Adiabatic eigenstates of an electron in a deformable anharmonic continuum

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Abstract
The adiabatic eigenstates of an electron placed in a deformable continuum with elastic anharmonicity are analysed in the framework of a scaling analysis. The polaron solutions in an anharmonic continuum are compared with the solutions in a harmonic approximation. An adiabatic treatment of the ground state of a carrier in an anharmonic continuum is presented here. This procedure enables the author to obtain some information about the size of the polaron and its stability in an anharmonic crystal. The estimates of anharmonic corrections for α-sexithiophene and Mo_2S_3 show that the anharmonicity can affect the electrical-transition properties of materials in a situation in which the charge carriers are polarons.

1. Introduction

The problem of the motion of an electron in a deformable crystal has been attracting the interest of many solid-state physicists for a long time. Since Landau [1] pointed out the possibility of self-trapping of an electron in a deformable lattice as early as in 1933, studies of the effect of the electron–lattice interaction on the electronic states have employed both a variety of models and a variety of approaches [16]. In particular, rather distinct models of the electron–lattice interaction, such as the long-range interaction of an electron with the electric dipoles associated with longitudinal-optical-mode displacements [2, 3, 17] and the short-range interaction characteristic of nonpolar crystals, have been intensively investigated [4–8, 18, 19]. For long-wave longitudinal (optical) phonons this interaction is characterized by the dimensionless coupling constant $\alpha = (1/\varepsilon_\infty - 1/\varepsilon_0)e^2/2l_0\hbar\omega_0$, where ε_0 and ε_∞ are the static and high-frequency dielectric constants, and $l_0 = (\hbar/2m^*\omega_0)^{1/2}$ is a length scale. Here ω_0 is the limiting frequency of longitudinal phonons and m^* is the band effective mass of the electron. In addition, much attention has been focused on the difference in behaviour of an electron in a three-dimensional continuum in comparison with a one dimensional quasi-crystal [9, 16]. The author emphasizes that all referenced theories are based on the treatment of a problem in a *harmonic* approximation, in which a strain constant S is a parameter solely responsible for deformation. In fact, the parameter of elastic anharmonicity G is not equal to zero in a real crystal [10]. Therefore, one may include the anharmonicity in the theoretical model of a polaron. There is considerable current interest in anharmonic effects in experimental

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studies of polarons in semiconductor quantum dots [15, 20–22]. Generally speaking, the anharmonicity can affect the polaron state in many ways. In the first place, the anharmonicity affects the ground state energy of a polaron E and its size l_p. Secondly, the polaron decay can be triggered by the instability of its phonon component [15]. In a related paper, Verzelen *et al* [15] suggested that the anharmonicity driven instability of optical phonons leads in semiconductor quantum dots to a decay of polaron states which otherwise would be everlasting. The phenomenological approach [15] was dealing with a problem of a decay of polaronic state in the case of a weak electron–phonon coupling, $\alpha \approx 0.15$. In this approximation, the energy of the polaron state was assumed not to be affected by the anharmonicity. In contrast to this assumption, the estimate (see below) shows that in many cases the anharmonic correction ΔE_{anh} to the energy of polaron is not negligible. This correction is especially large ($\Delta E_{anh}/E \sim 0.01$–$0.1$) in the case of a strong electron–phonon coupling, $\alpha \gg 1$, when the relevant deformation of a lattice is not small.

In the following we consider the anharmonic crystal with a strong electron–phonon coupling and study how the anharmonicity affects the ground state energy of a polaron, its size and its stability. The calculation of the ground state energy, the polaron mobility and the polaron mass m_p in an anharmonic crystal from the second quantized formulation or from the variational method is a very complex task. We shall adopt a different approach based on a scaling analysis. The scaling analysis enables us to obtain some important information on how the anharmonicity affects the polaron in systems with both distinct models of the electron–phonon interaction and dimensionality. The scaling analysis is ideally suited for this goal and it has been previously used in the theory of polaron in the harmonic approximation [7]. In order to simplify the problem as far as possible, the author presents an adiabatic treatment of the ground state of an electron placed in a deformable anharmonic continuum. The adiabatic approach is applied in the limit of a strong electron–phonon coupling [12] $\alpha > 10$. In the adiabatic limit, the size of a polaron is given by $l_p \approx 10 l_0/\alpha$. The condition for the applicability of the continuum approximation is $l_p > r_0$, where r_0 is the lattice constant. As a result, we find the following condition for the applicability of the scaling analysis: $10 < \alpha < 10 l_0/r_0$. Since $l_0 > r_0$ one may expect that the approach adopted in this paper holds within a fairly wide range of the electron–phonon constant α. In the present paper, we shall estimate the magnitude of an anharmonic effect for two typical compounds. A scaling analysis below provides definitive predictions as to the degree of spatial localization of the adiabatic eigenstates of an electron and their dependence on range and strength of the electron–lattice interaction. It is noted that the behaviour of the adiabatic ground eigenstate of an electron may vary *continuously* or *discontinuously* when the elastic anharmonicity is included, depending on the dimensionality of the system and on the character of the electron–lattice interaction.

