(\beta\Omega/2)\ . \tag{3.5}$$

Next consider the term

$$\left\langle \frac{\delta}{\sqrt{2}} \int_0^\beta dt \Big/ |\eta| \right\rangle_{S_0} = \frac{\delta}{\sqrt{2}} \int_0^\beta dt \int (d^3k/k^2 2\pi^2) \exp\langle i\mathbf{k}\cdot\boldsymbol{\eta}\rangle_{S_0}\ . \tag{3.6}$$

Now

$$\langle \exp(i\mathbf{k}\cdot\boldsymbol{\eta})\rangle_{S_0} = (1/\rho_0)\int D\eta(t)\exp\left[i\mathbf{k}\cdot\int \boldsymbol{\eta}(t)\delta(t-\tau)dt\right]\exp(-\beta S_0)$$
$$= \rho_2(f_2=\delta(t-\tau)k)/\rho_2\quad (f_2=0)$$
$$= \exp[-k^2 H(t,t)/2]\ . \tag{3.7}$$

Inserting (3.7) in (3.6), performing the integration over k, and inserting the expression of $H(t,t)$ from (2.2), we obtain

$$\left\langle \frac{\delta}{\sqrt{2}} \int_0^\beta dt \Big/ |\eta| \right\rangle_{S_0} = \frac{\delta}{\sqrt{\pi}} \int_0^\beta dt \sqrt{\omega \sinh\omega\beta} \Big/ \sqrt{\sinh[\omega(\beta-t)]\sinh\omega t}\ .$$

Since we are interested only in the limiting value as $\beta\to\infty$, we need not perform this integration in detail. It is sufficient to know that for large values of β,

$$\left\langle \frac{\delta}{\sqrt{2}} \int_0^\beta dt \Big/ |\eta| \right\rangle_{S_0} \to \beta\delta\sqrt{2\omega/\pi} + O(1)\ . \tag{3.8}$$

We now consider the evaluation of the term $\langle S_1\rangle_{S_0}$. For this purpose, let us write S_1 in the form

$$S_1 = \sqrt{2}\pi\alpha \int_0^\beta dt \int_0^\beta ds \int d^3k/k^2[1/(2\pi)^3]G(t,s)\exp(i\mathbf{k}\mathbf{a})$$
$$\times[\exp(i\mathbf{k}\cdot\mathbf{b}_+)+\exp(-i\mathbf{k}\cdot\mathbf{b}_+)+\exp(i\mathbf{k}\cdot\mathbf{b}_-)+\exp(-i\mathbf{k}\cdot\mathbf{b}_-)]\ , \tag{3.9}$$

where

$$\mathbf{a} = [\boldsymbol{\mu}(t)-\boldsymbol{\mu}(s)]/\sqrt{2};\quad \mathbf{b}\pm = [\boldsymbol{\eta}(t)\pm\boldsymbol{\eta}(s)]/\sqrt{2}\ . \tag{3.10}$$

Since the trial action S_0 is separable in coordinates μ and ν, we can write

$$\langle \exp(i\mathbf{k}\cdot\mathbf{a})[\exp(i\mathbf{k}\cdot\mathbf{b}_+)+\exp(-i\mathbf{k}\cdot\mathbf{b}_-)+\exp(i\mathbf{k}\cdot\mathbf{b}_-)+\exp(-i\mathbf{k}\cdot\mathbf{b}_-)]\rangle$$
$$= \langle \exp(i\mathbf{k}\cdot\mathbf{a})\rangle_{S_0[\mu]}\langle[\exp(i\mathbf{k}\cdot\mathbf{b}_+)+\exp(-i\mathbf{k}\cdot\mathbf{b}_+)+\exp(i\mathbf{k}\cdot\mathbf{b}_-)+\exp(-i\mathbf{k}\cdot\mathbf{b}_-)]\rangle_{S_0[\eta]}\ , \tag{3.11}$$

where $S_0[\mu]$ is the nonlocal quadratic action in $\boldsymbol{\mu}$ and $S_0[\eta]$ corresponds to the action of a harmonic oscillator. Now

