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2001 J. Phys.: Condens. Matter 13 1499

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Crossover from large to small bipolarons

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Received 29 November 2000

Abstract

A variational procedure is developed to study the properties of the bipolaron in the Fröhlich model including explicitly the electron band structure and taking into account the long-range repulsive electron–electron interaction. Adopting two different *ansatz* for the longitudinal optical phonon distribution function, the large-bipolaron and small-bipolaron limits are obtained. The evolution of the bipolaron ground state as a function of the electron–phonon coupling constant and of the bare-electronic bandwidth is discussed and the bipolaron phase diagram is presented. A clear crossover from the large-bipolaron to the small-bipolaron regime takes place.

1. Introduction

In the last few years infrared spectroscopy and transport measurements have indicated the presence of polaronic carriers in cuprates and manganites [1]. From a theoretical point of view, the Fröhlich [2] and Holstein [3] polaron models have been used to describe the electron–phonon interaction. In both models perturbative methods provide a correct description of the regimes of large and small electron–phonon coupling constants, but they fail in the intermediate region, which is the most interesting in these materials. The Feynman path-integral technique [4] overcomes this difficulty in the Fröhlich case. Within this model, relaxing the effective-mass approximation, it has been shown that it is possible to go from a large- to a small-polaron solution for intermediate values of the electron–phonon coupling constant [5–8]. In the Holstein model the regime characterized by intermediate couplings and electronic and phononic energy scales that are not well separated has been analysed using quantum Monte Carlo simulations [9, 10], numerical exact diagonalizations for small clusters [11, 12], dynamical mean-field theory [13], the global local variational model [14] and the density matrix renormalization group [15]. In the crossover region a linear superposition of states representing the small- and large-polaron wave functions also provides a very accurate description of the polaron features [16, 17]. It turns out that in both models the ground-state energy and the effective mass are continuous functions of the electron–phonon coupling.

Another important subject in condensed-matter physics is the pairing of electrons or holes in real space that has been experimentally observed in many physical systems, such as transition metal oxides [18–20], superconducting materials [21, 22], conjugated polymers [23]

and alternating-valence compounds [24]. In some cases the bipolaron formation is considered the main mechanism [19, 20, 22] of the coupling. The bipolaron has been the subject of numerous studies stimulated also by the discovery of high- T_c cuprates and the belief that the interplay between electron–electron and electron–phonon interactions plays an important role in these materials [25]. Indeed, several authors have proposed a Bose–Einstein bipolaron condensation below T_c , either occurring directly [26] or with the cooperation of fermionic charges [27, 28].

Theoretically the bipolaron formation has been treated in the Fröhlich and Holstein schemes. In the first case the long-range repulsive Coulomb interaction is taken into account [29–36] and it was found that the bipolaron forms only if the Fröhlich electron–phonon coupling constant α is larger than a critical α_c and the ratio η between the high-frequency and static dielectric constants is sufficiently small. Such a value has been estimated to be $\alpha_c \simeq 6.8$ [32] or $\alpha_c \simeq 6$ [33] depending on the approximations used. For any fixed α , there is a value η_c such that for $\eta > \eta_c$ the two charge carriers cannot bind. For α very large, $\eta_c = 0.14$ [37].

In the Holstein–Hubbard model the bipolaron formation has also been faced [38–41]. Two different regimes for the bipolaron ground state have been found when the electron–phonon coupling constant increases: a neighbouring-site bipolaron in the intermediate-coupling regime and an on-site bipolaron in the strong-coupling limit [42]. The properties of the intersite bipolaron have also been investigated by variational and exact-diagonalization methods and by combining density matrix and Lanczos algorithms [43–46]. The influence of the Hubbard interaction U on the bipolaron formation and the transition between the two bipolaronic regimes are still not completely understood.

In this paper we take into account the long-range repulsive electron–electron interaction and we study, by a variational procedure, the bipolaron formation in the Fröhlich model beyond the effective-mass approximation, i.e. the electron band structure is explicitly considered and the Fröhlich coupling is used to describe the electron–phonon matrix element. The bipolaron formation is studied mainly in the weak- and strong-coupling regimes (large and small bipolarons) by evaluating both the bipolaron ground-state and binding energies and the average distance between the two interacting electrons. In particular the binding energy is calculated by comparing the bipolaron ground-state energy with that of two free polarons [6] obtained when the relative distance between the charge carriers becomes infinite. We stress that the variational procedure adopted in this paper is similar to that implemented in reference [6] for the single-polaron problem.

For weak electron–phonon coupling constant, by exploiting the distinctive characteristic of this regime, i.e. the slow variation of the main quantities in the unit cell of the crystal, we will determine, for different values of η and the ratio between the bandwidth Δ and the phonon energy $\hbar\omega$, the critical values of α (α_c) defining the transition from two free large polarons to a large bipolaron. We find that the values of α_c increase with Δ and the binding energy is a decreasing function of η . Another interesting result is that, due to the interaction with phonons, the recoil energy of the electron pair plays an important role in the large-bipolaron formation that turns out to be less restrictive in comparison with the mere Fröhlich bipolaron: indeed, for a given finite bandwidth, α_c is smaller than the value calculated within the effective-mass approximation. In the regime of strong electron–phonon coupling, when the small-bipolaron formation takes place, we find that the electrons localize at a relative distance comparable to the lattice parameter of the crystal. Finally the crossover between the small- and large-bipolaron solutions occurs. The values of α where the transition occurs will be indicated in the following by α_c^{bip} .

In sections 2 and 3 the model and the variational procedure are presented; in section 4 the results are discussed.

2. The model

The Hamiltonian for two electrons (or two holes) in a periodic potential interacting with the longitudinal optical phonons and with each other through the Coulomb force can be given by

$$H = E_b(-i\vec{\nabla}_{\vec{r}_1}) + E_b(-i\vec{\nabla}_{\vec{r}_2}) + \frac{e^2}{\varepsilon_\infty r} + \sum_{\vec{q}} \hbar\omega_{\vec{q}} a_{\vec{q}}^\dagger a_{\vec{q}} + \sum_{\vec{q}} \left[V_{\vec{q}} a_{\vec{q}} (e^{i\vec{q}\cdot\vec{r}_1} + e^{i\vec{q}\cdot\vec{r}_2}) + \text{h.c.} \right] \quad (1)$$

where \vec{r}_1 and \vec{r}_2 indicate the positions of the two electrons, $\vec{\nabla}_{\vec{r}_1}$ and $\vec{\nabla}_{\vec{r}_2}$ the relative gradient operators, $\vec{r} = \vec{r}_1 - \vec{r}_2$ the relative distance, ε_∞ the high-frequency dielectric constant, ω the longitudinal optical phonon frequency, $V_{\vec{q}}$ the strength of the electron–phonon interaction, $a_{\vec{q}}$ ($a_{\vec{q}}^\dagger$) the phonon annihilation (creation) operator and $E_b(-i\vec{\nabla}_{\vec{r}_1})$ and $E_b(-i\vec{\nabla}_{\vec{r}_2})$ the operators obtained with the substitution in the bare-electronic band $E_b(\vec{k})$ for the crystalline momentum \vec{k} with $-i\vec{\nabla}_{\vec{r}_1}$ and $-i\vec{\nabla}_{\vec{r}_2}$ respectively. In equation (1) the Umklapp terms in the electron–phonon and electron–electron interactions have been neglected and $V_{\vec{q}}$ is the Fröhlich interaction

