

Corrections to the continuum approximation of the Fröhlich polaron: The ground-state energy

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(Received 30 November 1987; revised manuscript received 8 March 1988)

Corrections to the continuum approximation in the formulation of the dielectric polaron are investigated. The starting point is the small-polaron Hamiltonian of Emin with an arbitrary electron-phonon interaction potential. The kq representation of Zak is then used. From this Hamiltonian and with an appropriate interaction potential, corrections to the effective-mass approximation in the Fröhlich Hamiltonian are calculated from a perturbative expansion for a slowly varying electron-phonon interaction. This results in a renormalization of the interaction. A Debye cutoff is also imposed on the phonon wave vectors. The ground-state energy of the polaron is then calculated with use of the Fock approximation. It is found that in weak coupling and in strong coupling with small Debye cutoff the corrections to the continuum approximation are small, decrease the polaron self-energy, and are proportional to α/L , where α is the electron-phonon coupling constant and L is the wave vector at which the Debye cutoff is made. In strong coupling, for a large cutoff, the self-energy is also reduced but much more drastically and the strong-coupling behavior in α^2 disappears. Polar crystals for which a large polaron is involved can all be classified in the first limit and the corrections to the continuum approximation are rather small, the largest one being of the order of 14% for LiF.

I. INTRODUCTION

The polaron is the quasiparticle formed by an electron in an insulator in interaction with the phonons. This interaction gives rise to a lattice distortion around the electron. A distinction is made between a small and a large polaron, according to the radius of this distortion. A small polaron is considered when the radius is smaller or equal to the lattice parameter while a large polaron is considered when this radius is larger than a unit cell. In a polar material, the large polaron is usually called the dielectric polaron or Fröhlich polaron. In this case, the lattice is treated as a polarizable continuum and the effective-mass approximation is used for the electron. In the literature, this is known as the continuum approximation. In the case of a small polaron, the electron is considered as interacting with its nearest neighbors only and the effective-mass approximation is not done from the beginning. This gives rise to the possibility of self-trapping for the polaron.

In these two cases, the small and the large polaron, only limits are considered. For the large polaron, the effect of the local neighborhood and the effect of the lattice distortion on the local band structure are neglected. For the small polaron, the effects of long-range interactions are neglected. Real crystals corresponding to these limiting cases can be found. Large polarons are found in crystals for which the electron-phonon interaction is small: the III-V compounds, for example.¹ Small polarons are found in crystals of large electron-phonon coupling with a narrow conduction band: the metallic oxides, for example.² However, some crystals do not correspond to any of these limits. This is the case of some perovskites for which the polaron radius is of the order of the lattice parameter and which do not satisfy either the

small- or the large-polaron definition criteria.³ In this paper, this case will be called intermediate polaron.

It is important to know more about the properties of the intermediate polaron. First, because it will enable us to describe better, on theoretical grounds, the optical and transport properties of crystals like the perovskites and the alkali halides. Second, it will help to find the limits of validity of existing models by comparing the theoretical predictions of the limiting cases with those of a more appropriate description. Third, it can help to define a qualitative behavior for the intermediate polaron. For example, is it a state characterized by a mixture or coexistence of small and large polarons as suggested by Eagles,⁴ or is it a single state characterized by properties intermediate between those of the small and the large polarons? To provide an answer to all these questions, a good description of the intermediate polaron is needed.

Here, the polaron problem will be formulated in the kq representation of Zak.⁵ This representation uses a position variable (q) to describe the polaron wave function, in the interior of a unit cell, while a momentum variable (k), in the first Brillouin zone, is used to describe the "translationally invariant" motion of the polaron in the periodic lattice. This representation is well suited to describe the polaron problem since the interaction of the electron with the neighboring atoms in the unit cell can be described simultaneously with the translationally invariant motion. Using this representation, the polaron Hamiltonian can be written in a form which is valid in the two previously discussed limits. Then, it is easy to take the continuum limit and to see under which conditions this can be done. It is also easy to obtain the corrections to this continuum limit when these conditions are just barely satisfied. Also, the small-polaron limit and the intermediate case can be discussed in this framework.