$$\langle \exp(i\mathbf{k}\cdot\mathbf{a})\rangle_{S_0[\mu]} = \int D\mu(t)\exp\left[-S_0 + i\mathbf{k}/\sqrt{2}\int[\delta(\tau-t)-\delta(\tau-s)]\mu(\tau)d\tau\right]\Big/\rho_1\quad (\mathbf{f}_1=\mathbf{0})$$
$$= \rho_1\{\mathbf{f}_1=\mathbf{k}[\delta(\tau-t)-\delta(\tau-s)]/\sqrt{2}\}/\rho_1\quad (\mathbf{f}_1=\mathbf{0})$$
$$= \exp[-(k^2C_-)/4]\ , \tag{3.12}$$

where the quantity C_- is defined as

$$C_- = C(t,t)+C(s,s)-2C(t,s)\ .$$

Similarly, it is easy to verify that

$$\langle \exp(i\mathbf{k}\cdot\mathbf{b}\pm)\rangle_{S_0[\eta]} = \rho_2\{\mathbf{f}_2=\mathbf{k}[\delta(\tau-t)\pm\delta(\tau-s)]\}/\rho_2\quad (\mathbf{f}_2=\mathbf{0})$$
$$= \exp[-(k^2H\pm)/4]\ , \tag{3.13}$$

where

$$H\pm = H(t,t)+H(s,s)\pm 2H(t,s)\ . \tag{3.14}$$

Since the result depends on k^2, it follows that

$$\langle \exp[+i(\mathbf{k}\cdot\mathbf{b}\pm)]\rangle_{S_0[\eta]} = \langle \exp[-i(\mathbf{k}\cdot\mathbf{b}\pm)]\rangle_{S_0[\eta]} = \exp[-(k^2H\pm)/4]\ . \tag{3.15}$$

Collecting all these terms, we have

$$\langle S_1\rangle_{S_0[\eta]}=2\sqrt{2}\pi\alpha\int_0^\beta dt\int_0^\beta ds\int d^3k/(2\pi)^3k^2G(t,s)\{\exp[-k^2(C_-+H_+)/4]+\exp[-k^2(C_-+H_-)/4]\}$$
$$=\alpha\sqrt{2}/\pi\int_0^\beta dt\int_0^\beta dsG(t,s)[1/\sqrt{(C_-+H_+)}+1/\sqrt{(C_-+H_-)}]\;. \quad (3.16)$$

This expression is complicated for evaluating in detail. However, we are interested in the limit $\beta\to\infty$. For large β, we approximate the quantities in the integrand.

Consider first the expression for C_-. We have

$$C_-=C(t,t)+C(s,s)-2C(t,s)$$
$$=2\{\sinh(\Omega t/2)\sinh[\Omega(\beta-t)/2]+\sinh(\Omega s/2)\sinh[\Omega(\beta-s)/2]\}/\Omega\sinh(\Omega\beta/2)$$
$$-4\cosh[\Omega(t-s)/2]\sinh(\Omega s/2)\sinh[\Omega(\beta-t)/2]/\Omega\sinh(\Omega\beta/2)\quad\text{for } t\geq s\;,$$
$$C_-\to\{1-\exp[-\Omega(t-s)]\}/\Omega \quad (3.17)$$

as $\beta\to\infty$. As C_- is symmetric in t and s, it follows that

$$C_-\to[1-\exp(\Omega|t-s|)]/\Omega \quad (3.18)$$

as $\beta\to\infty$. Similarly, it can be shown that as $\beta\to\infty$,

$$H\pm\to[1\pm\exp(-\omega|t-s|)]/\omega\;, \quad (3.19)$$

$$G(t,s)\to\exp(-|t-s|)\;. \quad (3.20)$$

Inserting these estimates in (3.16), we find that for large β,

$$\langle S_1\rangle_{S_0}=(\sqrt{2}/\pi)\alpha\int_0^\beta dt\int_0^\beta ds\exp[(-|t-s|)\chi(|t-s|)]$$
$$=2\alpha(\sqrt{2}/\pi)\int_0^\beta du(\beta-u)\exp(-u)\chi(u)\;, \quad (3.21)$$

where

$$\chi(u)\equiv[1/\Omega+1/\omega-\exp(-\Omega u)/\Omega+\exp(-\omega u)/\omega]^{-1/2}$$
$$+[1/\Omega+1/\omega-\exp(-\Omega u)/\Omega$$
$$-\exp(-\omega u)/\omega]^{-1/2}\;. \quad (3.22)$$