$$V_{\vec{q}} = i \frac{\hbar\omega}{q} \left(\frac{4\pi\alpha}{V} \right)^{1/2} R_p^{1/2}$$

where V is the volume of the system, α is a dimensionless parameter measuring the strength of the electron–phonon interaction and R_p is the polaron radius ($R_p = \sqrt{\hbar/(2m\omega)}$ with m denoting the effective mass of $E_b(\vec{k})$ at $\vec{k} = 0$). In appendix I we show the limits of validity of equation (1). Introducing the centre-of-mass coordinates of the pair \vec{R}_c and the relative coordinates \vec{r} , the Hamiltonian becomes

$$H = E_b\left(-\frac{i}{2}\vec{\nabla}_{\vec{R}_c} - i\vec{\nabla}_{\vec{r}}\right) + E_b\left(-\frac{i}{2}\vec{\nabla}_{\vec{R}_c} + i\vec{\nabla}_{\vec{r}}\right) + \frac{e^2}{\varepsilon_\infty r} + \sum_{\vec{q}} \hbar\omega_{\vec{q}} a_{\vec{q}}^\dagger a_{\vec{q}} + \sum_{\vec{q}} \left[V_{\vec{q}} a_{\vec{q}} e^{i\vec{q}\cdot\vec{R}_c} \rho_{\vec{q}}(\vec{r}) + \text{h.c.} \right] \quad (2)$$

with

$$\rho_{\vec{q}}(\vec{r}) = e^{i\vec{q}\cdot\vec{r}/2} + e^{-i\vec{q}\cdot\vec{r}/2}.$$

3. Variational procedure

It is well known that in the Fröhlich model [2], within the effective-mass and continuum approximations, the variational approach proposed by Lee, Low and Pines [47] provides a good description only in the weak-coupling regime. Some of us [6] have shown that, relaxing the previous approximations and taking into account the electron band structure, a phonon wave function represented by a coherent state and similar in form to that used by Lee, Low and Pines [47] is able to provide a correct description of the polaron features both in the weak- and the strong-coupling regimes. For these reasons we adopt a variational procedure based on a bipolaron wave function which reduces to that of two free polarons described in reference [6] when the relative distance between the two interacting electrons becomes infinite. In appendix I we propose the following trial wave function for the bipolaron problem

$$|\psi_{\vec{Q}}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{Q}\cdot\vec{R}_c} \exp\left(\sum_{\vec{q}} (f_{\vec{q}}(\vec{r}) e^{i\vec{q}\cdot\vec{R}_c} a_{\vec{q}} - f_{\vec{q}}^*(\vec{r}) e^{-i\vec{q}\cdot\vec{R}_c} a_{\vec{q}}^\dagger)\right) \varphi(\vec{r}) |0\rangle \quad (3)$$

where \vec{Q} is the total crystalline momentum, $f_{\vec{q}}(\vec{r})$ denotes the distribution function of the phonons, $\varphi(\vec{r})$ represents the relative wave function of the two electrons and $|0\rangle$ indicates

the phonon vacuum state. We will study the solutions in the singlet state, so the trial wave function (3) has to be even under the exchange of the spatial coordinates of the two electrons (or equivalently under the transformation $\vec{r} \rightarrow -\vec{r}$). Clearly the calculations can be performed for a triplet state too. We stress that the phonon distribution function depends on the relative coordinate of the two interacting charge carriers, so the wave function (3) contains, on average, the retardation effects of the electron–electron interaction mediated by the exchange of the longitudinal optical phonons.

The expectation value of the Hamiltonian (1) reads

$$\begin{aligned}
E(\vec{Q}) = \langle \psi_{\vec{Q}} | H | \psi_{\vec{Q}} \rangle = & \sum_n E_n e^{i\vec{Q} \cdot \vec{R}_n / 2} \int d\vec{r} \varphi(\vec{r}) \varphi(\vec{r} + \vec{R}_n) e^{-\sigma_{1n}(\vec{r})} \\
& + \sum_n E_n e^{i\vec{Q} \cdot \vec{R}_n / 2} \int d\vec{r} \varphi(\vec{r}) \varphi(\vec{r} + \vec{R}_n) e^{-\sigma_{2n}(\vec{r})} + \sum_{\vec{q}} \hbar\omega \int d\vec{r} \varphi^2(\vec{r}) |f_{\vec{q}}(\vec{r})|^2 \\
& + \langle \varphi | \frac{e^2}{\varepsilon_{\infty} r} | \varphi \rangle - \sum_{\vec{q}} \left[V_q \int d\vec{r} \varphi(\vec{r})^2 f_{\vec{q}}^*(\vec{r}) (e^{i\vec{q} \cdot \vec{r} / 2} + e^{-i\vec{q} \cdot \vec{r} / 2}) + \text{c.c.} \right] \quad (4)
\end{aligned}$$

where

$$\sigma_{1n}(\vec{r}) = \frac{1}{2} \sum_{\vec{q}} \left[|f_{\vec{q}}(\vec{r})|^2 + |f_{\vec{q}}(\vec{r} + \vec{R}_n)|^2 - 2f_{\vec{q}}(\vec{r}) f_{\vec{q}}^*(\vec{r} + \vec{R}_n) e^{-i\vec{q} \cdot \vec{R}_n / 2} \right] \quad (5)$$

and

$$\sigma_{2n}(\vec{r}) = \frac{1}{2} \sum_{\vec{q}} \left[|f_{\vec{q}}(\vec{r})|^2 + |f_{\vec{q}}(\vec{r} + \vec{R}_n)|^2 - 2f_{\vec{q}}^*(\vec{r}) f_{\vec{q}}(\vec{r} + \vec{R}_n) e^{-i\vec{q} \cdot \vec{R}_n / 2} \right]. \quad (6)$$

In the following the numerical calculations will be performed by assuming that the bare-electron band $E_f(\vec{Q})$ has cubic symmetry and by retaining only the nearest-neighbouring coefficients E_n so that the bare band structure acquires the characteristic form of the tight-binding approximation:

$$E_b(\vec{Q}) = E_0 + 2E_1 [\cos(Q_x a) + \cos(Q_y a) + \cos(Q_z a)]. \quad (7)$$

We consider a suitable form of the relative wave function $\varphi(\vec{r})$:

$$\varphi(\vec{r}) = N r^\beta e^{-\gamma r} \quad (8)$$

with β and γ variational parameters and N the normalization coefficient

$$N = \frac{1}{(4\pi)^{1/2}} \left[\frac{(2\gamma)^{2\beta+3}}{\Gamma(2\beta+3)} \right]^{1/2}.$$

Here $\Gamma(x)$ indicates the gamma function. This relative wave function has already been used to calculate the large-bipolaron binding energy in the continuum approximation for the ground state and a class of excited states [33]. It takes into account the fact that because of the strong Coulomb interaction the electrons repel at small distance and the probability of being at the same point is zero. Since $\varphi(\vec{r})$ has spherical symmetry, we find that $\sigma_{1n}(\vec{r}) = \sigma_n(\vec{r}) = \sigma_{2n}(-\vec{r})$ and the expression for the energy (4) is simplified.