In this paper, we present the kq formulation of the polaron Hamiltonian and concentrate on the continuum limit of the large polaron. First, we present the polaron Hamiltonian, the kq representation, and write the polaron Hamiltonian in this representation. We discuss the Hamiltonian obtained and take its continuum limit. In Sec. III, lower-order corrections to the continuum approximation of the Fröhlich Hamiltonian are obtained and the Debye cutoff is introduced and discussed. In Sec. IV, the ground-state energy of the polaron is calculated, using second-order perturbation theory and the Fock approximation of Matz and Burkey,⁶ which is valid (it gives an upper bound to the ground-state energy) for any value of the electron-phonon coupling constant. These calculations give us the first corrections to the continuum approximation. Asymptotic limits are also considered. In Sec. V, numerical results are given for the ground-state energy, as a function of the electron-phonon coupling constant and of parameters depending on the dimensions of the unit cell. Applications are done to the case of polar crystals and the corrections to the continuum approximation are given for typical cases. We conclude by discussing the validity of the continuum approximation for polar crystals. We also discuss the limitations and the possible extensions of the present discussions.

II. THE POLARON HAMILTONIAN IN THE kq REPRESENTATION

We consider the case of an electron interacting with the longitudinal-optical (LO) phonons in a polar crystal. Optical phonons with wave number near the center of the Brillouin zone, the only ones that interact strongly with the electron, have no dispersion. In this case, the lattice contribution of the polaron Hamiltonian is the same as that used by Emin⁷ to describe his molecular crystal model of the small polaron. This Hamiltonian, in the r representation, is⁷

$$H_E = \frac{\hat{p}^2}{2m} + \sum_{\mathbf{G}} U(\mathbf{r}-\mathbf{G}) + \sum_l \hbar\omega_0 b_l^\dagger b_l + \sum_l [v_l(\mathbf{r})b_l + v_l^*(\mathbf{r})b_l^\dagger], \quad (1)$$

where m , \mathbf{r} , and \mathbf{p} are, respectively, the electron mass, position, and momentum, and $U(\mathbf{r}-\mathbf{G})$ is the static contribution of the atoms in the \mathbf{G} th unit cell to the electron's potential energy. b_l and b_l^\dagger are the phonon second quantization operators and ω_0 is the zone-center frequency of a LO phonon. The last term in Eq. (1) was used by Emin to describe the electron-lattice interaction energy in the molecular crystal model. In our case, this term will be used to describe a general linear electron-lattice interaction. A more specific form of $v_l(\mathbf{r})$ will be given later when the continuum limit will be taken in the case of the dielectric polaron.

The kq representation⁵ corresponds to a choice of coordinates that is well adapted to the symmetry of a crystal having the usual lattice periodicity. In this representation, \mathbf{k} is the quasimomentum and is a conserved quantity

for a free electron. As \mathbf{k} does not carry complete quantum-mechanical information about the electron motion in a periodic structure (\mathbf{k} is given in the first Brillouin zone within a reciprocal-lattice vector), partial information about the electron position can also be given. The quasicordinate \mathbf{q} will describe the position of the electron in a unit cell without specifying in which unit cell it is. The kq representation is obtained from the following transformation:⁵

$$\mathbf{p} = -i\hbar\partial/\partial\mathbf{q} \quad (2a)$$

and

$$\mathbf{r} = i\partial/\partial\mathbf{k} + \mathbf{q}, \quad (2b)$$

where \mathbf{r} and \mathbf{p} are the electron position and momentum in the usual position representation, \mathbf{k} is restricted to the first Brillouin zone, and \mathbf{q} is limited to a unit cell.