2. Estimate of an anharmonic correction

To begin, we will estimate the magnitude of the anharmonic correction for the elastic strain energy of a polaron. We assume that the elastic strain energy E_S due to the local dilation $\Delta(\vec{r})$ of a deformable anharmonic continuum is given by the following expression [10]:

$$E_s = \frac{1}{2} S \int \mathrm{d}\tau^1 \Delta^2(\vec{r}^1) - \frac{1}{3} G S \int \mathrm{d}\tau^1 \Delta^3(\vec{r}^1) \qquad (1)$$

where $\vec{r}^1$ here is the coordinate, S is a strain constant, G is a dimensionless Grüneisen coefficient, which characterizes the anharmonicity, and τ^1 are the space coordinates. The first term (or E_s^h) in the right-hand side of equation (1) is the harmonic part of the elastic energy and the second term (or E_s^{anh}) is the anharmonic correction with an accuracy to the

cubic term. At this point we can estimate the magnitude of the anharmonic correction or the parameter $\mu = E_s^{anh}/E_s^h \approx 0.7G|\Delta|$. For the sake of simplicity, we shall follow the well known model of a small polaron given by Toyozawa [6]. He assumes that the crystal has deformed in such a way that the volume dilation $\Delta(\vec{r}) < 0$ is given by

$$\Delta(\vec{r}) = \begin{cases} \Delta = \text{const} & (|\vec{r}| < R_0) \\ 0 & (|\vec{r}| > R_0) \end{cases} \tag{2}$$
$$\tag{3}$$

where R_0 is the radius of the dilation (in his model, R_0 is of the same order of magnitude as the lattice constant r_0). One can estimate the dilation Δ from the condition of self-trapping of an electron inside the three-dimensional square-well [6]:

$$\frac{2m^* R_0^2 E_1 |\Delta|}{\hbar^2} \geqslant \left(\frac{\pi}{2}\right)^2 \tag{4}$$

where E_1 is the deformation potential constant. It is now of interest to estimate the anharmonic effect for two specific materials: α-sexithiophene (α-6T), which is used as a thin-film transistor [13], and a linear chain compound, Mo_2S_3 [14]. It is generally accepted [13, 14] that the polarons are responsible for the transport mechanism in both materials. The relevant parameters of α-6T are [13] $\alpha = 15$, $R_0 = 3.8 \times 10^{-8}$ cm, $m^* = 2.6\,m_e$, $E_1 = 5.3$ eV, $G \approx 2$, $\hbar\omega_0 = 0.007$ eV. Inserting these values into equation (4) gives $\Delta > 0.05$ and $\mu = E_s^{anh}/E_s^h \approx 0.7G|\Delta| > 0.07$. The appropriate energy of a polaron [12] and the anharmonic correction to this energy are $|E_{pol}| \approx 0.1\alpha^2\hbar\omega_0 = 0.15$ eV, $\Delta E_{anh} > 0.007$ eV. One can see that $\Delta E_{anh} > k_b T_T = 0.005$ eV for a characteristic transition temperature $T_T = 45$ K. This estimate shows that the anharmonic correction should affect the intrinsic transport properties of organic-field transistors. The relevant parameters of Mo_2S_3 are [23–25] $R_0 \approx 3.2 \times 10^{-8}$ cm, $m^* \approx 7.2\,m_e$, Fermi energy $E_F \approx 0.09$ eV, Young's modulus $Y \approx 2 \times 10^{12}$ dyn cm^{-2} and phonon frequency $\omega_0 \sim 10^{13}$ s^{-1}. These parameters allow us to estimate the phonon energy $\hbar\omega_0 \approx 0.005$ eV and the electron–phonon coupling constant $\alpha \approx 17$. The dilation $\Delta = 0.13$ calculated in [14] for Mo_2S_3 corresponds to an anharmonic correction $\Delta E_{anh} > 0.01$ eV. The anharmonic correction ΔE_{anh} has the same order of magnitude as the energy difference $E \sim 10$–20 meV between wells in a double-well potential [14]. The double-well potential model describes first-order phase transitions between a weakly conducting ground state and a relatively highly conducting metastable state. The author concludes from this estimate that the anharmonic correction affects the low-T carrier transport and the electrical noise in Mo_2S_3.

3. Ground-state energy

The calculation of the ground-state energy of the electron coupled with a deformable continuous anharmonic medium is based on an approach of Emin and Holstein [7]. In this approach, the motion of an excess electron is sufficiently rapid compared to the motion of the heavy massed atoms, so that the electron may be assumed to adjust to the instantaneous positions of the atoms. If the kinetic energy of the lattice atoms is neglected, the ground state energy of the coupled electron–atom system is supposed to be the minimum of the sum of the electron's ground-state energy E_{e1} and the strain energy E_s of the deformable continuum. We shall consider the problem of an anharmonic continuum containing defect, so the Hamiltonian H_e of an electron placed in a deformable continuum is [7]

$$H_e = T_e + V_d(\vec{r}) + \int \mathrm{d}\tau^1 Z(\vec{r}, \vec{r}^1) \Delta(\vec{r}^1) \tag{5}$$

where T_e is the electron's kinetic energy operator; the second term is the contribution to the potential energy of an electron at $\vec{r}$ associated with the presence of the defect. The author takes the defect potential to be coulombic $V_d(\vec{r}) \propto |\vec{r}|^{-1}$. The final term, or the electron–continuum (electron–lattice) interaction, depicts a linear dependence of the potential energy of an electron at $\vec{r}$ on the dilation associated with each point of the continuum $\Delta(\vec{r^1})$; $Z(\vec{r}, \vec{r^1})$ is a function which characterizes the strength and range of the electron–continuum interaction. Following [7], we consider two kinds of interaction of the carrier with an elastic continuum: the long-range interaction of an electron with the deformation-induced electric polarization $Z(\vec{r}, \vec{r^1}) = E_L |\vec{r} - \vec{r^1}|^{-2}$, and the local interaction or the continuum version of the short-range interaction of the molecular-crystal model $Z(\vec{r}, \vec{r^1}) = E_S \delta(\vec{r} - \vec{r^1})$. Generalizing, we write the interaction function as the sum of these contributions:

$$Z(\vec{r}, \vec{r^1}) = E_L |\vec{r} - \vec{r^1}|^{-2} + E_S \delta(\vec{r} - \vec{r^1}). \tag{6}$$