The functional derivative of the energy $E(\vec{Q})$ with respect to $f_{\vec{q}}(\vec{r})$ provides the following expression for the phonon distribution function $f_{\vec{q}}(\vec{r})$:

$$f_{\vec{q}}(\vec{r}) = \frac{V_q \rho_{\vec{q}}(\vec{r}) \varphi^2(r)}{\varphi^2(r) \hbar\omega + 2\varepsilon(\vec{Q}, \vec{q}, \vec{r}) - \varepsilon_1(\vec{Q}, \vec{r}) - \varepsilon_2(\vec{Q}, \vec{r})} \quad (9)$$

where

$$\begin{aligned}\varepsilon(\vec{Q}, \vec{q}, \vec{r}) &= \sum_n E_n e^{(i/2)\vec{R}_n \cdot (\vec{Q} - \vec{q})} \varphi(r) \varphi(\vec{r} - \vec{R}_n) e^{-\sigma_n^*(\vec{r})} f_{\vec{q}}(\vec{r} - \vec{R}_n) \\ \varepsilon_1(\vec{Q}, \vec{r}) &= \sum_n E_n e^{(i/2)\vec{R}_n \cdot \vec{Q}} \varphi(r) \varphi(\vec{r} + \vec{R}_n) e^{-\sigma_n(\vec{r})}\end{aligned}$$

and

$$\varepsilon_2(\vec{Q}, \vec{r}) = \sum_n E_{-n} e^{-(i/2)\vec{R}_n \cdot \vec{Q}} \varphi(r) \varphi(\vec{r} - \vec{R}_n) e^{-\sigma_{-n}^*(\vec{r})}.$$

We acknowledge the presence of a recoil term in $f_{\vec{q}}(\vec{r})$, even though this makes the consideration more complex than in the polaron case [6]. Equation (9) is very complicated, so we adopt two approximations able to take into account different physical descriptions of the problem emphasizing the large- and small-bipolaron limits.

3.1. Small-bipolaron limit

We assume that the phonon distribution function $f_{\vec{q}}(\vec{r})$ depends on the relative distance \vec{r} between the electrons only through the relation

$$f_{\vec{q}}(\vec{r}) = C_{\vec{q}} \rho_{\vec{q}}(\vec{r}) = C_{\vec{q}} (e^{i\vec{q} \cdot \vec{r}/2} + e^{-i\vec{q} \cdot \vec{r}/2}) \quad (10)$$

where $C_{\vec{q}}$ is a function to be determined variationally. In the above form of $f_{\vec{q}}(\vec{r})$, $C_{\vec{q}}$ is independent of \vec{r} and, although only in averaged form, contains all the effects due to the recoil energy. Indeed we have exploited the feature that in this regime the phonon contribution to the energy depends only on the average electronic configuration. The phonon distribution function has the right property of exchange between the spatial coordinates of two electrons in a singlet state. We obtain

$$\begin{aligned}E(\vec{Q}) &= 2 \sum_n E_n e^{i\vec{Q} \cdot \vec{R}_n/2} e^{-\sigma_n} S_n(\gamma, \beta) + \frac{2\alpha R_p \hbar \omega}{1 - \eta} \frac{\gamma}{\beta + 1} \\ &+ 2 \sum_{\vec{q}} \hbar \omega |C_{\vec{q}}|^2 (1 + h(\vec{q})) - 2 \sum_{\vec{q}} \left[V_{\vec{q}} C_{\vec{q}}^* (1 + h(\vec{q})) \rho_{\vec{q}}(\vec{r}) + \text{c.c.} \right] \quad (11)\end{aligned}$$

where

$$\begin{aligned}\sigma_n &= \sum_{\vec{q}} |C_{\vec{q}}|^2 (1 - e^{-i\vec{q} \cdot \vec{R}_n}) \\ h(\vec{q}) &= \frac{4\pi N^2}{q} \frac{\Gamma(2\beta + 2)}{(4\gamma^2 + q^2)} \sin \left[(2\beta + 2) \arctan \left(\frac{q}{2\gamma} \right) \right]\end{aligned}$$

and

$$S_n(\gamma, \beta) = \int d\vec{r} \varphi_1(\vec{r}) \varphi_2(\vec{r} + \vec{R}_n)$$

with

$$\varphi_1(\vec{r}) = \varphi(\vec{r}) \exp \left(i \sum_{\vec{q}} |C_{\vec{q}}|^2 \sin(\vec{q} \cdot \vec{r}) \right)$$

and

$$\varphi_2(\vec{r} + \vec{R}_n) = \varphi(\vec{r} + \vec{R}_n) \exp \left(-i \sum_{\vec{q}} |C_{\vec{q}}|^2 \sin[\vec{q} \cdot (\vec{r} + \vec{R}_n)] \right).$$

From equation (11) it is simple to obtain the Euler equation $\partial E / \partial C_{\vec{q}}^* = 0$; thus,

$$C_{\vec{q}} = \frac{V_q(1 + h(\vec{q}))}{A(\vec{q})} \quad (12)$$

where

$$A(\vec{q}) = \hbar\omega(1 + h(\vec{q})) + 2 \left[\bar{\varepsilon}(\vec{Q} - 2\vec{q}) - \bar{\varepsilon}(\vec{Q}) \right]$$

with

$$\bar{\varepsilon}(\vec{Q}) = \sum_n E_n e^{i\vec{Q} \cdot \vec{R}_n / 2} e^{-\sigma_n} S_n(\gamma, \beta).$$

Substituting equation (12) in (11), the lowest value of the energy is

$$\begin{aligned} E(\vec{Q}) = 2E_0 + \frac{2\alpha R_p}{1 - \eta} \hbar\omega \frac{\gamma}{\beta + 1} \\ + 4E_1 e^{-\sigma} S(\gamma, \beta) \left[\cos\left(\frac{Q_x a}{2}\right) + \cos\left(\frac{Q_y a}{2}\right) + \cos\left(\frac{Q_z a}{2}\right) \right] \\ + 2 \sum_{\vec{q}} \frac{|V_q|^2 (1 + h(\vec{q}))^3}{A^2} - 4 \sum_{\vec{q}} \frac{|V_q|^2 (1 + h(\vec{q}))^2}{A} \end{aligned} \quad (13)$$

where

$$\sigma = \sum_{\vec{q}} \frac{|V_q|^2 (1 + h(\vec{q}))^2}{A^2} (1 - \cos(q_z a)) \quad (14)$$

$$S(\gamma, \beta) = \int d\vec{r} \varphi(r) \varphi(|\vec{r} + \vec{a}|)$$

and $\vec{a} = (0, 0, a)$. We notice that the value of σ has to be calculated self-consistently through equation (14).

The numerical calculations show that: (a) there is a region where $0 < \alpha < 1.33$ and $0 < \Delta < 5.4$ in which the small bipolaron cannot form; (b) in this region the total energy is minimized for $\beta = \gamma = 0$, i.e. it is coincident with twice that of two free small polarons; (c) outside this region, the values of β and γ minimizing the energy (13) are found only when $\gamma \gg bz$, where bz is the radius of the Brillouin zone. The consequences of this fact can be understood analytically.