We now write the polaron Hamiltonian in the kq representation, using Eqs. 2. We obtain

$$H_E = -\frac{\hbar^2}{2m}\partial^2/\partial\mathbf{q}^2 + \sum_{\mathbf{G}} U(\mathbf{q}+i\partial/\partial\mathbf{k}-\mathbf{G}) + \sum_l \hbar\omega_0 b_l^\dagger b_l + \sum_l [v_l(\mathbf{q}+i\partial/\partial\mathbf{k})b_l + v_l^*(\mathbf{q}+i\partial/\partial\mathbf{k})b_l^\dagger]. \quad (3)$$

Note that the phonon operators are left unchanged by this transformation. The second term of the right-hand side of this equation is just the potential energy of an electron, located at \mathbf{q} in a unit cell, and moving in the periodic potential of the crystal. Because of its periodicity, once the sum over the lattice vectors \mathbf{G} is done, it does not depend on $\partial/\partial\mathbf{k}$. In the following, it will be written $W(\mathbf{q})$.

It can also be shown that \mathbf{R} , the position coordinate of a unit cell in the direct lattice, and \mathbf{k} are conjugate coordinates:⁵

$$\mathbf{R} = i\partial/\partial\mathbf{k} \quad (4a)$$

and

$$\mathbf{k} = -i\partial/\partial\mathbf{R}. \quad (4b)$$

The commutator of \mathbf{R} and \mathbf{k} is thus equal to i . With these new definitions, H_E can be written:

$$H_E = -\frac{\hbar^2}{2m}\partial^2/\partial\mathbf{q}^2 + W(\mathbf{q}) + \sum_l \hbar\omega_0 b_l^\dagger b_l + \sum_l [v_l(\mathbf{q}+\mathbf{R})b_l + v_l^*(\mathbf{q}+\mathbf{R})b_l^\dagger]. \quad (5)$$

Note that even if \mathbf{k} does not appear explicitly in this equation, it will appear in the wave functions since \mathbf{R} is the coordinate conjugate to \mathbf{k} .⁵

Equation (5) contains exactly the same physics as the Emin Hamiltonian [Eq. (1)]. As such, it has exactly the same eigenvalues. Equation (5) is thus an adequate starting point to discuss the properties of the small polaron. A treatment similar to that of Emin should lead to exactly the same results concerning the small-polaron properties. In that case, $v_l(\mathbf{q}+\mathbf{R})$ depends both on \mathbf{q} , the elec-

tron coordinate in the unit cell, and on \mathbf{R} , the specific cell in which the electron is located. In the model used by Emin, v_l corresponds to a deformation potential coupling at the level of a unit cell. This is a good description for the small polaron and it can lead to self-trapping because the electron-phonon interaction can renormalize the periodic potential at the level of a unit cell.

The other limit, that of the large polaron, is more interesting. Then, $v_l(\mathbf{q} + \mathbf{R})$ is nearly a constant over a unit cell. It changes significantly only over several unit cells. This is the case of the $1/r^2$ dependence for the dielectric polaron in the continuum approximation. In this limit, to first order, v_l depends only on \mathbf{R} . The \mathbf{q} and \mathbf{R} are again decoupled as it is seen from (5). The \mathbf{q} part of the Hamiltonian is easily diagonalized, resulting in the m th energy band of the free electron. The result is

$$H = \mathcal{E}_m(\hat{\mathbf{k}}) + \sum_l \hbar\omega_0 b_l^\dagger b_l + \sum_l [v_l(\mathbf{R})b_l + v_l^*(\mathbf{R})b_l^\dagger]. \quad (6)$$