For analytical simplicity we consider two extreme cases of the choice of parameters: (a) $\omega=\Omega$; (b) $\Omega=0$. We may evaluate the term in Eq. (3.22) explicitly if we set $\omega=\Omega$. This choice seems proper only for very large values of α (Ref. 8) (for a strongly coupled system):

$$\chi(u)=\sqrt{\Omega/2}[1+1/\sqrt{1-\exp(-\Omega u)}], \quad (3.23)$$

and

$$\lim_{\beta\to\infty}(1/\beta)\langle S_1\rangle_{S_0}$$
$$\to2\alpha(\sqrt{\Omega}/\pi)\left[1+\int_0^\beta\exp(-u)du/\sqrt{1-\exp(-\Omega u)}\right]$$
$$\simeq4\alpha\sqrt{(\Omega/\pi)}\;. \quad (3.24)$$

On the other hand, for the case $\Omega=0$, $C_-\to u$. Further,

$$\chi(u)=\sqrt{\omega}\{[\omega u+1+\exp(-\omega u)]^{1/2}$$
$$+[\omega u+1-\exp(-\omega u)]^{1/2}\}\;, \quad (3.25)$$

and

$$\lim_{\beta\to\infty}(1/\beta)\langle S_1\rangle_{S_0}\to4\alpha\sqrt{(2\omega/\pi)}\;. \quad (3.26)$$

The choice $\Omega=0$ implies that α is small. However, note that α has to be larger than some minimum value to form a bound pair. We may now combine all these results to write the expression for the ground-state energy of the bipolaron. In the strong-coupling limit, where we let $\omega=\Omega$, we have

$$\lim_{\beta\to\infty}(1/\beta)\langle S_{\text{eff}}-S_0\rangle$$
$$=-3\Omega/2+\delta\sqrt{(2\Omega/\pi)}-4\alpha\sqrt{(\Omega/\pi)}\;, \quad (3.27)$$

and since $E_0=3\Omega$, the inequality (3.1) becomes

$$E\leq[E_0+\lim(1/\beta)\langle S_{\text{eff}}-S_0\rangle_{S_0}]$$
$$=3\Omega/2+\delta\sqrt{(2\Omega/\pi)}-4\alpha\sqrt{(\Omega/\pi)},\quad\sqrt{\Omega}\geq0\;. \quad (3.28)$$

The ground-state energy is obtained by minimizing this expression with respect to the variational parameter Ω, that is, by letting

$$dE/d\Omega=\tfrac{3}{2}+(\delta/2)\sqrt{(2/\Omega\pi)}-2\alpha\sqrt{(1/\pi\Omega)}=0\;, \quad (3.29)$$

which yields

$$\Omega=(2/9\pi)(2\sqrt{2}\alpha-\delta)^2,\quad\alpha\geq\delta/(2\sqrt{2})\;,$$
$$\Omega=0,\quad\alpha\leq\delta/(2\sqrt{2})\;. \quad (3.30)$$

Hence, in the strong-coupling limit, the ground-state energy is given by

$$E\leq-\tfrac{1}{3}\pi(2\sqrt{2}\alpha-\delta)^2,\quad\alpha\geq\delta/(2\sqrt{2})$$
$$E\leq0,\quad\alpha\leq\delta/(2\sqrt{2})\;. \quad (3.31)$$

In the weak-coupling limit, $\Omega=0$, $E_0=3\omega/2$, and

$$\lim_{\beta\to\infty}(1/\beta)\langle S_{\text{eff}}-S_0\rangle_{S_0}$$
$$=-3\omega/4+\delta\sqrt{(2\omega/\pi)}-4\alpha\sqrt{(2\omega/\pi)}\;. \quad (3.32)$$

The inequality (3.1) now reads

$$E\leq[E_0+\lim(1/\beta)\langle S_{\text{eff}}-S_0\rangle_{S_0}]$$
$$=3\omega/4+(\delta-4\alpha)\sqrt{(2\omega/\pi)}\;. \quad (3.33)$$

Minimization of E with respect to ω yields

$$\omega=(8/9\pi)(4\alpha-\delta)^2, \quad \alpha\geq\delta/4$$
$$\omega=0, \quad \alpha\leq\delta/4 , \tag{3.34}$$

and the estimate of the bipolaron energy in the weak-coupling limit reads

$$E\leq(-\tfrac{1}{3}\pi)(4\alpha-\delta)^2, \quad \alpha\geq\delta/4 ;$$
$$E_0\leq0, \quad \alpha\leq\delta/4 . \tag{3.35}$$

Note that for a negative-energy state, a minimum value of α is necessary whether one uses the parameters $\omega=\Omega$ or $\Omega=0$. The choice of parameters only changes the qualitative bounds on the energy E. Moreover as $\alpha\to0$, $E\leq0$, which is consistent physically.