In the aforesaid limit $\gamma \gg bz$, we have

$$h(\vec{q}) \simeq \frac{\gamma}{(\beta + 1)q} \sin\left(\frac{\beta + 1}{\gamma} q\right) \quad (15)$$

$$S(\gamma, \beta) \simeq 0 \quad (16)$$

and therefore

$$C_{\vec{q}} = C_q = \frac{V_q}{\hbar\omega} \quad (17)$$

showing that the effects due to the correlation introduced by the electron recoil are negligible in this regime. Then the self-energy becomes

$$E(\vec{Q} = 0) = 2E_0 - 2 \sum_{\vec{q}} \frac{|V_q|^2}{\hbar\omega} + \frac{2\alpha R_p}{1 - \eta} \hbar\omega \frac{\gamma}{\beta + 1} - 2 \sum_{\vec{q}} \frac{|V_q|^2}{\hbar\omega} h(\vec{q}) = 2E_p + E_b. \quad (18)$$

The first two terms to the right-hand side of (18) give twice the polaron self-energy $2E_p$ in the small-polaron limit. The sum of the third and the fourth terms, E_b , is the energy due to the

electronic repulsion and to the phonon field when the electrons are in the relative wave function $\varphi(r)$. E_b is the binding energy of the bipolaron and is a function of the ratio $\gamma/(\beta + 1)$:

$$E_b = 2\alpha R_p \frac{\gamma}{\beta + 1} \left[\frac{1}{1 - \eta} - \frac{2}{\pi} \text{Si} \left(\frac{\beta + 1}{\gamma} b_z \right) \right] \quad (19)$$

where $\text{Si}(x)$ is the sine integral. The highest bipolaron binding energy, found when $\eta = 0$, is

$$E_m = -0.45\alpha \frac{R_p}{a} \hbar\omega.$$

We observe that the above procedure does not allow us to calculate the values of β and γ separately; only the ratio $(\beta + 1)/\gamma = 0.75a$ is fixed. The radial probability distribution

$$g(r) = 4\pi N^2 \frac{(2\gamma)^{2\beta+3}}{\Gamma(2\beta+3)} r^{2\beta+2} e^{-2\gamma r}$$

is peaked around the position $0.75a$. On increasing γ (and consequently β), this function becomes more localized.

We tried to understand this fact more deeply, adopting the same procedure but assuming as the relative wave function

$$\varphi(r) = N e^{-\chi^2(r-r_0)^2/2}$$

where N is the normalization coefficient, χ and r_0 are variational parameters. The results of the new calculation are: (a) the energy is minimized for $r_0 = 0.73a$; (b) the energy is a decreasing function of χ which tends to the asymptotic limit $\chi \rightarrow \infty$. Therefore the relative function approximates to a δ -function localized at $r_0 = 0.73a$.

The same occurs using the former function

$$\varphi(\vec{r}) = N r^\beta e^{-\gamma r}.$$

However, in this case the theory allows one to find only the distance of the largest probability of the presence of the electrons, and not the quantities γ and β independently. Furthermore the energies calculated through the two trial wave functions differ by a few per cent. This indicates that the results are nearly independent of the relative wave function adopted. Since in the Fröhlich large-bipolaron formation the wave function (8) was employed, for consistency it is reasonable to use the same form of relative function for the large- and small-bipolaron limits. We conclude that: (a) the small bipolaron cannot form in the region where $0 < \alpha < 1.33$ and $0 < \Delta < 5.4$; (b) outside this region the highest value of η for which the bipolaron can form is $\eta = 0.14$; (c) the binding energy increases linearly with α for fixed polaron radius R_p .

3.2. Large-bipolaron limit

To obtain the large-bipolaron limit, we observe that in the expression for the energy (4) there are terms of the type $\int d\vec{r} \varphi(r) F(\vec{r} + \vec{R}_n)$, where $F(\vec{r} + \vec{R}_n)$ is

$$F(\vec{r} + \vec{R}_n) = \varphi(\vec{r} + \vec{R}_n) e^{-\sigma_n(\vec{r})}.$$

The attempt now is to consider $F(\vec{r} + \vec{R}_n)$ as a slowly varying function of \vec{R}_n and expand it to the second order. In this way we assume implicitly that $\varphi(r)$ and $f_{\vec{q}}(\vec{r})$ are slowly varying on the unit cell of the crystal, but we preserve the condition that the electronic band has a finite width. One could note that this behaviour of $\varphi(\vec{r})$ and $f_{\vec{q}}(\vec{r})$ implies that the Fourier transform is different from zero only around the centre of the Brillouin zone. Consequently even if we do not expand the band energy around $\vec{Q} = 0$, the results should be coincident with those obtained within the effective-mass approximation. We will find that this does not occur. Thus it will be clear that the two approximations are independent. The physical reason for this is

the following: taking the bandwidth finite, we prevent the kinetic energy from becoming very large. In appendix II it is shown that, after a very lengthy but straightforward calculation, we obtain for the energy

$$\begin{aligned}
E = & 2E_0 + 2 \int d\vec{r} \varphi(r)^2 \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) + a^2 \int d\vec{r} \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) \varphi(r) \nabla^2 \varphi(r) \\
& + \sum_{\vec{q}} \hbar\omega \int d\vec{r} \varphi(r)^2 |f_{\vec{q}}(\vec{r})|^2 - \sum_{\vec{q}} \left[V_q \int d\vec{r} \varphi(r)^2 f_{\vec{q}}^*(\vec{r}) \rho_{\vec{q}}(\vec{r}) + \text{c.c.} \right] \\
& + a^2 \int d\vec{r} \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) f_{\vec{q}}^*(\vec{r}) (\vec{\nabla} \varphi^2 \cdot \vec{\nabla} f_{\vec{q}}(\vec{r}) + \varphi^2 \nabla^2 f_{\vec{q}}(\vec{r})) \\
& - \left[\frac{2}{i} \sum_{\vec{q}} \int d\vec{r} \vec{\nabla} \varphi^2 \cdot \vec{\nabla} \left\{ \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) \right\} - \text{c.c.} \right] |f_{\vec{q}}(\vec{r})|^2 \\
& - a^2 \sum_{\vec{q}} \int d\vec{r} \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) |f_{\vec{q}}(\vec{r})|^2 ((\vec{\nabla} \varphi)^2 + \varphi(r) \nabla^2 \varphi(r)) \\
& + a^2 \sum_{\vec{q}} \int d\vec{r} \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, \vec{r}\right) f_{\vec{q}}^*(\vec{r}) (\vec{\nabla} \varphi^2 \cdot \vec{\nabla} f_{\vec{q}}(\vec{r}) + \varphi^2 \nabla^2 f_{\vec{q}}(\vec{r})) \\
& + \frac{a^2}{2} \sum_{\vec{q}} \int d\vec{r} \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, \vec{r}\right) |f_{\vec{q}}(\vec{r})|^2 \nabla^2 \varphi^2 + \langle \varphi | \frac{\varphi^2}{r} | \varphi \rangle
\end{aligned} \tag{20}$$

where

$$\begin{aligned}
\Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, \vec{r}\right) &= \tilde{E}\left(\frac{\vec{Q}}{2} - \vec{q}, \vec{r}\right) - \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) \\
\tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) &= \sum_{n \neq 0} E_n e^{i\vec{Q} \cdot \vec{R}_n / 2} e^{-\delta_n(\vec{r})}
\end{aligned}$$

and

$$\delta_n(\vec{r}) = \sum_{\vec{q}} |f_{\vec{q}}(\vec{r})|^2 (1 - e^{-i\vec{q} \cdot \vec{R}_n / 2}).$$

In all of the above equations the bare-electronic band of (7) has been explicitly considered. The Euler equation $\delta E / \delta f_{\vec{q}}^*(\vec{r}) = 0$ gives

$$\begin{aligned}
& a^2 \tilde{E}\left(\frac{\vec{Q}}{2} - \vec{q}, \vec{r}\right) \nabla^2 f_{\vec{q}}(\vec{r}) + a^2 \tilde{E}\left(\frac{\vec{Q}}{2} - \vec{q}, \vec{r}\right) \frac{\vec{\nabla} \varphi^2}{\varphi^2} \cdot \vec{\nabla} f_{\vec{q}}(\vec{r}) \\
& + \left[2 \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) + \hbar\omega + a^2 \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) \frac{\varphi \nabla^2 \varphi}{\varphi^2} \right] f_{\vec{q}}(\vec{r}) \\
& = V_q (e^{i\vec{q} \cdot \vec{r} / 2} + e^{-i\vec{q} \cdot \vec{r} / 2}).
\end{aligned} \tag{21}$$