In this equation, $\mathcal{E}_m(\mathbf{k})$ is the electronic energy of the m th band and $\hat{\mathbf{k}}$ is a wave-number operator that does not commute with \mathbf{R} , as can be seen from (4b). For small eigenvalues of $\hat{\mathbf{k}}$, a quadratic form can be used for the band energy, using the effective-mass approximation:

$$H = -\frac{\hbar^2}{2m^*} \frac{\partial^2}{\partial \mathbf{R}^2} + \sum_l \hbar\omega_0 b_l^\dagger b_l + \sum_l [v_l(\mathbf{R})b_l + v_l^*(\mathbf{R})b_l^\dagger], \quad (7)$$

where m^* is the effective conduction-band mass. If $v_l(\mathbf{R})$ is chosen as being equal to $Ce^{i\mathbf{l}\cdot\mathbf{R}}/l$, the Fröhlich Hamiltonian is found, where C is proportional to the square root of the electron-phonon coupling constant α . To this Hamiltonian, which is used to describe the large polaron in the continuum approximation, we will add, using the kq representation, corrections due to the discreteness of the crystal lattice.

III. CORRECTIONS TO THE CONTINUUM APPROXIMATION

In this section, we calculate second-order corrections to the continuum approximation in the Fröhlich Hamiltonian. From these, we obtain the corrections to the ground-state energy of the free polaron. Our starting point will be the Emin Hamiltonian written in the kq representation [Eq. (5)] in which we substitute a long-range electron-phonon interaction term characteristic of polar crystals [$v_l(\mathbf{r})$ equal to $V_l e^{i\mathbf{l}\cdot\mathbf{r}}$ and V_l proportional to l^{-1}].¹

$$H = -\frac{\hbar^2}{2m} \partial^2 / \partial \mathbf{q}^2 + W(\mathbf{q}) + \sum_l \hbar\omega_0 b_l^\dagger b_l + \sum_l (V_l e^{i\mathbf{l}\cdot(\mathbf{q}+\mathbf{R})} b_l + V_l^* e^{-i\mathbf{l}\cdot(\mathbf{q}+\mathbf{R})} b_l^\dagger), \quad (8)$$

where

$$V_l = -\frac{i}{l} \left[\frac{2\pi e^2 (\epsilon_\infty^{-1} - \epsilon_0^{-1})}{\hbar\omega_0 \Sigma} \right]^{1/2} \hbar\omega_0,$$

and Σ is the system volume. ϵ_0 and ϵ_∞ are the low- and high-frequency dielectric constants, respectively. ω_0 is the LO-phonon frequency.

It has been shown, in the last section, that if the electron-phonon interaction potential $v_l(\mathbf{q} + \mathbf{R})$ does not depend on \mathbf{q} , the Emin Hamiltonian reduces to the Fröhlich Hamiltonian in the continuum approximation. We now want to obtain corrections to the continuum approximation in the case where the interaction potential varies only slowly within a unit cell. This is similar to the impurity problem that was treated by Zak, using the kq representation.^{5,8} We will use the same treatment here, assuming that $v_l(\mathbf{q} + \mathbf{R})$ varies slowly over a unit cell. This is equivalent to saying that its dependence on \mathbf{q} is weak. This is plausible in the case of a $1/l$ potential, since in that case the long wavelengths are the most important.

Following a procedure described by Zak,^{5,8} an expansion of the Hamiltonian in the derivatives of a slowly varying potential $\mathcal{V}(\mathbf{r})$ can be obtained. The corrections to the effective-mass approximation can be calculated to second order and the following Hamiltonian is obtained:

$$H = \mathcal{E}_m(\hat{\mathbf{k}}) + \mathcal{V}(\mathbf{R}) + A_{ij}^{(m)} \frac{\partial^2 \mathcal{V}(\mathbf{R})}{\partial R_i \partial R_j} + B_{ij}^{(m)} \frac{\partial \mathcal{V}(\mathbf{R})}{\partial R_i} \frac{\partial}{\partial R_j}. \quad (9)$$

