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Exact equations for bipolarons in the strong-coupling limit

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Abstract. Equations for the bipolaron wavefunction, ground-state energy and effective mass are derived which are exact in the strong-coupling limit. The results are obtained for large bipolarons in an arbitrary number of spatial dimensions (D). We apply our results to the cases $D = 1, 2, 3$.

1. Introduction

Two identical charged particles (electrons), placed in a polar or ionic crystal, interact with the lattice vibrations which induces an attractive retarded force between them. Under certain conditions, a bound state can exist of two electrons surrounded by a common cloud of virtual phonons. Such a quasi-particle is referred to as a *bipolaron*. Interest in bipolaron properties has been renewed by the possibility of a *bipolaron mechanism for high-T_c superconductivity*: bipolarons act as charged bosons undergoing a Bose–Einstein condensation in real space. For large bipolarons, such a mechanism was studied by Vinetskii and Pashitskii [1] and then developed by Emin and Hillery [2]. The Antwerp group [3] and Bassani *et al* [4] recently published some papers concerning the stability region for bipolaron formation and the possibility of a bipolaron mechanism for high-T_c superconductivity.

The prerequisite for such theories is the very existence of bipolarons. Previously, various bipolaron characteristics such as their ground-state energy, effective mass, radius and number of virtual phonons (see review article [5] and references therein) have been investigated. The main conclusion of the majority of the published papers is that bipolarons can exist in a particular range of critical values for the coupling constants of the competing interactions: the attractive electron–phonon (α) and repulsive Coulomb (U) interaction. For bipolaron formation, the repulsive force should be weak enough while the electron–phonon interaction has to be sufficiently strong to overcome the repulsion. Previously, the critical values of the coupling constants were determined by different authors using different variational upper estimates for the bipolaron energy. The advantages of such variational approaches are obvious: these methods lead to estimates of the bipolaron characteristics for the whole range of values of the electron–phonon coupling constant, especially the intermediate values.

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Polaron effects [6] are important for many polar dielectrics and semiconductors of the $A^{III}B^{V}$ and the $A^{II}B^{VI}$ groups. Such materials have electron–phonon coupling constants in the range of small and intermediate values. In addition to mobile charge carriers in solid-state systems, there are also different classes of systems with anomalously high values of the electron–phonon coupling constant, for example, protein globules and solvated electrons in liquids (see, e.g., papers by the Pushchino group [7]).

The goal of the present paper is to derive exact equations describing bipolarons in the strong-coupling limit. The same limit for the single polaron was investigated in early papers by Pekar, Landau and Pekar, Bogolubov, and Tyablikov [8]. Numerical calculations for 3D (bulk) polarons have been performed by Miyake [9] and for 2D polarons by Wu *et al* [10]. In a recent paper by Bogolubov [11], the procedure for deriving the strong-coupling equations was simplified. Here we generalize it to the case of the bipolaron and improve this approach to avoid divergences.

The formation of the bipolaron and the existence of excited states of both polarons [12–14] and bipolarons is important in electron transfer processes in a broad variety of condensed matter. A lot of work has already been performed on the 2D and 3D bipolaron ground state [3, 4, 15, 16].

The main advantages of the approach used in this paper are that: (i) apart from the purely theoretical interest in strongly coupled electron–phonon systems, the equations can serve as a test for the accuracy of the so-called 'all-coupled variational' approach to bipolaron characteristics; (ii) in addition to the variational equation, a Schrödinger equation is also derived with which it becomes possible to investigate the excited states of the strongly coupled bipolaron (which are not attainable with the usual variational approach [14] and which, as far as we know, have not yet been investigated); and (iii) the equations are applied to the case of the 1D bipolaron (tackling the divergences which are inherent to this problem). A very thorough study of the 1D bipolaron and its excited states can then be performed by solving the nonlinear effective Schrödinger equation (see [17]). Apart from the characteristics and discussion on the existence of the bipolaron and its excited states, some pecularities appear because of the nonlinearity of the equation.

In many systems, the electrons (or holes) move in planes (e.g. quantum wells, CuO_2-planes in high-T_c superconductors) or along one direction (e.g. quantum wires, polymers). Therefore, we will consider bipolarons in a space with an arbitrary number D of dimensions. Note that at $D = 2$ the bipolaron effects are enlarged [4, 15, 16] compared with the $D = 3$ case.

The present paper is organized as follows. In section 2, we derive the exact equations for the bipolaron characteristics in the strong-coupling limit. In section 3, we study the equation for the bipolaron ground-state energy and effective mass. Section 4 deals with the special case of one-dimensional bipolarons.