Table I gives numerical estimates of the free energy for various values of the parameters α and δ. These have been obtained by minimizing with respect to both ω and Ω.

Next we turn to the question of the stability of the bipolaron. As has been mentioned earlier, the bipolaron pair can be formed if the electron-phonon interaction characterized by the constant α is sufficiently large to overcome the Coulomb repulsion between the electron (hole) pairs. Hence we can assert that the bipolaron would be stable if its binding energy, defined by the relation

$$W=2E_0-E>0 ,$$

where E_0 is the energy of the individual polarons with respect to the bottom of the conduction band. E_0 is the case of the strong-coupling limit is given by

$$E_0=-\gamma_p\alpha^2 ,$$

where γ_p is Pekar's constant. Hence the condition for stability yields

$$-2\gamma_p\alpha^2+(\tfrac{1}{3}\pi)(2\sqrt{2}\alpha-\delta)^2\geq0 ,$$

which implies

$$\alpha\geq\delta/[\sqrt{2}(2-\sqrt{3\pi\gamma_p})] . \tag{3.36}$$

The value of γ_p is $\approx1/3\pi$. Therefore, for stability, α has to be necessarily larger than $\delta/\sqrt{2}$. A similar condition can be derived using the E of Eq. (3.35), which corresponds to choice $\Omega=0$. However, since for a given $\alpha\geq\delta/4$ the bound on E of Eq. (3.34) lies below the bound of Eq. (3.35), the value of α/δ described by Eq. (3.36) gives a lower bound for the stability of the bipolaron.

B. Effective mass of the bipolaron

The effective mass of the bipolaron can be obtained by considering the response of the system under a small perturbative force. Such a definition of effective mass for the polaron problem has been given by Saitoh.[30] As mentioned in Sec. II, we have now to consider the effective action S_{eff} given by (2.9) and the corresponding trial action S_0 containing the force term. Since $S_{\text{eff}}-S_0=S_{\text{eff}}-S_0$, the expectation value

$$\langle\tilde{S}_{\text{eff}}-\tilde{S}_0\rangle_{\tilde{S}_0}=\langle S_{\text{eff}}-S_0\rangle_{\tilde{S}_0}$$
$$=\langle S_{\text{eff}}-S_0\rangle_{S_0}+\beta E(|\mathbf{f}|) ,$$

where the first term on the right is the contribution for $\mathbf{f}=\mathbf{0}$ and the second term is the contribution that depends explicitly on force parameter $\mathbf{f}$. The first term has already been evaluated in Sec. III A. The diagonal density matrix

$$\rho(0,0/\beta;\mathbf{f})=\rho_0(0,0/\beta;\mathbf{f})\times\exp(-\langle S_{\text{eff}}-S_0\rangle_{S_0})\exp[-\beta E(|\mathbf{f}|)] . \tag{3.37}$$

The effective mass m^* is then related to the coefficient of $-|\mathbf{f}|^2/2$ in the exponent of the density matrix $\rho(0,0/\beta;|\mathbf{f}|)$. We enumerate the various terms in this context. First, the coefficients of the $|\mathbf{f}|^2/2$ term in the exponent of $\rho_0(0,0/\beta;\mathbf{f})$ reads

$$J_1=\int_0^\beta dt\int_0^\beta ds\, C(t,s) . \tag{3.38}$$

Next, the term proportional to $-f^2/2$ in $\exp[-\beta E(f)]$ can be shown to be given by a sum of the terms J_2 and J_3, given by

$$J_2=-\tfrac{1}{2}J_1 , \tag{3.39}$$

TABLE I. The estimates of the free energy for various values of α and δ in the strong-coupling limit.