The first-order contribution is absent for a crystal having the symmetry of inversion. The interband contributions have been neglected in (9). The coefficients $A_{ij}^{(m)}$ and $B_{ij}^{(m)}$ are c -numbers and can be calculated if one knows the periodic part of the Bloch wave function [$u_{mk}(\mathbf{q})$] for the band m . An order of magnitude for these coefficients can be obtained if the tight-binding approximation is used for the band structure.⁵ If we assume the absence of degeneracy for the atomic levels and if the corresponding atomic wave functions $a_m(\mathbf{r})$ are real, we find⁵

$$A_{ij}^{(m)} = \frac{1}{2} \sum_{\mathbf{R}} \int d^3 r x_i x_j a_m(\mathbf{r} + \mathbf{R}) a_m(\mathbf{r}) \quad (10a)$$

and

$$B_{ij}^{(m)} = 0. \quad (10b)$$

For a crystal of cubic symmetry, a further simplification occurs:

$$A_{ij}^{(m)} = \frac{1}{6} \left[\int d^3 r r^2 a_m^2(\mathbf{r}) \right] \delta_{ij}. \quad (11)$$

This can be written as

$$A_{ij}^{(m)} = \frac{1}{6} \langle r^2 \rangle = a^2. \quad (12)$$

In Eq. (12), a , the root mean square of the electron orbit radius for the level corresponding to the conduction band, is defined. In what follows, a^2 will be approximated by the square of half the nearest-neighbor distance divided by 6.

Using these approximations, the polaron Hamiltonian becomes, replacing $\mathcal{E}_m(\hat{\mathbf{k}})$ by the effective-mass approximation,

$$H = -\frac{\hbar^2}{2m^*} \nabla_{\mathbf{R}}^2 + \sum_l \hbar \omega_0 b_l^\dagger b_l + V(\mathbf{R}) + a^2 \sum_{i,j} \frac{\partial^2 V(\mathbf{R})}{\partial R_i \partial R_j} \quad (13)$$

with

$$V(\mathbf{R}) = \sum_l (V_l e^{i\mathbf{l}\cdot\mathbf{R}} b_l + V_l^* e^{-i\mathbf{l}\cdot\mathbf{R}} b_l^\dagger).$$

m^* is the effective conduction-band mass. The last term of (13) is easily evaluated. Its effect is to renormalize V_l to $V_l(1-a^2 l^2)$ in $V(\mathbf{R})$. The resulting large-polaron Hamiltonian, including the corrections to the continuum approximation, is thus, in a dimensionless system ($\hbar \omega_0 = 2m^* = \hbar = 1$),

$$H = -\nabla_{\mathbf{R}}^2 + \sum_l b_l^\dagger b_l + \sum_l (B_l e^{i\mathbf{l}\cdot\mathbf{R}} b_l + B_l^* e^{-i\mathbf{l}\cdot\mathbf{R}} b_l^\dagger), \quad (14)$$

where B_l is given by

$$B_l = V_l(1-a^2 l^2). \quad (15)$$

In this dimensionless system, we have

$$V_l = -\frac{i}{l} \left[\frac{4\pi\alpha}{\Omega} \right]^{1/2},$$

$$\alpha = \frac{e^2}{2\hbar\omega_0\tau_0} (\epsilon_\infty^{-1} - \epsilon_0^{-1}),$$

$$\tau_0 = \left[\frac{\hbar}{2m^*\omega_0} \right]^{1/2},$$

where Ω is the dimensionless volume of the system and α is the electron-phonon coupling constant. τ_0 is often called the quantum radius of the polaron. It is the natural unit of length in the polaron problem.