This is a very complicated non-linear equation, because $f_{\vec{q}}(\vec{r})$ appears in non-linear form in $\tilde{E}(\vec{Q}/2 - \vec{q}, \vec{r})$ and $\Delta E(\vec{Q}/2, \vec{q}, \vec{r})$, which also depend explicitly on \vec{r} . The main approximation is now to replace $|f_{\vec{q}}(\vec{r})|^2$ in $\delta_n(\vec{r})$ and $\varphi \nabla^2 \varphi / \varphi^2$ with their average value for the state $\varphi(r)$. Therefore the polarization effects are taken into account through quantities depending

on the average relative position of the electron pair. Equation (21) becomes then

$$\begin{aligned}
& a^2 \tilde{E} \left(\frac{\vec{Q}}{2} - \vec{q} \right) \nabla^2 f_{\vec{q}}(\vec{r}) + a^2 \tilde{E} \left(\frac{\vec{Q}}{2} - \vec{q} \right) \frac{\vec{\nabla} \varphi^2}{\varphi^2} \cdot \vec{\nabla} f_{\vec{q}}(\vec{r}) \\
& + \left[2 \Delta E \left(\frac{\vec{Q}}{2}, \vec{q} \right) + \hbar\omega - a^2 \Delta E \left(\frac{\vec{Q}}{2}, \vec{q} \right) \frac{\gamma^2}{2\beta + 1} \right] f_{\vec{q}}(\vec{r}) \\
& = V_q (e^{i\vec{q} \cdot \vec{r}/2} + e^{-i\vec{q} \cdot \vec{r}/2})
\end{aligned} \tag{22}$$

where

$$\begin{aligned}
\tilde{E}(\vec{Q}) &= \sum_{n \neq 0} E_n e^{i\vec{Q} \cdot \vec{R}_n} e^{-\delta_n} \\
\delta_n &= \sum_{\vec{q}} \langle \varphi | f_{\vec{q}}(\vec{r}) |^2 \varphi \rangle (1 - e^{-i\vec{q} \cdot \vec{R}_n/2}) \\
\Delta E \left(\frac{\vec{Q}}{2}, \vec{q} \right) &= \tilde{E} \left(\frac{\vec{Q}}{2} - \vec{q} \right) - \tilde{E} \left(\frac{\vec{Q}}{2} \right).
\end{aligned} \tag{23}$$

An equation formally similar to (22) was obtained in the theory of the large-bipolaron formation in the effective-mass approximation [33]. In that case the solution of the equivalent of equation (22) was exactly written as a series containing both confluent hypergeometrical functions and spherical harmonics. The physical meaning of this result is that the phonon distribution function $f_{\vec{q}}(\vec{r})$ does not have spherical symmetry, as it must occur for the presence of the two electrons. It was found that when the bipolaron radius $(\beta + 1)/\gamma$ is much larger than the polaron radius R_p , $f_{\vec{q}}(\vec{r})$ has a simple asymptotic form and the energy becomes that of two independent Fröhlich polarons. The same mathematical procedure can be applied to equation (22), producing for the asymptotic distribution function

$$f_{\vec{q}}(\vec{r}) = -\frac{V_q}{M_{\vec{q}}} (e^{i\vec{q} \cdot \vec{r}/2} + e^{-i\vec{q} \cdot \vec{r}/2}) = -\frac{V_q}{M_{\vec{q}}} \rho_{\vec{q}}(\vec{r}) \tag{24}$$

where

$$M_{\vec{q}} = \hbar\omega - a^2 \tilde{E} \left(\frac{\vec{Q}}{2} - \vec{q} \right) \left(\gamma^2 + \frac{q^2}{4} \right) + \Delta E \left(\frac{\vec{Q}}{2}, \vec{q} \right) \left(2 - \frac{\gamma^2 a^2}{2\beta + 1} \right) \tag{25}$$

is always positive if $2 - \gamma^2 a^2 / (2\beta + 1) > 0$. We stress that even in this simple case the calculation of $f_{\vec{q}}(\vec{r})$ must be done in a self-consistent way, because the phonon distribution function enters $M_{\vec{q}}$ through δ_n . Once this has been done, equation (20) allows one to calculate the energy of two separated large polarons in a band with finite width. In this limit we do not take into account the distortion of $f_{\vec{q}}(\vec{r})$ due to the presence of the second electron. When the two electrons are at finite relative distance, we should follow the same procedure as is used in reference [33] to calculate $f_{\vec{q}}(\vec{r})$. Now this is very difficult to do; we simplify the calculation, considering only the first angular term [48], so we adopt as the trial phonon distribution function the following:

$$f_{\vec{q}}(\vec{r}) = -\frac{V_q}{M_{\vec{q}}} (e^{i\vec{q} \cdot \vec{r}/2} + e^{-i\vec{q} \cdot \vec{r}/2}) (p_1 + p_2 (\hat{q} \cdot \hat{r})^2) \tag{26}$$

where p_1 and p_2 are variational parameters and \hat{q} and \hat{r} the unit vectors in the directions of \vec{q} and \vec{r} respectively. It is necessary to use $(\hat{q} \cdot \hat{r})^2$ to be sure that the wave function (3) is even for the exchange of the spatial coordinates of the two electrons. Using the above expression of $f_{\vec{q}}(\vec{r})$, the energy (20) is calculated numerically taking into account the self-consistent condition (23). The energy is finally minimized with respect to the parameters p_1 , p_2 , γ and β . The explicit

calculations are performed for $\vec{Q} = 0$. Considering the simple cubic bare band (7) and taking into account that the relative wave function $\varphi(r)$ has spherical symmetry, the coefficients δ_n reduce to a unique complex number $\delta = w + is$ whose real and imaginary parts are given by the implicit coupled equations

$$\begin{aligned} w &= \sum_{\vec{q}} \int d\vec{r} |f_{\vec{q}}(\vec{r})|^2 \varphi^2(r) \left[1 - \cos\left(\frac{q_z a}{2}\right) \right] \\ s &= \sum_{\vec{q}} \int d\vec{r} |f_{\vec{q}}(\vec{r})|^2 \varphi^2(r) \sin\left(\frac{q_z a}{2}\right) \end{aligned} \quad (27)$$

because $f_{\vec{q}}(\vec{r})$ depends on w and s through $M_{\vec{q}}$. At $Q \simeq 0$, we find exactly $s = 0$.