The electronic energy, E_{e1}, for a given strain field, $\Delta(\vec{r})$, is given by

$$E_{e1} = \int d\tau \, \Psi^*(\vec{r}) H_e \Psi(\vec{r}) \tag{7}$$

where $\Psi(\vec{r})$ is the lowest-energy eigenfunction of H_e. The ground-state energy of the coupled system corresponds to a situation in which a dilation $\Delta(\vec{r})$ is such as to yield the lowest total energy $E = E_{e1} + E_s$. Minimizing the energy E with respect to $\Delta(\vec{r})$, one finds that $\Delta(\vec{r})$ is the root of the equation

$$\Delta^2(\vec{r}) - \frac{1}{G} \Delta(\vec{r}) + \frac{1}{G} \Delta_0(\vec{r}) = 0. \tag{8}$$

The last term of equation (8) is proportional to the dilation $\Delta_0(\vec{r})$ calculated in a harmonic approximation [7]:

$$\Delta_0(\vec{r}) = -S^{-1} \int d\tau^1 |\Psi(\vec{r^1})|^2 Z(\vec{r^1}, \vec{r}). \tag{9}$$

The solution of equation (8) corresponding to the minimum total energy is given by

$$\Delta(\vec{r}) = \frac{1}{2G} - \frac{1}{2G} \sqrt{1 - 4G \Delta_0(\vec{r})}. \tag{10}$$

Expanding the last term $\sqrt{1 - 4G\Delta_0(\vec{r})} \approx 1 - 2G\Delta_0(\vec{r}) - 2G^2\Delta_0^2(\vec{r})$ in a Taylor series with two terms we calculate the dilation $\Delta(\vec{r})$ in an anharmonic approximation as the sum of two terms: the harmonic term $\Delta_0(\vec{r})$ and the anharmonic correction which is proportional to the Grüneisen coefficient G:

$$\Delta(\vec{r}) = \Delta_0(\vec{r}) + G\Delta_0^2(\vec{r}). \tag{11}$$

Since from equation (9) $\Delta_0 < 0$, the anharmonic correction will always decrease the magnitude of the dilation $|\Delta| < |\Delta_0|$. The dilation $\Delta(\vec{r})$ in terms of the parameters of our problem is given by

$$\Delta(\vec{r}) = -S^{-1} \int d\tau^1 |\Psi(\vec{r^1})|^2 Z(\vec{r}, \vec{r^1})$$
$$+ GS^{-2} \int d\tau^1 |\Psi(\vec{r^1})|^2 Z(\vec{r^1}, \vec{r}) \int d\tau^{11} |\Psi(\vec{r^{11}})|^2 Z(\vec{r^{11}}, \vec{r}). \tag{12}$$

Following the approach of [7] we utilize equation (12) to express the ground state energy in terms of the ground-state electronic eigenfunctions. The result is

$$E = T_e - V_d - V_{int} + E_s \tag{13}$$

where the terms in the right-hand side of equation (12) are found to be

$$T_e = \frac{\hbar^2}{2m^*} \int d\tau |\nabla\Psi(\vec{r})|^2 \tag{14}$$

$$V_d = -\int d\tau |\Psi(\vec{r})|^2 V_d(\vec{r}) \tag{15}$$

$$V_{int} = V_{int}^h + V_{int}^{anh}. \tag{16}$$

The harmonic and the anharmonic contributions to V_{int} are given by

$$V_{int}^h = S^{-1} \int d\tau |\Psi(\vec{r})|^2 \int d\tau' Z(\vec{r}, \vec{r}') \int d\tau'' Z(\vec{r}''\vec{r}'|\Psi(\vec{r}'')|^2 \tag{17}$$

$$V_{int}^{anh} = -GS^{-2} \int d\tau |\Psi(\vec{r})|^2 \int d\tau^1 Z(\vec{r}, \vec{r}^1) \int d\tau^{11} |\Psi(r^{\vec{1}1})|^2 Z(\vec{r}^1, r^{\vec{1}1})$$
$$\times \int d\tau^{111} |\Psi(r^{\vec{1}11})|^2 Z(r^{\vec{1}11}, r^{\vec{1}1}). \tag{18}$$