In Eq. (8), the polaron Hamiltonian was written in the kq representation. Consequently, \mathbf{k} is limited to the first Brillouin zone and \mathbf{q} is limited to a unit cell in the direct space. In writing Eq. (14), a perturbation expansion has been done for a slowly varying electron-phonon interaction potential. The unperturbed state was then the continuum approximation. As a consequence, \mathbf{R} , the variable conjugate to \mathbf{k} , which, in the exact problem, was a discrete variable indicating the position of a unit cell in the crystal, has to be considered as a continuous variable in (14). On the other hand, the phonon variables have not been modified by the use of the kq representation or by the perturbation expansion done on the electronic variables. Because a phonon wavelength cannot be shorter than the dimension of a unit cell, the phonon wave vectors must be restricted to the first Brillouin zone. In the present work, we will use the simplification introduced by Debye and make the Debye cutoff approximation: the phonon wave vectors will be limited to a sphere of radius equal to the Debye wave vector $L = \pi/a^*$, where a^* is the lattice parameter. Note that this cutoff is necessary to obtain finite values for the ground-state energy of the polaron. Because of the l^2 term in B_l , an

infinite value would be obtained for the energies without this cutoff. This is reminiscent of the case of the piezoelectric polaron for which such a cutoff is necessary to obtain finite energies.

The use of a Debye cutoff is not new in polaron theory. It was used by Schultz⁹ who applied this cutoff in a path-integral approach. It was also done by Lee and Pines¹⁰ in the context of a unitary transform technique. Sumi and Toyozawa¹¹ also considered the Debye cutoff when they studied an electron interacting with both acoustic- and optical-phonon modes. This cutoff was used to study the error introduced by the continuum approximation. They all found that this error was small for polar crystals of interest. In what follows, we find energies comparable or equal to those found by the above authors if corrections to the effective-mass approximations are neglected. In the present paper, in addition to the Debye cutoff on the phonon wave vectors, we consider corrections to the continuum approximation of the Fröhlich Hamiltonian brought by relaxing the effective band mass approximation: the electron-phonon interaction is included in the tight-binding band-structure calculation from the beginning. These corrections will then be calculated using the kq representation together with a perturbative expansion for departures from the effective-mass approximation.

IV. CALCULATION OF THE GROUND-STATE ENERGY

In this section, we calculate the ground-state energy of the polaron at zero temperature, starting from (14). First, a second-order perturbation theory will be used for weak coupling and, second, results valid for any coupling will be obtained from the Fock approximation.

For small electron-phonon coupling, second-order perturbation theory can be used to obtain the ground-state energy of the polaron. We obtain

$$E_0 = P^2 - \sum_l \frac{|B_l|^2}{(1+l^2-2\mathbf{P}\cdot\mathbf{l})}, \quad (16)$$

where \mathbf{P} is the momentum of the polaron. If the angular integrals are done, we find

$$E_0 = P^2 - \frac{\alpha}{\pi P} \int_0^L dl \frac{(1-a^2 l^2)^2}{l} \tanh^{-1} \left[\frac{2lP}{(1+l^2)} \right]. \quad (17)$$

For small P , this reduces to

$$E_0 = -\alpha_E + P^2(1-\alpha_M/6), \quad (18)$$

with

$$\alpha_E = \frac{2\alpha}{\pi} \tan^{-1} L - \frac{4a^2\alpha}{\pi} (L - \tan^{-1} L)$$

and

$$\alpha_M = \frac{2\alpha}{\pi} \left[\tan^{-1} L + \frac{L}{1+L^2} - \frac{2L}{(1+L^2)^2} \right] - \frac{4a^2\alpha}{\pi} \left[3 \tan^{-1} L - \frac{5L}{1+L^2} + \frac{2L}{(1+L^2)^2} \right].$$

From (18), an effective mass can be written:

$$m^{**} = \frac{m^*}{1 - \alpha_M/6} \tag{19}$$

In these equations, the a^4 terms coming from (17) have been discarded because these terms were not kept in the expansion of Eq. (9). α_E denotes the renormalization, arising from the Zak corrections and from the Debye cutoff, of the electron-phonon coupling constant present in the polaron self-energy. α_M refers to the same quantity, but in the effective-mass expression. If the limits $a \rightarrow 0$ (removal of the Zak correction to the continuum approximation) and then $L \rightarrow \infty$ (elimination of the Debye cutoff) are taken, we find $\alpha_E = \alpha_M = \alpha$, the usual value for the continuum approximation in second-order perturbation theory.¹² If these limits are taken in the inverse order, divergences occur, since the cutoff was necessary to evaluate the energies. We can summarize Eqs. (18) and (19) by noting that the net effect of these two corrections is to reduce the effective strength of the electron-phonon coupling constant both in the polaron self-energy and in its effective mass.