4. Discussion of results and conclusions

We have calculated numerically the self-energy $E(Q = 0)$ for the small and large bipolarons as a function of the bandwidth Δ and of the electron–phonon coupling constant α . The results for $\Delta = 20$ (in units of $\hbar\omega$) are shown in figure 1 together with twice the polaron self-energy E_{2pol} obtained in reference [6] (conditions: $\gamma = \beta = 0$; E_{2pol}^l is the energy of two polarons in the large-polaron limit and E_{2pol}^s is that in the small-polaron limit). As in the polaron case, we stress the appearance of two regimes, the large-bipolaron and small-bipolaron ones. The quantity α_c^{bip} (α_c^{pol}) indicates the crossover from large to small bipolarons (polarons). The large-bipolaron solution denoted by E_l describes the ground state for weak coupling, the small-bipolaron solution denoted by E_s that for strong coupling. The crossover between the two regimes is sharp and becomes more apparent with increasing Δ . Furthermore we remark

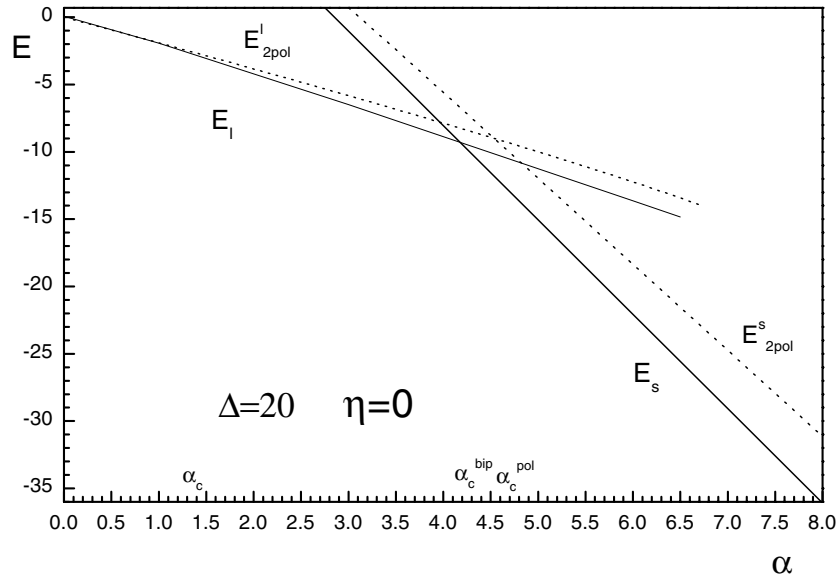


Figure 1. The bipolaron self-energy $E(Q = 0)$ for small and large bipolarons as a function of the electron–phonon coupling constant α for $\Delta = 20$ and $\eta = 0$. E_l and E_s (solid lines) denote the large- and small-bipolaron solutions respectively. E_{2pol}^l (dotted line) gives twice the large-polaron self-energy and E_{2pol}^s (dotted line) twice the small-polaron self-energy as calculated in reference [6]. The energies are given in units of $\hbar\omega$.

that the α_c^{bip} -values are little smaller than α_c^{pol} -values. We observe, however, that for α smaller than 1.5, the large bipolaron does not form, so the two charge carriers behave as two free large polarons.

In figure 2 we show the phase diagram for the bipolaron in the plane (α, Δ) . There are four regions with different features of the bipolaron or polaron states. The modifications of the states between two confining regions occur sharply. The main conclusions are the following.

- In region I, the lowest energy is that of two free large polarons.
- In region II, between the curves α_c and α_c^{bip} , the large bipolaron is the stable phase. When Δ increases, α_c and the self-energy approach the values calculated in the effective-mass approximation [33], whereas α_c^{bip} increases indefinitely. Therefore for Δ very large, the large bipolaron is the prominent phase.
- In region III, below the curve α_c^{bip} , the small bipolaron has the lowest energy. In the limit $\Delta \gg \hbar\omega$ the transition to the small-bipolaron state occurs as long as the electron–phonon coupling is very strong.
- In region IV ($0 < \alpha < 1.33$ and $0 < \Delta < 5.4 \hbar\omega$), the small bipolaron cannot form, because the total energy is equal to twice that of two free small polarons.

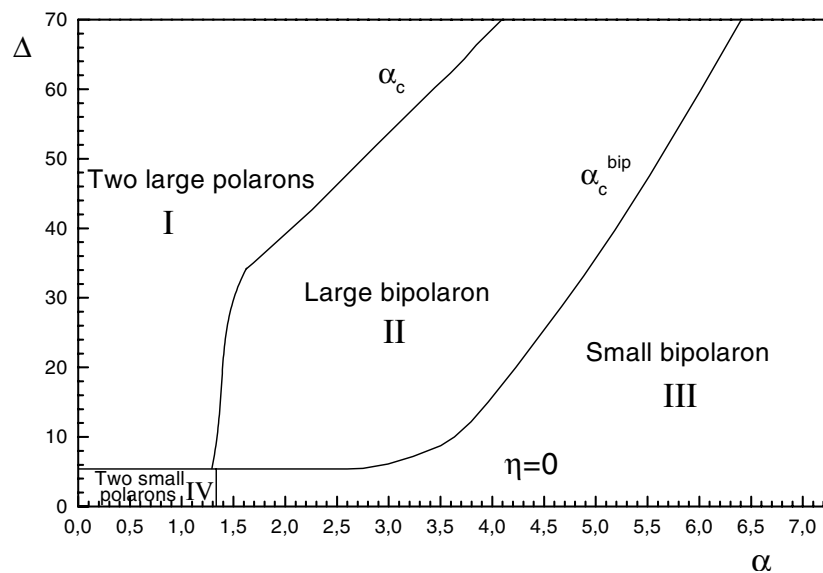


Figure 2. The bipolaron phase diagram for $\eta = 0$. In the plane (α, Δ) four stable regions are indicated: I: the region of two large polarons; II: the region of the large bipolaron; III: the region of the small bipolaron; IV: the region of two small polarons. The quantity α_c (solid line) defines the transition from two free large polarons to a large bipolaron; α_c^{bip} (solid line) indicates the crossover from the large to the small bipolaron. Δ is given in units of $\hbar\omega$.

Clearly, in regions I and IV the Coulomb interaction overcomes the attractive forces mediated by the electron–phonon interaction and the exchange effects. We stress, however, the fact that the formation of a large bipolaron from two free large polarons is less restrictive compared with the mere Fröhlich bipolaron. Indeed, for $\Delta = 20 \hbar\omega$, the quantity α_c is only 1.5, smaller than the value obtained in reference [33]. Therefore, for fixed Δ , on increasing α two free large polarons bind to form the large bipolaron; moreover the large-bipolaron state evolves as a function of the coupling constant, undergoing a clear transition to the small-bipolaron state. From the comparison with the results of reference [6], it is apparent that the

transition from the large- to the small-bipolaron regime occurs for nearly the same parameter values of the polaron crossover.

We notice that in region II the bipolaron radius is always larger than the lattice constant a and in region III it is of the order of the quantity a independently of the coupling constant. These results confirm the nature of the bipolaron solutions and the formation of an intersite small bipolaron.

Finally, in figure 3 we show the behaviour of the binding energy as a function of η for different values of Δ . On increasing Δ , the binding energy and η_c decrease, getting near the values estimated in the continuum approximation.