The strain energy of the continuum $E_s = E_s^h + E_s^{anh}$ is the sum of the harmonic and the anharmonic contributions, respectively:

$$E_S^h = \frac{1}{2} V_{int}^h \tag{19}$$

$$E_S^{anh} = \frac{2}{3} V_{int}^{anh}. \tag{20}$$

One can see that expressions (17) and (19) for the harmonic contributions to the energy are exactly the same as were derived in [7]. The ground-state energy E calculated from equations (13), (16), (19) and (20) may be rewritten as

$$E = (T_e - V_d - \tfrac{1}{2} V_{int}^h) - \tfrac{1}{3} V_{int}^{anh} \tag{21}$$

where the term in parenthesis is the harmonic contribution to the energy and the last term is the anharmonic correction $V_{int}^{anh} < 0$. We can conclude that, since the above energy is, by definition, the minimum energy of the coupled system, any alteration of the wave function $\Psi(\vec{r})$ must necessarily increase the energy E. The scaling analysis makes use of the so-called scaling factor [7] $0 < R < \infty$, which is related to the spatial extent of the electron's wave function and which has the dimensionality of $\vec{r}$. In other words, if we change the length scale of the (normalized) eigenfunction, replace $\Psi(\vec{r})$ by $R^{-d/2}\Psi(\vec{r}/R)$, where d is the dimensionality of the system, the energy (now a function of R) must have its minimum at the scale corresponding to the actual eigenstate, at $R = 1$. Introducing $Z(\vec{r}, r^{\vec{1}})$ from equation (6) and wave function $R^{-d/2}\Psi(\vec{r}/R)$ into equations (17) and (18), we calculate V_{int}^h, V_{int}^{anh} and the ground-state energy $E(R)$:

$$E(R) = T_e/R^2 - \tfrac{1}{2}(V_{int}^s/R^d + V_{int}^{S,L}/R^2 + V_{int}^L/R^{(4-d)}) - V_d/R$$
$$- \tfrac{1}{3}[V_{int}^{anh,L}/R^{(6-d)} + V_{int}^{anh,S}/R^{2d} + V_{int}^{anh,L^2S}/R^4 + V_{int}^{anh,S^2L}/R^{(2+d)}] \tag{22}$$

where the last term in the brackets is the anharmonic correction to the ground-state energy $E(R) = E(R)^h + E(R)^{anh}$, and the sum of the first three terms is the adiabatic energy $E(R)$ in a harmonic approximation. The appropriate terms of equation (22) are given by

$$V_{int}^S = (E_S^2/S \int d\tau |\Psi(\vec{r})|^4 \tag{23}$$

$$V_{int}^L = (E_L^2/S) \int d\tau \int d\tau' \int d\tau'' |\Psi(\vec{r})|^2 |\Psi(\vec{r}'')|^2/|\vec{r} - \vec{r}'|^2|\vec{r}' - \vec{r}''|^2 \tag{24}$$

$$V_{int}^{S,L} = (2E_S E_L/S) \int d\tau \int d\tau'' |\Psi(\vec{r})|^2 |\Psi(\vec{r}'')|^2/|\vec{r} - \vec{r}''|^2 \tag{25}$$

$$V_{int}^{anh,S} = -GS^{-2}E_S^3 \int d\tau |\Psi(\vec{r})|^6 \tag{26}$$

$$V_{int}^{anh,L} = \left\{ -GS^{-2}E_L^3 \int d\tau \int d\tau' \int d\tau'' \int d\tau''' |\Psi(\vec{r})|^2 |\Psi(\vec{r}'')|^2 |\Psi(\vec{r}''')|^2 \right\}$$
$$\times \{|\vec{r}-\vec{r}'|^2 |\vec{r'''}-\vec{r}'|^2 |\vec{r}''-\vec{r}'|^2\}^{-1} \tag{27}$$

$$V_{int}^{anh,L^2S} = -3GS^{-2}E_L^2 E_S \int d\tau |\Psi(\vec{r})|^2 \int d\tau' |\Psi(\vec{r}')|^2 |(\vec{r}-\vec{r}')|^{-2} \int d\tau'' |\Psi(\vec{r}'')|^2 |\vec{r}''-\vec{r}'|^{-2} \tag{28}$$

$$V_{int}^{anh,S^2L} = -3GS^{-2}E_S^2 E_L \int d\tau \int d\tau' |\Psi(\vec{r})|^4 |\Psi(\vec{r}')|^2 / |(\vec{r}-\vec{r}')|^2. \tag{29}$$

We note that the harmonic terms V_{int}^S, V_{int}^L and $V_{int}^{S,L}$ are the same, as calculated in [7].

4. Large polaron in a three-dimensional anharmonic continuum

At this point we can obtain several results of polaron theory in an anharmonic continuum and compare them with well known results of adiabatic theory of polarons in a harmonic approximation [7]. Consider first the polaron problem characterized by the study of a three-dimensional defect-free continuum in which the electron interacts with a continuum solely via the long-range component of the electron–continuum interaction: $d = 3$, $V_d = 0$, $V_{int}^S = V_{int}^{S,L} = V_{int}^{anh,S} = V_{int}^{anh,L^2S} = V_{int}^{anh,S^2L} = 0$. As one can see from equation (22), the ground-state energy is given by

$$E(R) = T_e/R^2 - \tfrac{1}{2}V_{int}^L/R - \tfrac{1}{3}V_{int}^{anh,L}/R^3 \tag{30}$$