2. Basic equations

The Fröhlich Hamiltonian for two electrons interacting with the phonon field is written as follows

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \sum_k \hbar\omega_k a_k^\dagger a_k + U(|r_1 - r_2|) + \sum_k [a_k V_k (e^{ik\cdot r_1} + e^{ik\cdot r_2}) + a_k^\dagger V_k^* (e^{-ik\cdot r_1} + e^{-ik\cdot r_2})] \tag{2.1}$$

where $r_i(p_i)$ are the position (momentum) operators of the ith electron, m is the electron band mass and $a_k^\dagger$ (a_k) are the creation (annihilation) operators of phonons with wavevector k and frequency ω_k. The potential $U(|r_1 - r_2|)$ corresponds to the direct (Coulomb) interaction between electrons and the quantities V_k are the Fourier transforms of the electron–phonon interaction. The total momentum of the system is conserved: one can readily verify that the operator

$$\hat{P} = -i\hbar\nabla_{r_1} - i\hbar\nabla_{r_2} + \sum_k \hbar k a_k^\dagger a_k \tag{2.2}$$

commutes with Hamiltonian (2.1). Therefore, we will consider states for which the total momentum is a c-number $\mathcal{P}$, introducing a Lagrange multiplier v. Instead of (2.1), we consider the new Hamiltonian

$$H(v) = H - v \cdot \left(p_1 + p_2 + \sum_k \hbar k \, a_k^\dagger a_k - \mathcal{P} \right). \tag{2.3}$$

The Lagrange multiplier v is given by $\partial H(v)/\partial \mathcal{P} = v$, which implies that v is the average velocity of the system. This allows us to define a total bipolaron effective mass m^* at small velocities:

$$\mathcal{P} = m^* v + \mathcal{O}(v^2). \tag{2.4}$$

The first step is to transform Hamiltonian (2.3) into $H'(v) = U_1 H(v) U_1^{-1}$ using the unitary transformation

$$U_1 = \exp\left[-i \frac{r_1 + r_2}{2\hbar} \left(2mv - a \sum_k \hbar k a_k^\dagger a_k \right) \right]. \tag{2.5}$$

Under this transformation, the total momentum is transformed as follows

$$\hat{P}' = U_1 \hat{P} U_1^{-1} = p_1 + p_2 + 2mv + (1 - a) \sum_k \hbar k a_k^\dagger a_k. \tag{2.6}$$

The goal of transformation (2.5) is: (i) to reveal the motion of the centre of mass (CM) of the two electrons (which is not the same as *the bipolaron CM*); and (ii) to take into account the recoil effects. The idea for using parameter a was suggested in [18] and allows us to treat the weak- and strong-coupling limits at the same time. When $a = 1$, transformation (2.5) generalizes the well known Lee–Low–Pines transformation by using the CM coordinate of two electrons instead of a single electron coordinate.

With the above transformation, the Hamiltonian takes the form

$$\begin{aligned} H'(v) = {} & \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(|r_1 - r_2|) - mv^2 + v \cdot \mathcal{P} \\ & + \sum_k a_k^\dagger a_k \left[\hbar\omega_k - \hbar k \cdot v - \frac{a}{2m} \hbar k \cdot (p_1 + p_2) \right] + \frac{a^2}{4m} \left(\sum_k \hbar k \, a_k^\dagger a_k \right)^2 \\ & + \sum_k \left[a_k V_k e^{-iak \cdot (r_1 + r_2)/2} (e^{ik \cdot r_1} + e^{ik \cdot r_2}) + \text{HC} \right]. \end{aligned} \tag{2.7}$$

The second step is performed using transformation $H''(v) = U_2 H'(v) U_2^{-1}$ with

$$U_2 = \exp\left[\sum_k (c_k^*(v)a_k - c_k(v)a_k^\dagger)\right] \tag{2.8}$$

to shift the phonon field operators $a_k \to a_k + c_k(v)$ by c-numbers $c_k(v)$. By this shift, one can describe a polaron in the strong-coupling limit as an electron captured by a potential well generated by a large classical component of the phonon field. The resulting Hamiltonian can be split into two parts: $H''(v) = H_0(v) + H_{\rm int}(v)$. The first term is the non-interacting part which contains the energy of the free-phonon field and the energy of the electrons moving in an effective potential

$$\begin{aligned} H_0(v) = {} & \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(|r_1 - r_2|) - mv^2 + v\cdot\mathcal{P} \\ & + \sum_k |c_k(v)|^2 \left[\hbar\omega_k + \frac{a^2}{4m}(\hbar k)^2 - \hbar k\cdot\left(v + \frac{a}{2m}(p_1+p_2) - \frac{a^2}{4m}\sum_l \hbar l |c_{l(v)}|^2\right)\right] \\ & + \sum_k a_k^\dagger a_k \left[\hbar\omega_k + \frac{a^2}{4m}(\hbar k)^2 - \hbar k\cdot\left(v + \frac{a}{2m}(p_1+p_2) - \frac{a^2}{2m}\sum_l \hbar l |c_l(v)|^2\right)\right] \\ & + \sum_k \left[c_k(v) V_k e^{-iak\cdot(r_1+r_2)/2}(e^{ik\cdot r_1} + e^{ik\cdot r_2}) + \text{HC}\right]. \end{aligned} \tag{2.9}$$

The other part $H_{\rm int}$ of Hamiltonian (2.3) can be written in a normal-ordered form and will play no role in what follows.