We now turn to a formalism valid for any value of α . It is the Fock approximation of Matz and Burkey.⁶ This treatment is chosen for many reasons: it is simple to use, it gives an upper bound to the ground-state energy, and it is valid for any value of the electron-phonon coupling constant.¹³ Also, the energies obtained from this formalism are the same as those obtained by Gross,¹⁴ using unitary transforms, and by Feynman¹⁵ in its rigid oscillator approximation. This formalism predicts a self-trapping phase transition around $\alpha = 6$ in the continuum model, a result which is not found within the more precise Feyn-

man path-integral formalism¹⁶ (using the Feynman two-particle model). However, the asymptotic results coincide and the energies predicted by the two methods are quantitatively nearly the same. In the present case, as the corrections to the continuum approximation only are considered, the Fock approximation can be used without problem. In this context, an upper bound to the ground-state energy can be written¹³ (here, \mathbf{r} has been substituted for \mathbf{R} to indicate a continuum variable):

$$E_0 = \int d^3r \Phi_0^*(\mathbf{r}) \hat{p}^2 \Phi_0(\mathbf{r}) + \sum_{l,n} \int d^3r \int d^3r_1 |B_l|^2 \exp[i\mathbf{l} \cdot (\mathbf{r} - \mathbf{r}_1)] \times \frac{\Phi_n(\mathbf{r}) \Phi_n^*(\mathbf{r}_1)}{\epsilon_0 - 1 - \epsilon_n} \Phi_0^*(\mathbf{r}) \Phi_0(\mathbf{r}_1), \tag{20}$$

where the $\{\Phi_n(\mathbf{r})\}$ form a complete variational model spectrum, the ϵ_n 's being its eigenvalues. Here we will use the usual Gaussian model spectrum of variational parameter β . This is the best one-parameter spectrum for the free polaron.^{6,14,15} Note that (20) differs from the usual expressions for E_0 for two reasons: first, the electron-phonon interaction potential has been renormalized from V_l to B_l , because of the Zak correction to the continuum approximation and, second, a Debye cutoff at L is present for the l summation.

Evaluation of (20) with a Gaussian spectrum (of variational parameter β)^{6,13} and a Debye cutoff (L) gives

$$E_0 = T + T_1 + T_2, \tag{21}$$

where

$$T = 3\beta^2/2, \\ T_1 = - \left[\frac{2}{\pi} \right]^{1/2} \alpha\beta \int_0^\infty dt \frac{e^{-t}}{(1 - e^{-2\beta^2 t})^{1/2}} \phi \left[\frac{L}{2^{1/2}\beta} (1 - e^{-2\beta^2 t})^{1/2} \right], \\ T_2 = \frac{2^{3/2} a^2 \alpha \beta}{\pi} \int_0^\infty dt \frac{e^{-t}}{(1 - e^{-2\beta^2 t})^{1/2}} \left[\frac{\pi^{1/2} \beta^2}{(1 - e^{-2\beta^2 t})} \phi \left[\frac{L}{2^{1/2}\beta} (1 - e^{-2\beta^2 t})^{1/2} \right] - \frac{2^{1/2} \beta L e^{-L^2(1 - e^{-2\beta^2 t})/2\beta^2}}{(1 - e^{-2\beta^2 t})^{1/2}} \right].$$

This equation has to be minimized with respect to β . $\phi(x)$ is the error function. All the a^2 contributions coming from the Fock approximation are present. Because (21) was derived from a perturbative expansion in a^2 , the a^4 contributions arising from (20) have not been written since they would not have been complete: the expansion in (9) was truncated to the second order.