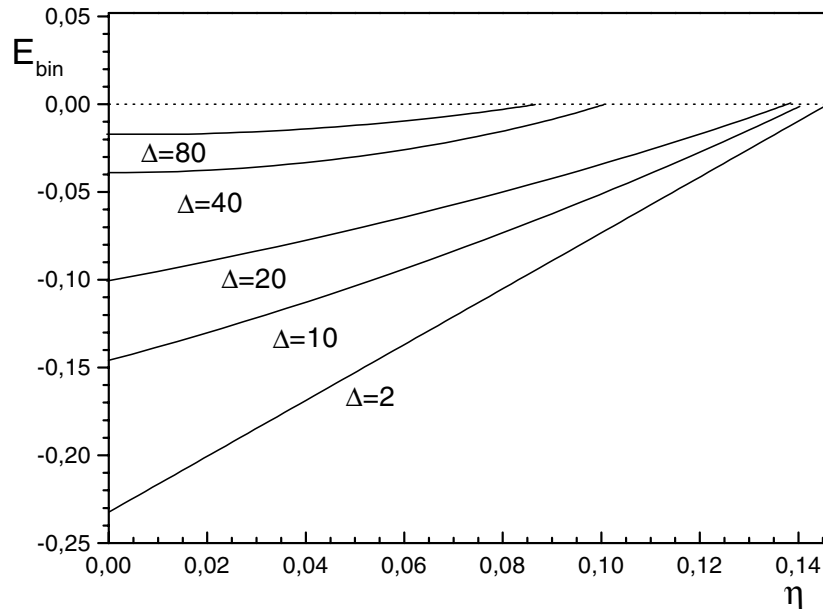


Figure 3. The bipolaron binding energy E_{bin} (in units of $e^2/\epsilon_\infty a$) as a function of η for different values of Δ (in units of $\hbar\omega$). The definition of the quantity α has been used [2].

We stress the fact that the crossover between large and small bipolarons can have interesting consequences for different materials. Indeed there are experimental results [19, 20, 22] consistent with the presence of bipolarons in WO_{3-x} , in manganites and in $\text{Ba}_{0.69}\text{K}_{0.31}\text{BiO}_3$. Recent experimental data support the crossover between large and small polarons in manganites (phase transition and optical properties) [1]. Therefore we believe that the bipolaron formation and the crossover between large and small bipolarons can play an important role in the physics even of manganites and cuprates.

We point out that the Fröhlich interaction is not an essential requirement because the proposed approach can be extended to different expressions for the electron–phonon matrix element. However, the comparison of our results with those obtained in the Holstein–Hubbard model [43, 44, 46] is not easy because we have taken into account a long-range electron–electron interaction.

In conclusion, by means of a variational procedure we have investigated the properties of the Fröhlich bipolaron, relaxing the effective-mass approximation and taking into account the long-range electron–electron repulsive interaction. The evolution of the bipolaron ground state as a function of the electron–phonon coupling constant α and of the width Δ of the

bare-electronic band has been discussed and the bipolaron phase diagram has been presented. In the proposed approach a clear transition from the large-bipolaron to the small-bipolaron regime takes place. As in the polaron case [16, 17], a variational linear superposition of the large-bipolaron and the small-bipolaron solutions provides better estimates of the bipolaron ground-state and binding energies just in the crossover regime, since for intermediate values of the electron–phonon coupling constant the two wave functions are not orthogonal and the off-diagonal matrix elements of the Hamiltonian (1) are different from zero. Work in this direction is in progress and the results will be discussed elsewhere.

Appendix I

The most general Hamiltonian of two electrons (or two holes) in a periodic potential interacting with the longitudinal optical phonons and with each other through the Coulomb force is given by [6, 49]

$$H_{gen} = \frac{p_1^2}{2m} + V(\vec{r}_1) + \frac{p_2^2}{2m} + V(\vec{r}_2) + \frac{e^2}{\varepsilon_\infty r} + \sum_{\vec{q}} \hbar \omega a_{\vec{q}}^\dagger a_{\vec{q}} + \sum_{\vec{q}} \left[W_q(\vec{r}_1) a_{\vec{q}} e^{i\vec{q}\cdot\vec{r}_1} + \text{h.c.} \right] + \sum_{\vec{q}} \left[W_q(\vec{r}_2) a_{\vec{q}} e^{i\vec{q}\cdot\vec{r}_2} + \text{h.c.} \right] \quad (\text{AI.1})$$

where \vec{r}_1 and \vec{r}_2 indicate the positions of the two electrons, \vec{p}_1 and \vec{p}_2 denote the momenta of the two charges, $V(\vec{r})$ is the single-particle potential periodic on the Bravais lattice, $\vec{r} = \vec{r}_1 - \vec{r}_2$ the relative distance, ε_∞ the high-frequency dielectric constant, ω the longitudinal optical phonon frequency, $W_q(\vec{r})$ the lattice-periodic general form of the electron–phonon coupling, $a_{\vec{q}}$ ($a_{\vec{q}}^\dagger$) the phonon annihilation (creation) operator. The quantity $W_q(\vec{r})$ can be expanded as

$$W_q(\vec{r}) = \sum_{\vec{G}} V_q(\vec{G}) e^{i\vec{G}\cdot\vec{r}}$$

where \vec{G} is a vector of the reciprocal lattice. In the polaron and bipolaron problem it is commonly assumed that only $V_q(\vec{G} = 0) = V_q$ is different from zero, which means that the electron–phonon interaction is considered slowly varying in the unit cell and accordingly the Umklapp processes are neglected. The Hamiltonian is invariant under translations by Bravais lattice vectors, so it can be proved [49] that the eigenvalue problem admits generalized Bloch eigenfunctions:

$$|f_{\vec{Q}}\rangle = e^{i\vec{Q}\cdot\vec{R}_c} U[\vec{r}_1, \vec{r}_2, (a_{\vec{q}}, a_{\vec{q}}^\dagger)] |0\rangle$$

where \vec{R}_c denotes the centre-of-mass coordinate, $(a_{\vec{q}}, a_{\vec{q}}^\dagger)$ the set of phonon annihilation and creation operators and U is an operator function satisfying the equation

$$U[\vec{r}_1 + \vec{a}, \vec{r}_2 + \vec{a}, (a_{\vec{q}} e^{-i\vec{q}\cdot\vec{a}}, a_{\vec{q}}^\dagger e^{i\vec{q}\cdot\vec{a}})] = U[\vec{r}_1, \vec{r}_2, (a_{\vec{q}}, a_{\vec{q}}^\dagger)]$$

for any Bravais lattice vector \vec{a} . We stress that the wave function depends on a wave vector \vec{Q} and it can be written as [50]

$$|f_{\vec{Q}}\rangle = \sum_{n_1, n_2} |\psi_{\vec{Q}}(\vec{R}_{n_1}, \vec{R}_{n_2})\rangle a(\vec{r}_1 - \vec{R}_{n_1}) a(\vec{r}_2 - \vec{R}_{n_2}) \quad (\text{AI.2})$$

where $a(\vec{r} - \vec{R}_n)$ is a Wannier function and $|\psi_{\vec{Q}}(\vec{R}_{n_1}, \vec{R}_{n_2})\rangle$ is a function that under a translation by any Bravais lattice vector \vec{a} is multiplied by the factor $e^{i\vec{Q}\cdot\vec{a}}$. Exploiting the slow variation

of the electron–phonon interaction on the unit cell and taking only the direct term in the electron–electron interaction [51], we adopt the standard procedure of reference [50] to give an eigenvalue equation for $|\psi_{\vec{Q}}(\vec{R}_{n_1}, \vec{R}_{n_2})\rangle$. The new Hamiltonian operator is

$$H = \sum_{m_1} E_{m_1} e^{-i\vec{R}_{m_1} \cdot \vec{\nabla}} + \sum_{m_2} E_{m_2} e^{-i\vec{R}_{m_2} \cdot \vec{\nabla}} + \frac{e^2}{\epsilon_{\infty} r} + \sum_{\vec{q}} \hbar \omega_{\vec{q}} a_{\vec{q}}^{\dagger} a_{\vec{q}} + \sum_{\vec{q}} \left[V_{\vec{q}} a_{\vec{q}} (e^{i\vec{q} \cdot \vec{R}_{n_1}} + e^{i\vec{q} \cdot \vec{R}_{n_2}}) + \text{h.c.} \right]. \quad (\text{AI.3})$$