where the first and the second terms correspond to the harmonic approximation and the third term is an anharmonic correction. It is convenient to introduce the dimensionless parameter $\beta = 2V_{int}^{anh,L}/3V_{int}^L (0 < \beta < 1)$, which characterizes the magnitude of an anharmonicity ($\beta = 0$ corresponds to the harmonic approximation). The comparison of the function $E(R)$ from equation (30) with the function $E(R)$ calculated in a harmonic approximation [7] is illustrated in figure 1. One can see that there are solutions which possess a solitary minimum at $R = 1$ for both approximations. This means that the electron exists in a finite-radius, bound state with a polaron always being energetically stable. This is the case of an electron interacting with optical phonons under the condition that the size of the self-trapped state is large compared to the lattice constant. The most sophisticated treatment of this 'large' polaron is due to Feynman [3] with the path-integral method, substantially extended in the past decade [16]. The relevant energy of the large polaron $E = E_{el} + E_S$, the electron's energy E_{el} and the strain energy E_S are explicitly calculated from equation (30) and from the condition for minimum of the energy

$$\frac{\partial E(R)}{\partial R}\bigg|_{R=1} = 0$$

$$E = -\frac{1}{4}V_{int}^L(1-\beta) \tag{31}$$

$$E_{el} = -\tfrac{3}{4}V_{int}^L(1+\beta) \tag{32}$$

$$E_S = \frac{V_{int}^L}{2}(1+2\beta) \tag{33}$$

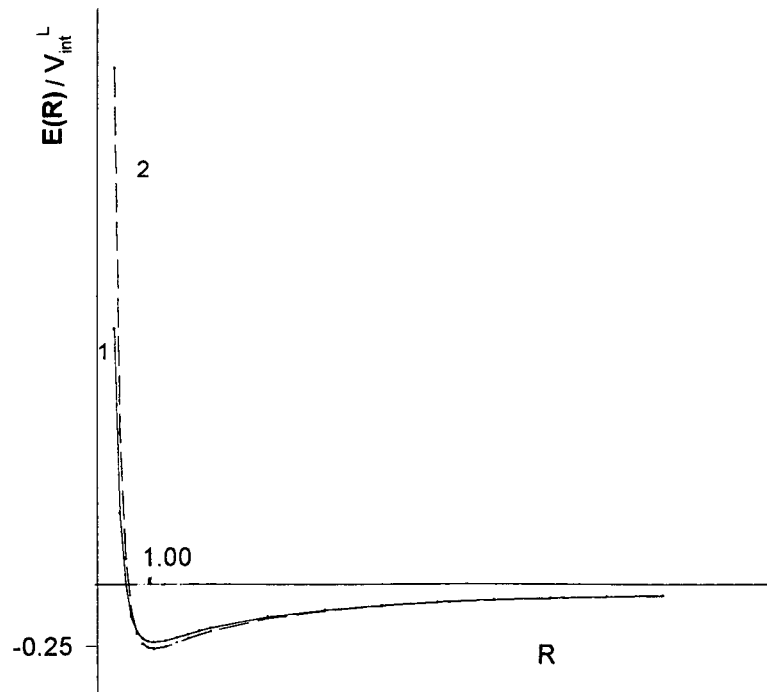$$K = E_{el}/E_S = -\frac{3}{2}\frac{(1+\beta)}{(1+2\beta)}. \tag{34}$$

Figure 1. The ground-state energy $E(R)$ of a large polaron in a three-dimensional continuum with the long-range electron–continuum interaction: 1, the anharmonic approximation ($\beta = 0.1$); 2, the harmonic approximation ($\beta = 0$).

The behaviour of E, E_{e1} and E_S as a function of β is illustrated in figure 2. One can see from equation (31) that the energy E of a polaron in an anharmonic continuum is larger than the energy calculated in a harmonic approximation. The anharmonic correction to the result of Pekar [11] ($K = -3{:}2$) depends on the parameter of anharmonicity β and $K > -3{:}2$ for an anharmonic continuum. One does see that the anharmonic correction for a 3D crystal with the long-range interaction does not change dramatically the results of the theory of polarons in a harmonic approximation. This is an example where the adiabatic ground eigenstate changes *continuously* if we include the anharmonic correction. We shall see below that it is not the case for a three-dimensional continuum with a solely short-range component of the electron-continuum interaction.

5. Large polaron in a one-dimensional anharmonic continuum

The situation to be considered is that of a carrier which interacts with the defect-free one-dimensional continuum solely via the short-range component of the electron-continuum interaction. Emin and Holstein [7] have solved this problem for a harmonic continuum and they have shown that this problem is equivalent to the Pekar problem discussed above with V_{int}^{S} simply replacing V_{int}^{L}. We shall compare this result with the solution for an anharmonic continuum where $V_{int}^{L} = V_{int}^{anh,L} = V_{int}^{anh,L^2 S} = V_{int}^{anh,S^2 L} = 0$, and the ground-state energy from equation (22) is given by