α	δ	β	ω	Ω	E_0
5.12	5.01	25	4.16	5.55	−12.76
6.12	10	40	0.471	1.1	−11.217
10	15	15	9.19	17.0	−25.79
9	9	15	11.6	18.0	−32.85
7	7	15	9.185	13.0	−21.16
7	6	15	10.452	14.0	−23.63
7	5	15	11.6	15.0	−23.306
6	7	15	4.631	7.0	−14.3
6	6	15	6.08	8.5	−16.15
6	5	15	7.707	10	−18.26
6	4	15	9.47	11.5	−20.72

$$J_3 = -\sqrt{2}\alpha/\sqrt{\pi}\int_0^\beta dt\int_0^\beta ds\, G(t,s)I^2 \times[(C_- + H_+)^{-3/2} + (C_- + H_-)^{-3/2}] , \quad (3.40)$$

where

$$I = \int_0^\beta d\tau[C(\tau,t) - C(\tau,s)] . \quad (3.41)$$

We have to evaluate J_1 and J_2. For this purpose, we use the definition (2.20), and show that

$$\int_0^t C(\tau,t)d\tau = \{t\sinh[\Omega(\beta - t/2)]\sinh(\Omega t/2)\}/[\Omega\sinh(\Omega\beta/2)] , \quad (3.42)$$

$$\int_t^\beta C(\tau,t)d\tau = \{(\beta - t)\sinh(\Omega t/2)\sinh[\Omega(\beta - t/2)]\}/[\Omega\sinh(\Omega\beta/2)] , \quad (3.43)$$

so that

$$\int_0^\beta C(\tau,t)d\tau = \{\beta\sinh(\Omega t/2)\sinh[\Omega(\beta - t/2)]\}/[\Omega\sinh(\Omega\beta/2)] \quad (3.44)$$

and

$$J_1 = \int_0^\beta dt\int_0^\beta d\tau C(\tau,t) = \beta[(\Omega\beta/2)\cosh(\Omega\beta/2) - \Omega\sinh(\Omega\beta/2)]/[\Omega^2\sinh(\Omega\beta/2)] \to \beta^2/2\Omega \quad (3.45)$$

as $\beta\to\infty$. Similarly, $J_2 \to -\beta^2/(4\Omega)$ in the limit $\beta\to\infty$. We may use Eq. (3.44) to simplify the expression for I, which now reads

$$I = \{\beta\sinh[\Omega(\beta - t - s)/2]\sinh[\Omega(t - s)/2]\}/[\Omega\sinh(\beta\Omega/2)] . \quad (3.46)$$

We are interested in obtaining an estimate of the effective mass m^* in both the strong- as well as the weak-coupling limit and as $\beta\to\infty$ (that is, in the limit of zero temperature). The integrand in J_3 is a product of a function $g(t-s)$ and another function $h(t+s)$. In order to cast integral J_3 in a proper form, consider the auxiliary integral

$$J = \int_0^\beta dt\int_0^\beta ds\, g(t-s)h(t+s) . \quad (3.47)$$

By changing the variables to $u = t - s$ and $v = t + s$, we can show that

$$J = 2\int_0^\beta du\int_0^{\beta-u} dv\, g(u)h(v+\beta) , \quad (3.48)$$

provided that $h(\beta - v) = h(v+\beta)$, which is the case if h is chosen to be I^2. In order to evaluate J_2 in the limit of large β, we use the fact that $H\pm\to 1/\omega$ and $C\pm\to 1/\Omega$ in this limit, and also the fact that the kernel $G(t,s)\to\exp-|t-s| = \exp-|u|$. First note that by virtue of (3.48),

$$\begin{aligned}\int_0^\beta dt\int_0^\beta ds\, I^2G &= [2\beta^2/\Omega^2\sinh^2(\Omega\beta/2)]\int_0^\beta du\,\sinh^2(\Omega u/2)\exp(-u)\int_0^{\beta-u}\sinh^2(\Omega v/2)dv\\ &= [\beta^2/\Omega^2\sinh^2(\Omega\beta/2)]\int_0^\beta du\,\exp(-u)[\exp(u\Omega)/4 - \tfrac{1}{2}]\{[\sinh(\beta-u)\Omega]/\Omega - (\beta-u)\}\\ &= [\beta^2/\Omega^2\sinh^2(\Omega\beta/2)]\int_0^\beta du\,\exp(-u)[\exp(u\Omega)/4 - \tfrac{1}{2}]e^{(\beta-u)\Omega}/2\Omega + O(\beta)\\ &\simeq \beta^2/2\Omega^3\int_0^\beta du\,\exp(-u)[1 - 2\exp(-u\Omega)]\\ &\to \beta^2(\Omega-1)/[2\Omega^3(\Omega+1)] .\end{aligned} \quad (3.49)$$