Up to this point, the $c_k(v)$ are arbitrary c-numbers which will be determined by minimizing the energy. The energy is obtained by taking the expectation value of the Hamiltonian $H(v) = H_0(v) + H_{\rm int}(v)$ over the trial ket $|\Phi_v\rangle = \phi_v(r_1, r_2)|0\rangle$, where $|0\rangle$ denotes the phonon vacuum. With the above trial ket, the average $\langle H_{\rm int}(v)\rangle$ is equal to zero. We find the following energy functional:

$$\begin{aligned} E[\phi_v] = {} & \langle H_0(v)\rangle - E(\langle\phi_v|\phi_v\rangle - 1) \\ = {} & \left\langle\frac{p_1^2}{2m}\right\rangle + \left\langle\frac{p_2^2}{2m}\right\rangle + \langle U(|r_1 - r_2|)\rangle \\ & + \langle\phi_v|\phi_v\rangle(v\cdot\mathcal{P} - mv^2) - \frac{a}{2m}(p_1+p_2)\cdot\sum_k \hbar k |c_k(v)|^2 \\ & + \langle\phi_v|\phi_v\rangle \sum_k |c_k(v)|^2 \left(\hbar\omega_k + \frac{a^2}{4m}(\hbar k)^2 - \hbar k\cdot v + \frac{a^2}{4m}\hbar k\cdot\sum_l \hbar l |c_l(v)|^2\right) \\ & + 2\sum_k \left[V_k c_k(v)\rho_k(a) + V_k^* c_k^*(v)\rho_k^*(a)\right] + E(\langle\phi_v|\phi_v\rangle - 1) \end{aligned} \tag{2.10}$$

where E is a Lagrange multiplier and we have introduced the notation

$$\rho_k(a) = \tfrac{1}{2}\int dr_1\, dr_2\, e^{-iak\cdot(r_1+r_2)/2}(e^{ik\cdot r_1} + e^{ik\cdot r_2})\phi_v^*(r_1, r_2)\phi_v(r_1, r_2). \tag{2.11}$$

A variation with respect to E gives the conventional normalization of the wavefunction

$$\langle\phi_v|\phi_v\rangle = \int dr_1\, dr_2\, \phi_v^*(r_1, r_2)\phi_v(r_1, r_2) = 1. \tag{2.12}$$

Furthermore, note that Hamiltonian (2.3) is symmetrical under a permutation of the electrons. Therefore, the wavefunctions should be either symmetrical (para-bipolaron) or antisymmetrical (ortho-bipolaron): $\phi_v(r_1, r_2) = \pm\phi_v(r_2, r_1)$.

The variations of the functional $E[\phi_v]$ with respect to $c_k(v)$ and $c_k^*(v)$ determine these c-numbers as follows

$$c_k(v) = -\frac{2V_k^*\rho_k^*(a)}{\hbar\omega_k - \hbar k\cdot v - \dfrac{a}{2m}\hbar k\cdot\langle p_1 + p_2\rangle + \dfrac{a^2}{4m}\left[2\hbar k\cdot\sum_l \hbar l|c_l(v)|^2 + (\hbar k)^2\right]}. \tag{2.13}$$

The variation of the functional $E[\phi_v]$ with respect to v leads to a link between the average velocity and the total bipolaron momentum:

$$\mathcal{P} = 2mv + \sum_k \hbar k|c_k(v)|^2. \tag{2.14}$$

On the other hand, the averaging of operator $\hat{P}'' = U_2\hat{P}'U_2^{-1}$ with $\hat{P}'$ and U_2 defined by equations (2.6) and (2.8), respectively, results in

$$\langle\hat{P}''\rangle = \langle p_1 + p_2\rangle + 2mv + (1-a)\sum_k \hbar k|c_k(v)|^2. \tag{2.15}$$

Comparing equation (2.14) with (2.15), one obtains the relation

$$\langle p_1 + p_2\rangle = a\sum_k \hbar k\ |c_k(v)|^2 \tag{2.16}$$

which simplifies expression (2.13) for the coefficients $c_k(v)$ considerably:

$$c_k(v) = -\frac{2V_k^*\rho_k^*(a)}{\hbar\omega_k - \hbar k\cdot v + (a^2/4m)(\hbar k)^2}. \tag{2.17}$$