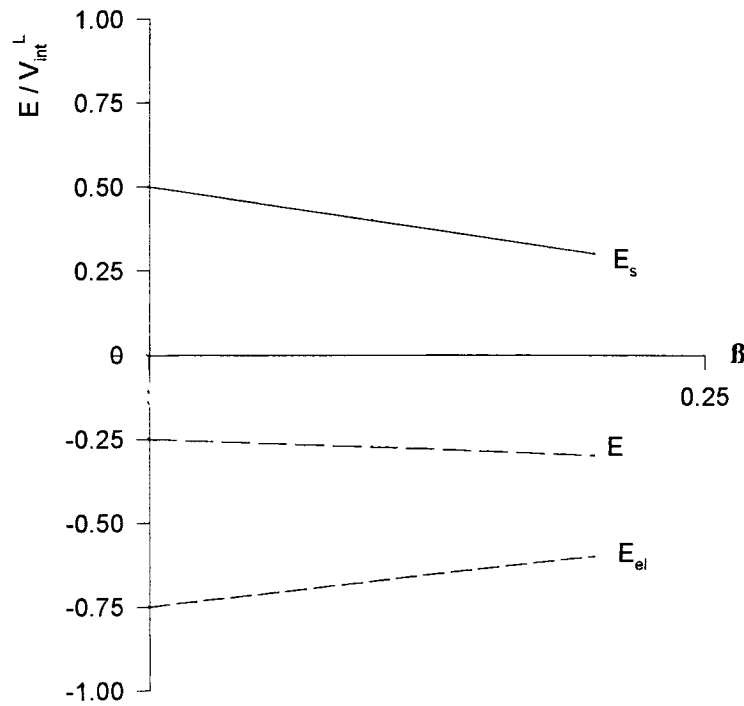$$E(R) = T_e/R^2 - \tfrac{1}{2} V_{int}^{S}/R + \tfrac{1}{3}|V_{int}^{anh,S}|/R^2. \tag{35}$$

Figure 2. The energy of a large polaron E, the energy of an electron E_{el} and the strain energy E_s in a three-dimensional anharmonic continuum with the long-range electron–continuum interaction.

One can see from equation (35) that the problem is still equivalent to the Pekar problem in a harmonic approximation with an appropriate term $(T_e + |V_{int}^{anh,s}|/3)$ replacing T_e. Hence, the polaronic solution corresponds to a large polaron ($R = 1$) with the energy of a polaron $E < 0$. The electron's energy E_{el} and the elastic energy E_S are given by

$$E = -\tfrac{1}{4} V_{int}^S \tag{36}$$

$$E_{el} = -\tfrac{3}{4} V_{int}^S (1 - \tfrac{8}{9}\beta_1) \tag{37}$$

$$E_S = \tfrac{1}{2} V_{int}^S (1 - \tfrac{4}{3}\beta_1) \tag{38}$$

where the parameter of anharmonicity $\beta_1 = 2|V_{int}^{anh,S}|/3V_{int}^S$ ($0 < \beta_1 < 1$). One can see from equation (36) that the anharmonic correction does not alter the result of the harmonic approximation and the energy E of the large polaron coincides with the energy E calculated in [7].

6. Small polaron in a three-dimensional anharmonic continuum

In contrast with the previously discussed one-dimensional problem, the adiabatic eigenstates of a carrier in a *three-dimensional* defect-free deformable continuum with an elastic anharmonicity where the electron–continuum interaction is solely short-ranged are quite different from the solution in a harmonic approximation. The relevant energy of the bound state $E(R)$ from equation (22) is given by

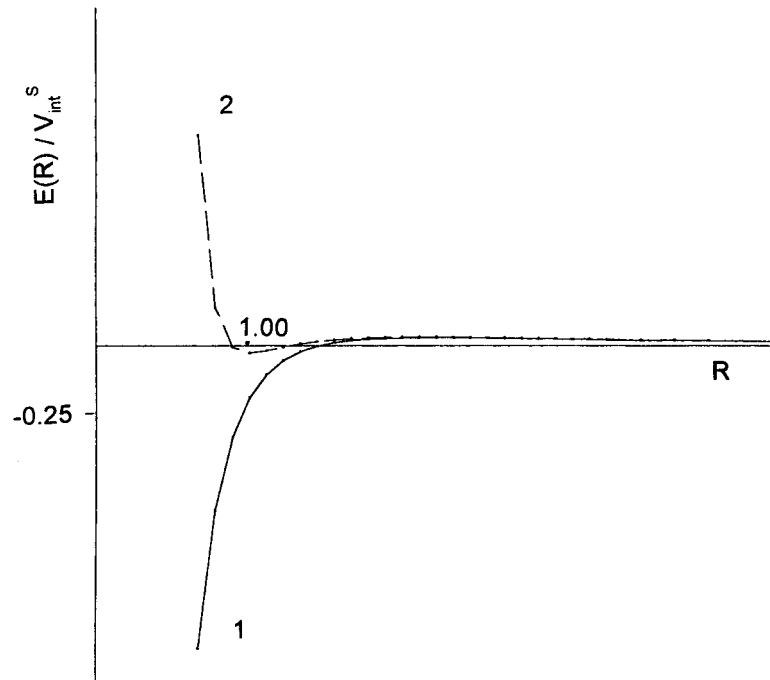$$E(R) = T_e/R^2 - \tfrac{1}{2} V_{int}^S/R^3 + \tfrac{1}{3}|V_{int}^{anh,S}|/R^6 \tag{39}$$

Figure 3. The ground-state energy $E(R)$ of a large polaron in a three-dimensional continuum with the short-range electron–continuum interaction: 1, the harmonic approximation ($\beta_2 = 0$); 2, the anharmonic approximation ($\beta_2 = 0.05$).