Using the above expression, we can write in the strong-coupling limit, where $\omega = \Omega$ $(H\pm = C\pm = 1/\Omega)$,

$$J_3 = -(2\alpha/\sqrt{2}\pi)(\Omega^{3/2}/\sqrt{2})(\beta^2/2\Omega^3)[(\Omega-1)/(\Omega+1)] = [\alpha(\Omega-1)/\sqrt{\pi}\Omega(\Omega+1)](\beta^2/2\Omega) . \quad (3.50)$$

For large β the effective mass m^* is then given by

$$1/m = J_1 + J_2 + J_3 = \beta^2/2\Omega\{(\tfrac{3}{2}) - (\alpha/\sqrt{\pi}\Omega)[(\Omega-1)/(\Omega+1)]\} . \quad (3.51)$$

We now normalize the mass m in the trial action to 2, since it is a sum of the masses of the two individual electrons; thus the coefficient of $-f^2/2$ in the trial action, which is $\beta^2/2\Omega$, must be replaced by $\frac{1}{2}$. Therefore the effective mass of the bipolaron is

$$1/m^* = \tfrac{1}{2}[\tfrac{3}{2} - (\alpha/\sqrt{\pi}\Omega)(\Omega-1)/(\Omega+1)] . \quad (3.52)$$

Inserting the value of Ω in (3.30), found by variational minimization of ground-state energy, and assuming that $[(\Omega-1)/(\Omega+1)]\simeq 1$, we obtain

$$1/m^* = \tfrac{1}{2}[\tfrac{3}{2} - 3\alpha/(4\alpha - \sqrt{2}\delta)] \quad (3.53)$$

and $\alpha > \sqrt{2}\delta$. Let us now consider the weak-coupling limit where $\Omega = 0$. Here, since the trial action does not contain the nonlocal quadratic part, $J_2 = 0$, while

$$J_1 = \beta^3/12 \ , \tag{3.54}$$

while J_3 is still given by (3.39) with $C\pm=0$ and

$$I = \tfrac{1}{2}(t-s)[\beta-(t+s)] \ . \tag{3.55}$$

Equation (3.55) can be obtained from (3.46) by taking the limit as $\Omega \to 0$. With (3.55) and $H\pm = 1/\omega$, the integration in (3.39) may be carried out as before to yield the result

$$\begin{aligned} J_3 &= (8\alpha/\sqrt{2}\pi)\omega^{3/2}\int_0^\beta du \int_0^{\beta-u} dv (u^2 v^2/4)\exp(-u) \\ &= +(2\alpha\omega^{3/2}/3\sqrt{2}\pi)\int_0^\beta du [u^2(\beta-u)^3\exp(-u)] \\ &\simeq (+4\alpha/3\sqrt{2\pi})\omega^{3/2}\beta^3 \ . \end{aligned} \tag{3.56}$$

Thus the effective mass m^* is given by

$$\begin{aligned} 1/m^* &= J_1 + J_2 \\ &= (\beta^3/12)[1+(16\alpha/\sqrt{2}\pi)\omega^{3/2}] \ . \end{aligned} \tag{3.57}$$

Once again we renormalize the mass in the trial action $(\beta^2/12)^{-1}$ as 2 and insert the value (3.34) for ω. Consequently, in the weak-coupling limit, the effective mass of the bipolaron takes the form

$$1/m^* = \tfrac{1}{2}[1+(4/\pi^2)(\tfrac{8}{3})^3\alpha(4\alpha-\delta)^3] \ . \tag{3.58}$$

IV. CONCLUSIONS

In this paper we have obtained analytical estimates for the ground-state energy E and the effective mass of the large bipolaron. As has been pointed out earlier, our definition of the effective mass of a bipolaron is different from the one used by Hiramoto and Toyozawa.[32]

The advantage of using the present definition is that it can be used even to describe the temperature-dependent effective mass, whereas the earlier definition due to Feynman has been found to be inadequate for this purpose.[31] Our analysis can also be used for studying the temperature variation of the free energy.

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