Introducing the notation $M = 2m/a^2$, we may represent the denominator of expression (2.17) as follows

$$\hbar\omega_k - \hbar k\cdot v + \frac{(\hbar k)^2}{2M} = \hbar\omega_k + \frac{(Mv - \hbar k)^2}{2M} - \frac{Mv^2}{2} \tag{2.18}$$

which corresponds to the energy difference of a free moving particle with momentum Mv and the state which has emitted one phonon with momentum $\hbar k$. Thus, the parameter M should be close to the bipolaron effective mass m^*, which is large in the strong-coupling limit or, equivalently, the parameter a is small in this limit. Notice that for $v \neq 0$ it is not permitted to choose $a = 0$ because this would result in an expression for $c_k(v)$ in which the denominator can be equal to zero for some value of the phonon momentum k. In theories without a cut-off this leads to divergences, which is the main theoretical disadvantage of the approach in [11]. Taking into account the electron recoil energy $(a^2/4m)(\hbar k)^2$, this difficulty is avoided. Also, for parameter a, in this recoil term, we obtain variationally an equation. Finally, the variational equation $\delta E[\phi_v]/\delta\phi_v^* = 0$ leads to the Schrödinger equation for the wavefunction $\phi_v(r_1, r_2)$ where the Lagrange multiplier E plays the role of the energy of the system. This equation, and the one for a, will be presented in the next section.

3. Bipolaron ground-state energy and effective mass

In order that the ground-state energy and the effective mass are well defined, one has to consider the limit of a slowly moving bipolaron. First, we consider the bipolaron effective mass. When v tends to zero, terms of order v^2 may be neglected. The wavefunction ϕ_v at $v = 0$ is denoted by ϕ_0 and all averages are now performed over ϕ_0 rather than over ϕ_v. Expanding $c_k(v)$ of equation (2.17) in powers of v and substituting it into equation (2.14), we arrive at the following expression for the bipolaron effective mass:

$$m^* = 2m + 8\sum_k (n \cdot \hbar k)^2 \frac{|V_k|^2 |\rho_k(a)|^2}{[\hbar\omega_k + (a^2/4m)(\hbar k)^2]^3} \tag{3.1}$$

where n is a vector of unit length in the direction of the total momentum $\mathcal{P}$ (or the average velocity v). For an isotropic electron–phonon interaction, one may replace $(n \cdot k)^2$ by k^2/D, where D is the number of space dimensions. In this case, equation (3.1) simplifies to

$$m^* = 2m + \frac{8}{D}\sum_k (\hbar k)^2 \frac{|V_k|^2 \, |\rho_k(a)|^2}{[\hbar\omega_k + (a^2/4m)(\hbar k)^2]^3}. \tag{3.2}$$

Now the bipolaron ground-state energy will be considered. At $v = 0$ one obtains, from equation (2.10), the energy functional

$$E[\phi_0] = \left\langle \frac{p_1^2}{2m} \right\rangle + \left\langle \frac{p_2^2}{2m} \right\rangle + \langle U(|r_1 - r_2|) \rangle + \langle \phi_0 | \phi_0 \rangle \sum_k |c_k|^2 \left[\hbar\omega_k + \frac{a^2}{4m} (\hbar k)^2 \right]$$
$$+ 2\sum_k [V_k c_k \rho_k(a) + V_k^* c_k^* \rho_k^*(a)] + E(\langle \phi_0 | \phi_0 \rangle - 1) \tag{3.3}$$

with the expression for the coefficients c_k

$$c_k = c_k(0) = -\frac{2V_k^* \rho_k^*(a)}{\hbar\omega_k + (a^2/4m)(\hbar k)^2}. \tag{3.4}$$

The equation for parameter a takes the form

$$\frac{\partial}{\partial a}\left[\sum_k \frac{|V_k|^2 \, |\rho_k(a)|^2}{\hbar\omega_k + (a^2/4m)(\hbar k)^2} \right] = 0. \tag{3.5}$$

The Schrödinger equation for the bipolaron at rest is determined by the functional derivative $\delta E[\phi_v]/\delta\phi_v^* = 0$ which results in the integral–differential equation

$$\left[\frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U(r_1, r_2; \phi_0) \right] \phi_0(r_1, r_2) = E_0 \phi_0(r_1, r_2) \tag{3.6}$$

with the effective potential

$$U(r_1, r_2; \phi_0) = U(|r_1 - r_2|) + 4\sum_k \frac{|V_k|^2 |\rho_k(a)|^2}{\hbar\omega_k + (a^2/4m)(\hbar k)^2}$$
$$- 2\sum_k \frac{|V_k|^2}{\hbar\omega_k + (a^2/4m)(\hbar k)^2} \left[\rho_k^*(a) e^{-iak\cdot(r_1+r_2)/2} (e^{ik\cdot r_1} + e^{ik\cdot r_2}) + \text{cc} \right]. \tag{3.7}$$

Note the translational degeneracy of equation (3.6): if $\phi_0(r_1, r_2)$ is a solution then $\phi_0(r_1 + r_0, r_2 + r_0)$ is also a solution to the same equation with the same energy. Choosing a particular solution means fixing a point somewhere in space. Afterwards, equation (3.6) and its solutions are completely determined.