where the first two terms in the right-hand side of equation (39) correspond to the harmonic approximation, and the last term is the anharmonic correction. The behaviour of $E(R)$ is shown in figure 3 for both the harmonic and the anharmonic problems. One sees from figure 3 that the character of an adiabatic solution changes *discontinuously* with the inclusion of an anharmonic correction. The only minima in the harmonic approximation which occur are at $R = \infty$, corresponding to an unbound electron in an unstrained continuum, and at $R = 0$, corresponding to an electron self-trapped in an infinitely deep and infinitesimally localized deformation-induced potential well. The last situation is the continuum analogue of a small-polaron state with an induced lattice deformation being essentially confined to a single unit cell. It was emphasized on the basis of an approximate adiabatic argument [6] and variational calculations [5, 6] that only these two situations, and no intermediate-range polaron, could exist in 3D systems characterized by a short-range electron–lattice interaction. The energy of a small polaron $E = -\infty$ in a harmonic approximation, but the anharmonic problem gives a finite magnitude of E. The anharmonic correction to the energy $E(R)$ (or the last term in the right-hand side of equation (39)) with a strong R^{-6} dependence at $R = 0$) does not affect the unbound electron state at $R = \infty$, but it alters $E(R)$ for $R < 1$, as one can see from figure 3. Instead of an infinitely deep potential well at $R = 0$ (harmonic approximation) there is a minimum with the finite energy $E < 0$ at some $0 < R_{min} < 1$. The author assumes that this minimum corresponds to a small-polaronic state in a harmonic approximation ($R = 0$) shifted to some position at $R = R_{min} > 0$ due to an anharmonic term. Hence, the anharmonic correction generates a quasi-polaronic state with a finite energy $E < 0$ and the degree of spatial localization (size of a polaron) which is *larger* than the degree of spatial localization calculated
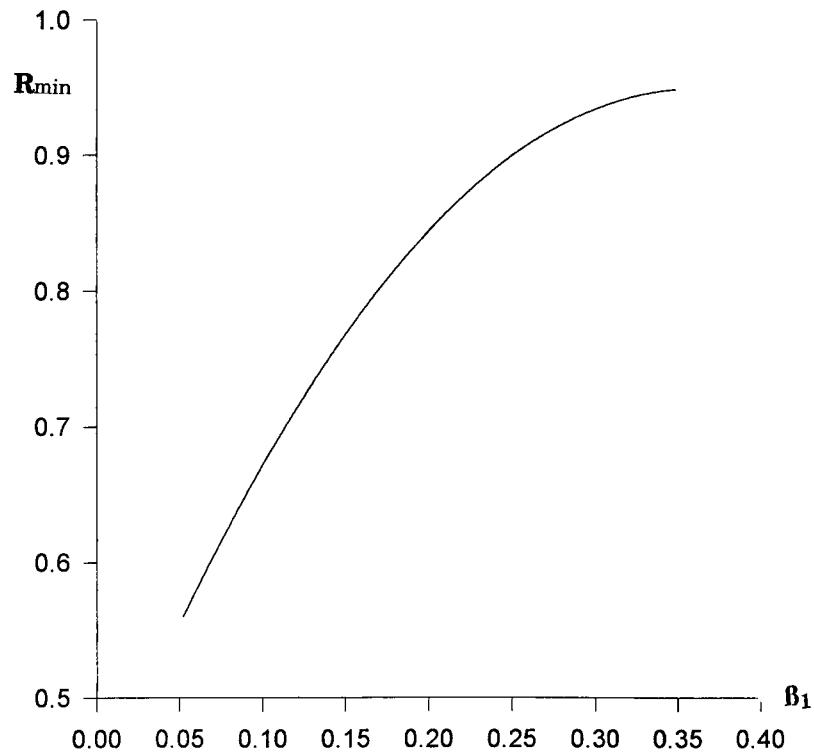
Figure 4. The parameter R_{min} of a size of a small polaron in a three-dimensional continuum with the short-range electron–continuum interaction.

in a harmonic approximation. Figure 4 shows how the parameter R_{min} depends on the degree of anharmonicity $\beta_2 = 2|V_{int}^{anh,S}|/V_{int}^S (0 < \beta_2 < 1)$. In spite of the fact that the discussed solution is rather virtual than a real eigenstate, these states are close to each other ($R_{min} > 0.5$ for a reasonable parameter of anharmonicity $\beta_2 \geqslant 0.05$).