In the above equation the bare-electron band has been taken as

$$E_b(\vec{k}) = \sum_n E_n e^{i\vec{k} \cdot \vec{R}_n}.$$

Since a phonon wave function represented by a coherent state provides a correct description of the polaron features [6, 17] and the particles are constantly scattered by each other through their direct interaction [49], our variational approach for the two-polaron problem can be set up adopting the trial wave function

$$|\psi_{\vec{Q}}(\vec{R}_{n_1}, \vec{R}_{n_2})\rangle = \sum_{\vec{k}} \exp\left(i\vec{Q} \cdot \left(\frac{\vec{R}_{n_1} + \vec{R}_{n_2}}{2}\right)\right) \exp\left(-i\left(\frac{\vec{k}}{2}\right) \cdot (\vec{R}_{n_1} - \vec{R}_{n_2})\right) \times \varphi(\vec{k}) \exp\left(\sum_{\vec{q}} \left[f_{\vec{q}}(\vec{R}_{n_1} - \vec{R}_{n_2}) a_{\vec{q}} \exp\left(i\vec{q} \cdot \left(\frac{\vec{R}_{n_1} + \vec{R}_{n_2}}{2}\right)\right) - \text{h.c.} \right]\right) |0\rangle \quad (\text{AI.4})$$

where \vec{Q} is the total crystalline momentum, \vec{k} is the relative momentum of the two particles, $f_{\vec{q}}$ denotes the variational distribution function of the phonons, $\varphi(\vec{k})$ takes into account the mutual scattering of the particles and $|0\rangle$ indicates the phonon vacuum state.

Provided that the interaction part of the Hamiltonian varies slowly with position, we can change our discrete variables to continuous variables, obtaining the Hamiltonian

$$H = E_b(-i\vec{\nabla}_{\vec{r}_1}) + E_b(-i\vec{\nabla}_{\vec{r}_2}) + \frac{e^2}{\epsilon_{\infty} r} + \sum_{\vec{q}} \hbar \omega_{\vec{q}} a_{\vec{q}}^{\dagger} a_{\vec{q}} + \sum_{\vec{q}} \left[V_{\vec{q}} a_{\vec{q}} (e^{i\vec{q} \cdot \vec{r}_1} + e^{i\vec{q} \cdot \vec{r}_2}) + \text{h.c.} \right] \quad (\text{AI.5})$$

where $\vec{\nabla}_{\vec{r}_1}$ and $\vec{\nabla}_{\vec{r}_2}$ are the gradient operators and $E_b(-i\vec{\nabla}_{\vec{r}_1})$ and $E_b(-i\vec{\nabla}_{\vec{r}_2})$ are the operators obtained with the substitution in the bare-electronic band $E_b(\vec{k})$ for the momentum \vec{k} with $-i\vec{\nabla}_{\vec{r}_1}$ and $-i\vec{\nabla}_{\vec{r}_2}$ respectively. Finally the bipolaron wave function reads

$$|\psi_{\vec{Q}}\rangle = \frac{1}{\sqrt{V}} e^{i\vec{Q} \cdot \vec{R}_c} \exp\left(\sum_{\vec{q}} (f_{\vec{q}}(\vec{r}) e^{i\vec{q} \cdot \vec{R}_c} a_{\vec{q}} - f_{\vec{q}}^*(\vec{r}) e^{-i\vec{q} \cdot \vec{R}_c} a_{\vec{q}}^{\dagger})\right) \varphi(\vec{r}) |0\rangle \quad (\text{AI.6})$$

where $\varphi(\vec{r})$ is the Fourier transform of $\varphi(\vec{k})$ and represents the relative wave function of the two particles.

Appendix II

In this appendix we derive the expression for the energy (24). First of all we note that in equation (4) there are terms of the type $\int d\vec{r} \varphi(\vec{r}) F(\vec{r} + \vec{R}_n)$, where $F(\vec{r} + \vec{R}_n)$ is

$$F(\vec{r} + \vec{R}_n) = \varphi(\vec{r} + \vec{R}_n) e^{-\sigma_{1n}(\vec{r})}.$$

We expand $F(\vec{r} + \vec{R}_n)$ to the second order in \vec{R}_n :

$$\int d\vec{r} \varphi(r) F(\vec{r} + \vec{R}_n) \approx \int d\vec{r} \varphi(r) F(\vec{r}, \vec{r}) + \int d\vec{r} \varphi(r) (\vec{R}_n \cdot \vec{\nabla}_n) F(\vec{r}, \vec{r}) + \frac{1}{2} \int d\vec{r} \varphi(r) (\vec{R}_n \cdot \vec{\nabla}_n)^2 F(\vec{r}, \vec{r})$$

where the $\vec{\nabla}_n$ specify the derivation with respect to terms in which $\vec{r} + \vec{R}_n$ appears. The zero-order term is then

$$\int d\vec{r} \varphi(r)^2 \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) \quad (\text{AII.1})$$

where we define

$$\tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) = \sum_{n \neq 0} E_n e^{i\vec{Q} \cdot \vec{R}_n / 2} e^{-\delta_n(\vec{r})}$$

with

$$\delta_n(\vec{r}) = \sum_{\vec{q}} |f_{\vec{q}}(\vec{r})|^2 (1 - e^{-i\vec{q} \cdot \vec{R}_n / 2}).$$

The first-order term is supplied by

$$- \left[\frac{1}{i} \sum_{\vec{q}} \int d\vec{r} \nabla \varphi^2 \cdot \vec{\nabla} \left\{ \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) \right\} - \text{c.c.} \right] |f_{\vec{q}}(\vec{r})|^2 \quad (\text{AII.2})$$

where

$$\Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) = \tilde{E}\left(\frac{\vec{Q}}{2} - \vec{q}, \vec{r}\right) - \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right).$$

Finally the second-order term is calculated supposing a slow variation of $\Delta E(\vec{Q}/2, \vec{q}, \vec{r})$ with respect to r , yielding

$$\begin{aligned} & \frac{a^2}{2} \int d\vec{r} \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) \varphi(r) \nabla^2 \varphi(r) + \frac{a^2}{4} \sum_{\vec{q}} \int d\vec{r} \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, \vec{r}\right) |f_{\vec{q}}(\vec{r})|^2 \nabla^2 \varphi^2 \\ & + \frac{a^2}{2} \int d\vec{r} \tilde{E}\left(\frac{\vec{Q}}{2}, \vec{r}\right) f_{\vec{q}}^*(\vec{r}) (\vec{\nabla} \varphi^2 \cdot \vec{\nabla} f_{\vec{q}}(\vec{r}) + \varphi^2 \nabla^2 f_{\vec{q}}(\vec{r})) \\ & - \frac{a^2}{2} \sum_{\vec{q}} \int d\vec{r} \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, r\right) |f_{\vec{q}}(\vec{r})|^2 ((\vec{\nabla} \varphi)^2 + \varphi(r) \nabla^2 \varphi(r)) \\ & + \frac{a^2}{2} \sum_{\vec{q}} \int d\vec{r} \Delta E\left(\frac{\vec{Q}}{2}, \vec{q}, \vec{r}\right) f_{\vec{q}}^*(\vec{r}) (\vec{\nabla} \varphi^2 \cdot \vec{\nabla} f_{\vec{q}}(\vec{r}) + \varphi^2 \nabla^2 f_{\vec{q}}(\vec{r})). \quad (\text{AII.3}) \end{aligned}$$

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