Alternatively, the above equations can also be formulated as a variational problem which is useful in numerical calculations. The ground-state energy E_0 can be defined as the minimum of the functional $E[\phi_0]$. The average kinetic energies of both electrons are equal due to symmetry and one arrives at the functional

$$E[\phi_0] = \bar{T} + \bar{U}$$

$$\bar{T} = \frac{\hbar^2}{m} \int \mathrm{d}r_1 \, \mathrm{d}r_2 \, |\nabla_1 \phi_0(r_1, r_2)|^2$$

$$\bar{U} = -4 \sum_k \frac{|V_k|^2 |\rho_k(a)|^2}{\hbar\omega_k + (a^2/4m)(\hbar k)^2} + \int \mathrm{d}r_1 \, \mathrm{d}r_2 \, U(|r_1 - r_2|) |\phi_0(r_1, r_2)|^2. \tag{3.8}$$

Now we specify the electron–phonon interaction for the case of the Pekar–Fröhlich optical polarons for which the phonon frequency does not depend on the wavevector: $\omega_k = \omega_D$. According to a paper by Peeters *et al* [19], one has in a D-dimensional space

$$V_k = -\mathrm{i}\hbar\omega_D \left(\frac{\alpha_D}{V k^{D-1}} \sqrt{\frac{\hbar}{2m\omega_D}} \left(2\sqrt{\pi}\right)^{D-1} \Gamma\left(\frac{D-1}{2}\right) \right)^{1/2} \tag{3.9}$$

where V is the volume of a D-dimensional 'crystal' and $\Gamma(x)$ is the gamma function. At $D = 3$, one arrives at the standard electron–phonon interaction with conventional phonon frequency $\omega_{3D} = \omega_{LO}$ and dimensionless electron–phonon coupling constant

$$\alpha_{3D} = \alpha = \frac{e^2}{\hbar} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right) \sqrt{\frac{m}{2\hbar\omega_{LO}}}. \tag{3.10}$$

Here, e is the electron charge and ϵ_∞ (ϵ_0) is the high-frequency (static) dielectric constant.

With parametrization (3.9), one obtains

$$\sum_k \frac{|V_k|^2}{\hbar\omega_k + (a^2/4m)(\hbar k)^2} \mathrm{e}^{\mathrm{i}k\cdot r} = \hbar\omega_D \frac{\alpha_D \sqrt{2}}{a} S\left(\frac{|r|}{a} \sqrt{\frac{m\omega_D}{\hbar}} \right) \tag{3.11}$$

where $S(r)$ can be expressed as a sum of modified Bessel and Struve functions:

$$S(r) = \int_0^1 \mathrm{d}x \, [1 - x^2]^{(D-3)/2} \mathrm{e}^{-2xr} \tag{3.12a}$$

$$S(r) = \frac{\sqrt{\pi}}{2} \Gamma\left(\frac{D-1}{2}\right) \left(-\frac{1}{r}\right)^{\frac{D}{2}-1} \left[I_{\frac{D}{2}-1}(-2r) + \mathbf{L}_{\frac{D}{2}-1}(-2r) \right]. \tag{3.12b}$$

To describe the direct interaction between electrons, we choose the Coulomb-type potential

$$U(|r_1 - r_2|) = \hbar\omega_D \frac{U_D}{|r_1 - r_2|} \sqrt{\frac{\hbar}{m\omega_D}}. \tag{3.13}$$

For $D = 3$, the dimensionless Coulomb coupling constant takes the form

$$U_{3D} = \frac{e^2}{\hbar\omega_{LO}\epsilon_\infty}\sqrt{\frac{m\omega_{LO}}{\hbar}} = \frac{\sqrt{2}\alpha}{1-\epsilon_\infty/\epsilon_0}. \tag{3.14}$$

Inserting equations (3.11) and (3.13) into (3.8), the average potential energy of a large bipolaron, gives

$$\begin{aligned}\bar{U} = \hbar\omega_D\Bigg\{ &- \frac{4\sqrt{2}\alpha_D}{a}\int \mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}r_1'\,\mathrm{d}r_2'\,|\phi_0(r_1,r_2)|^2|\phi_0(r_1',r_2')|^2 \\ &\times S\left(\sqrt{\frac{m\omega_D}{\hbar}}\left|\frac{r_1-r_1'}{a} - \frac{r_1+r_2-r_1'-r_2'}{2}\right|\right) \\ &+ U_D\sqrt{\frac{\hbar}{m\omega_D}}\int \mathrm{d}r_1\,\mathrm{d}r_2\,\frac{|\phi_0(r_1,r_2)|^2}{|r_1-r_2|}\Bigg\}\end{aligned} \tag{3.15}$$

where the symmetry of the wavefunctions is taken into account.