7. Electron interacting with both polar and acoustic mode in a three-dimensional anharmonic continuum

The problem of a polaron in a 3D defect-free continuum with both the short-range and the long-range electron–continuum interaction was studied in a harmonic approximation [7]. Two different situations were found, depending on whether $(T_e - V_{int}^{S,L}/2)^2$ is greater than or less than $3v_{int}^S v_{int}^L/2$. If the long-range component of the electron–continuum interaction is weak, two kinds of polaron, a small polaron and a finite-radius polaron, coexist. If the long-range component of the electron–continuum interaction is sufficiently strong, a large polaron shrinks in size until it undergoes a transition into a small-polaron state [7]. The author thinks that this transition has its origin only in the fact that the energy of a small polaron is infinite in a harmonic approximation. Indeed, the situation for an anharmonic continuum (where the energy of a small polaron is finite) is qualitatively distinct from the harmonic problem. In a reasonable approximation, we shall neglect the small terms V_{int}^{anh,L^2S} and V_{int}^{anh,S^2L} and keep
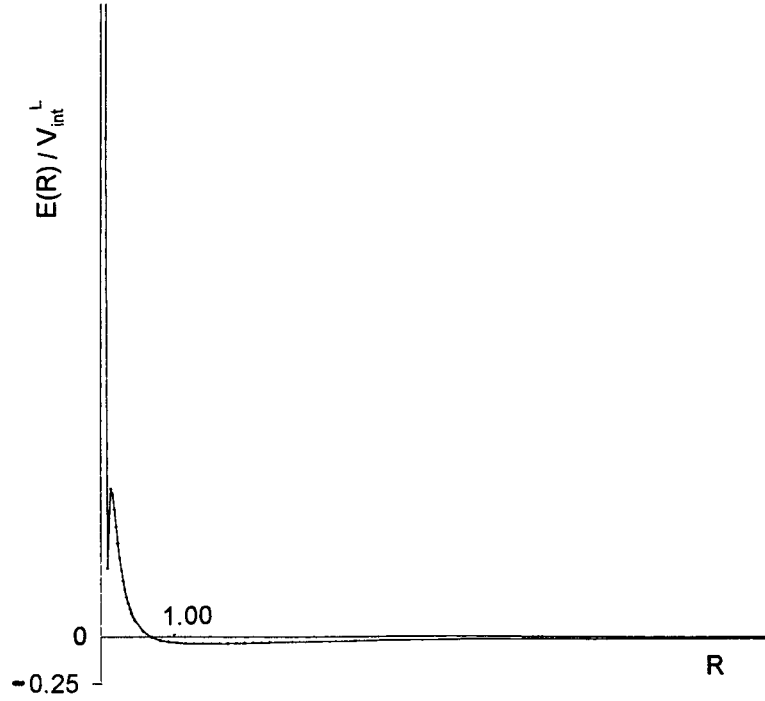
Figure 5. The transition of a small-polaron state into a large-polaron state in a three-dimensional anharmonic continuum with both strong long-range and weak short-range interactions.

the terms $V_{int}^{anh,L}$ and $V_{int}^{anh,S}$ in equation (22). The ground-state energy is given by

$$E(R) = \frac{(T_e - \frac{1}{2}V_{int}^{S,L})}{R^2} - \frac{1}{2}\frac{V_{int}^L}{R} - \frac{1}{2}\frac{(V_{int}^{S,L} - \frac{2}{3}|V_{int}^{anh,L}|)}{R^3} + \frac{1}{3}\frac{|V_{int}^{anh,S}|}{R^6}. \quad (40)$$

The author conducted a numerical calculation of $E(R)$ for $V_{int}^S \leqslant V_{int}^L$ (the long-range component of an interaction is greater than the short-range component) and it was found that a small-polaron state experiences a transition into a large-polaron state for any reasonable non-zero magnitude of parameter $V_{int}^{anh,S}$. This transition is shown in figure 5, where an unstable state with the energy $E > 0$ is also clearly seen. If the short-range component of an interaction is greater than the long-range component ($V_{int}^S > V_{int}^L$) a small-polaron state does not undergo a transition into a large-polaron state. In its turn, a finite-radius polaron experiences a transition into a small-polaron state. Therefore, in a 3D continuum with both the short-range and the long-range components of an electron–continuum interaction, the anharmonicity breaks the coexistence of a small polaron with a large polaron. There are only large polarons for the dominant long-range electron–continuum interaction or small polarons for the dominant short-range interaction. The energy of a large polaron ($V_{int}^S \leqslant V_{int}^L$) as follows from equation (40) is given by

$$E = -\frac{1}{4}[V_{int}^L - V_{int}^S - \frac{2}{3}V_{int}^{anh,L} + \frac{8}{3}|V_{int}^{anh,S}|]. \quad (41)$$

One sees from this expression that, as in the case of a solely long-range interaction, the anharmonicity destabilizes a large polaron, i.e. increases its ground-state energy.

8. Conclusion

This paper presents an adiabatic treatment of the ground state of an electron placed in a deformable anharmonic continuum. The author estimates the anharmonic effect for two materials—α-sexithiophene and Mo_2S_3. It is concluded that anharmonicity can affect the electrical-transition properties of crystals. The calculations were performed in the framework of an approach of Emin and Holstein, who employed the scaling analysis to the problem in a harmonic approximation. Systems with the dimensionality $D = 1$ and $D = 3$, where the interaction of an electron with a continuum is long ranged or short ranged, were studied. It was shown that the effect of an anharmonicity is different in 1D and 3D systems and it also depends on the range of the electron–continuum interaction. It was found that in a 3D continuum in which the electron interacts with the continuum solely via the long-range component of the electron-continuum interaction, the anharmonic correction increases the ground-state energy of a large polaron calculated in a harmonic approximation. The effect of an anharmonic correction was found to be much stronger in a problem of a small polaron in a 3D continuum, where the interaction of a carrier with a continuum is solely short ranged. The author notes that the anharmonicity affects the degree of spatial localization of a small-polaron state. It is found that in a 3D anharmonic continuum with both the long-range and the short-range interactions of an electron with a continuum, the anharmonicity breaks the coexistence of a small polaron with a large polaron. In a situation of an electron interacting with a 1D continuum solely via the short-range mode no anharmonic correction to the energy of a large polaron was found. It is concluded from these results that the anharmonic corrections can be important in the physics of polarons. The magnitude of these corrections depends on the dimensionality of the problem, the character of the electron-continuum interaction and the parameter of anharmonicity.

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