Note that in the strong-coupling limit $a \to 0$ and from equation (3.11) we have $\lim_{a\to 0} S(r/a)/a = 1/(2r)$, from which we obtain the average potential energy

$$\begin{aligned}\bar{U}_0 = \hbar\omega_D\sqrt{\frac{\hbar}{m\omega_D}}\Bigg\{ &- 2\sqrt{2}\alpha_D\int \mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}r_1'\,\mathrm{d}r_2'\,\frac{|\phi_0(r_1,r_2)|^2|\phi_0(r_1',r_2')|^2}{|r_1-r_1'|} \\ &+ U_D\int \mathrm{d}r_1\,\mathrm{d}r_2\,\frac{|\phi_0(r_1,r_2)|^2}{|r_1-r_2|}\Bigg\}.\end{aligned} \tag{3.16}$$

The energy functional (3.8) for 3D bipolarons with potential energy given by equation (3.16) appeared first in the pioneering paper by Pekar and Tomasevich [20] as a starting point for Pekar's adiabatic approach to the bipolaron problem. The very name *bipolaron* has been given to this quasiparticle in the cited paper albeit the authors reached a wrong conclusion on the bipolaron *unstability*. Here, we start from the Fröhlich-type Hamiltonian and find the same functional as the leading approximation.

4. Applications to 1D bipolarons

In what follows, we introduce the scaled electron–phonon coupling constant [19–21]

$$\alpha_D' = \alpha_D\sqrt{\pi}\frac{\Gamma[(D-1)/2]}{2\Gamma(D/2)}. \tag{4.1}$$

Similarly, we define a scaled Coulomb coupling constant U_D' so that the ratio $U_D/\alpha_D = U_D'/\alpha_D'$ remains the same. At $D = 3$, we have $\alpha_{3D}' = \alpha_{3D}$ and $U_{3D}' = U_{3D}$, but renormalization (4.1) of the electron–phonon coupling constant is necessary to obtain finite results when $D \to 1$. To derive the equation for the strong-coupling limit in its final form, it is convenient to perform a scaling

$$r_i \to \frac{r_i}{\alpha_D'}\sqrt{\frac{\hbar}{m\omega_D}} \qquad a = \frac{b}{\alpha_D'^2}. \tag{4.2}$$

To preserve the normalization of the wavefunction, one must also perform the scaling of the wavefunction

$$\phi_0\left(\frac{r_1}{\alpha'_D}\sqrt{\frac{\hbar}{m\omega_D}}, \frac{r_2}{\alpha'_D}\sqrt{\frac{\hbar}{m\omega_D}}\right) \to \left(\alpha'_D\sqrt{\frac{m\omega_D}{\hbar}}\right)^D \phi_0(r_1, r_2). \tag{4.3}$$

The effective potential then transforms as follows:

$$U(r_1, r_2; \phi_0) \to \hbar\omega_D\alpha_D'^2 U(r_1, r_2; \phi_0). \tag{4.4}$$

Finally, we arrive, therefore, at the Schrödinger equation ($p_i = -i\nabla_i$):

$$\left[\frac{p_1^2}{2} + \frac{p_2^2}{2} + U(r_1, r_2; \phi_0)\right]\phi_0(r_1, r_2) = \varepsilon_0\,\phi_0(r_1, r_2) \tag{4.5}$$

with dimensionless scaled energy: $\varepsilon_0 = E_0/(\hbar\omega_D\alpha_D'^2)$ and potential

$$\begin{aligned} U(r_1, r_2; \phi_0) = \frac{2\Gamma(D/2)}{\sqrt{\pi}\Gamma[(D-1)/2]}\Bigg\{&\frac{U'_D}{\alpha'_D}\frac{1}{|r_1 - r_2|} \\ &+ 4\sqrt{2}\frac{\alpha'_D}{b}\int \mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}r'_1\,\mathrm{d}r'_2\,|\phi_0(r_1, r_2)|^2|\phi_0(r'_1, r'_2)|^2 \\ &\times S\left(\left|\alpha'_D\frac{r_1 - r'_1}{b} - \frac{r_1 + r_2 - r'_1 - r'_2}{2\alpha'_D}\right|\right) \\ &- 4\sqrt{2}\frac{\alpha'_D}{b}\int \mathrm{d}r'_1\,\mathrm{d}r'_2\,|\phi_0(r'_1, r'_2)|^2\left[S\left(\left|\alpha'_D\frac{r_1 - r'_1}{b} - \frac{r_1 + r_2 - r'_1 - r'_2}{2\alpha'_D}\right|\right)\right. \\ &\left. + S\left(\left|\alpha'_D\frac{r_2 - r'_1}{b} - \frac{r_1 + r_2 - r'_1 - r'_2}{2\alpha'_D}\right|\right)\right]\Bigg\}. \end{aligned} \tag{4.6}$$

The average potential energy is determined by

$$\begin{aligned} \bar{U} = \frac{2\Gamma(D/2)}{\sqrt{\pi}\Gamma[(D-1)/2]}\Bigg\{&\frac{U'_D}{\alpha'_D}\int \mathrm{d}r_1\,\mathrm{d}r_2\,\frac{|\phi_0(r_1, r_2)|^2}{|r_1 - r_2|} \\ &- 4\sqrt{2}\frac{\alpha'_D}{b}\int \mathrm{d}r_1\,\mathrm{d}r_2\,\mathrm{d}r'_1\,\mathrm{d}r'_2\,|\phi_0(r_1, r_2)|^2|\phi_0(r'_1, r'_2)|^2 \\ &\times S\left(\left|\alpha'_D\frac{r_1 - r'_1}{b} - \frac{r_1 + r_2 - r'_1 - r'_2}{2\alpha'_D}\right|\right)\Bigg\}. \end{aligned} \tag{4.7}$$

The average kinetic energy is the same as that given in equation (3.8) except for the factor $\hbar^2/m$ (because of scaling (4.2), (4.3)).

Equation (3.2) for the bipolaron effective mass together with equation (3.9) and the same strong-coupling scaling leads to the expression

$$\frac{m^*}{m} = 2 + \alpha'^4\frac{4\sqrt{2}}{D}\frac{\Gamma(D/2)}{\pi^{1+D/2}}\int \frac{\mathrm{d}k}{k^{D-1}}\frac{k^2|\rho_k(b/\alpha_D'^2)|^2}{[1 + (b/4\alpha_D'^2)k^2]^3}. \tag{4.8}$$

To apply the above equations to the 1D bipolaron case, e.g. to equation (4.7), one has to use the relation

$$\lim_{D\to 1} \frac{\Gamma(D/2)}{\sqrt{\pi}\Gamma[(D-1)/2]} \frac{1}{|r|} = \delta(z) \tag{4.9}$$

where r is a D-dimensional vector and z is its component along the direction of the easy motion of the bipolaron. From equation (3.12), one obtains the expression

$$\lim_{D\to 1} \frac{\Gamma(D/2)}{\sqrt{\pi}\Gamma[(D-1)/2]} S(|r|) = \tfrac{1}{2}\mathrm{e}^{-2|z|}. \tag{4.10}$$

Inserting now equations (4.9) and (4.10) into (4.7), one arrives at the corresponding expressions for the average potential energy in 1D

$$\bar{U} = 2\frac{U'_{1D}}{\alpha'_{1D}} \int \mathrm{d}z_1 \, |\phi_0(z_1, z_1)|^2 - 4\sqrt{2}\frac{\alpha'_{1D}}{b} \int \mathrm{d}z_1 \, \mathrm{d}z_2 \, \mathrm{d}z'_1 \, \mathrm{d}z'_2 \, |\phi_0(z_1, z_2)|^2 |\phi_0(z'_1, z'_2)|^2$$
$$\times \exp\left(-\left|2\alpha'_{1D}\frac{z_1 - z'_1}{b} - \frac{z_1 + z_2 - z'_1 - z'_2}{\alpha'_{1D}}\right|\right). \tag{4.11}$$

To expand $\bar{U}$ in inverse powers of α', a change of variable is performed in the integral of equation (4.11)

$$z'_1 \to z_1 + z'_1 \frac{b/2\alpha'^2_{1D}}{1 - b/2\alpha'^2_{1D}} + (z'_2 - z_2)\frac{b/2\alpha'^2_{1D}}{1 - b/2\alpha'^2_{1D}} \tag{4.12}$$

resulting in the following representation for $\bar{U}$:

$$\bar{U} = 2\frac{U'_{1D}}{\alpha'_{1D}} \int \mathrm{d}z_1 \, |\phi_0(z_1, z_1)|^2 - \frac{2\sqrt{2}}{1 - b/2\alpha'^2_{1D}} \int \mathrm{d}z_1 \, \mathrm{d}z_2 \, \mathrm{d}z'_1 \, \mathrm{d}z'_2 \, \mathrm{e}^{-|z'_1|} |\phi_0(z_1, z_2)|^2$$
$$\times \left|\phi_0\left(z_1 + z'_1 \frac{b/2\alpha'_{1D}}{1 - b/2\alpha'^2_{1D}} + (z'_2 - z_2)\frac{b/2\alpha'^2_{1D}}{1 - b/2\alpha'^2_{1D}}, z'_2\right)\right|^2. \tag{4.13}$$

Taking the limit $\alpha'_{1D} \to \infty$ in equation (4.13), we write down the strong-coupling expansion up to terms of order $1/\alpha'^2_{1D}$

$$\bar{U} = \bar{U}_0 + \frac{1}{\alpha'^2_{1D}}\bar{U}_1 + \cdots \tag{4.14}$$

where the linear term disappears because of integration over z'_1 and where $\bar{U}_0$ and $\bar{U}_1$ are given by equations

$$\bar{U}_0 = 2\frac{U'_{1D}}{\alpha'_{1D}} \int \mathrm{d}z_1 \, |\phi_0(z_1, z_1)|^2 - 4\sqrt{2} \int \mathrm{d}z_1 \, \mathrm{d}z_2 \, \mathrm{d}z'_1 \, |\phi_0(z_1, z_2)|^2 |\phi_0(z_1, z'_2)|^2 \tag{4.15}$$

and

$$\bar{U}_1 = \sqrt{2}b^2 \int \mathrm{d}z_1 \, \mathrm{d}z_2 \, \mathrm{d}z'_2 \left[\frac{\partial}{\partial z_1}|\phi_0(z_1, z_2)|^2\right]\left[\frac{\partial}{\partial z_1}|\phi_0(z_1, z'_2)|^2\right]$$
$$- 2\sqrt{2}b \int \mathrm{d}z_1 \, \mathrm{d}z_2 \, \mathrm{d}z'_2 \, |\phi_0(z_1, z_2)|^2$$
$$\times \left[|\phi_0(z_1, z'_2)|^2 + (z'_2 - z_2)\frac{\partial}{\partial z_1}|\phi_0(z_1, z'_2)|^2\right]. \tag{4.16}$$

The minimum of the potential energy is reached at some finite value of b, as follows from equation (4.16). This means that a, which equals $b/\alpha_{1D}'^2$, will indeed tend to zero in the strong-coupling limit and that the parameter $M = 2m/a^2$ in equation (2.18) behaves, at large α_{1D}', as $M \sim \alpha_{1D}'^4$. To calculate the leading term of the strong-coupling expansion, one may deal with $\bar{U}_0$ only.

The corresponding effective potential in the nonlinear effective Schrödinger equation (4.5) can be obtained in the same manner and is of the form

$$U(z_1, z_2; \phi_0) = 4\sqrt{2} \int dz_1\, dz_2\, dz_2'\, \phi_0^2(z_1, z_2)\phi_0^2(z_1, z_2') - 4\sqrt{2} \int dz_1' [\phi_0^2(z_1, z_1') + \phi_0^2(z_2, z_1')] + 2\frac{U_{1D}'}{\alpha_{1D}'}\delta(z_1 - z_2). \tag{4.17}$$

The same limit $D \to 1$ for the effective mass of equation (4.8) creates no problems. Using the symmetry of the wavefunction $\phi_0(z_1, z_2)$, it can be written as follows:

$$\frac{m^*}{m} = 2 + 8\sqrt{2}\alpha_{1D}'^4 \int dz_1\, dz_2\, dz_2' \left[\frac{\partial}{\partial z_1}|\phi_0(z_1, z_2)|^2\right]\left[\frac{\partial}{\partial z_1}|\phi_0(z_1, z_2')|^2\right]. \tag{4.18}$$

We convince ourselves that, for large α_{1D}', the bipolaron effective mass and parameter M are both proportional to $\alpha_{1D}'^4$, that is, M is indeed close to m^*. Similar conclusions hold for $D = 2, 3$. For instance, at $D = 3$ we have, from equation (3.11),

$$S(r) = \frac{1}{2r}(1 - e^{-2r}). \tag{4.19}$$

At large α_{3D}, argument r will also be large and, as a consequence, the second term will not contribute. We arrive then at the conventional potential energy (3.16).

To conclude, we have presented a systematic study of the equations describing large bipolarons in a strong-coupling regime in spaces with an arbitrary dimensionality. Some of these equations are similar to the ones used previously for the 3D case. The numerical study of the 1D bipolaron case for the ground and excited states based on these equations is given in [17].

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