In (21), T results from the kinetic energy of the electron, T_1 results from the Fock term with a Debye cutoff, and T_2 results from the Zak corrections to the continuum approximation. If the limits $a \rightarrow 0$ and $L \rightarrow \infty$ are taken, the usual expression for the Fock approximation for the

free polaron is found

$$E_0 = \frac{3}{2}\beta^2 - \left[\frac{2}{\pi} \right]^{1/2} \alpha\beta \int_0^\infty dt \frac{e^{-t}}{(1 - e^{-2\beta^2 t})^{1/2}}. \tag{22}$$

If only $a = 0$ and L is finite, $T_2 = 0$ and we find an energy ($E_0 = T + T_1$) already derived by Schultz⁹ and by Sumi and Toyozawa¹¹ (in the case where the interaction with the acoustic phonons is neglected). The resulting expression contains the Debye cutoff but not the other corrections to the continuum approximation. In weak coupling, the minimization of E_0 gives $\beta = 0$. An asymptotic

expansion of (21) can then be done and we find

$$E_0 = -\frac{2\alpha}{\pi} \tan^{-1} L + \frac{4a^2\alpha}{\pi} (L - \tan^{-1} L). \quad (23)$$

This is the same result as that found from perturbation theory [Eq. (18)]. Without the Zak correction, it was found by Sumi and Toyozawa¹¹ in the same limit. The corrections to the continuum approximation can be obtained from the large- L limit ($L \gg 1$) of (23):

$$E_0 = -\alpha + \frac{2\alpha}{\pi L} + \frac{4a^2\alpha L}{\pi}. \quad (24)$$

The first term of this equation is the usual weak-coupling

ground-state energy, the second term is the correction coming from the Debye cutoff and the third term comes from the Zak corrections to the ground-state energy. The last two terms are of the same order of magnitude since a is proportional to L^{-1} . The correction coming from the Debye cutoff (the second term) is the same as that found by Schultz⁹ from the Feynman path-integral formalism.

In strong coupling, minimization of (21) will generate a large value of β . For these values of β , an asymptotic expansion of (21) can be obtained. This expansion cannot be easily done for T_2 in its actual form. It can, however, be rewritten in a more tractable form, after integrations by parts:

$$T_2 = \frac{4a^2\alpha}{\pi} \left\{ L - \left[\frac{\pi}{2} \right]^{1/2} \beta \phi \left[\frac{L}{\sqrt{2\beta}} \right] + \left[\frac{\pi}{2} \right]^{1/2} \beta (1 - 2\beta^2) \int_0^\infty dt \frac{e^{(2\beta^2-1)t}}{(1 - e^{-2\beta^2 t})^{1/2}} \left[(1 - e^{-2\beta^2 t})^{1/2} \phi \left[\frac{L}{\sqrt{2\beta}} \right] - \phi \left[\frac{L(1 - e^{-2\beta^2 t})^{1/2}}{\sqrt{2\beta}} \right] \right] \right\}. \quad (25)$$

We have to consider two limits: $\beta \gg L$ and $L \gg \beta$. First, for $\beta \gg L$ and for large values of β , $\exp(-2\beta^2 t) \rightarrow 0$ and we obtain

$$T_1 = - \left[\frac{2}{\pi} \right]^{1/2} \alpha \beta \phi \left[\frac{L}{\sqrt{2\beta}} \right] \quad (26a)$$

and

$$T_2 = \left[\frac{2}{\pi} \right]^{1/2} 2\alpha\beta^3 a^2 \times \left[\phi \left[\frac{L}{\sqrt{2\beta}} \right] - \left[\frac{2}{\pi} \right]^{1/2} \left[\frac{L}{\beta} e^{-(L^2/2\beta^2)} \right] \right]. \quad (26b)$$

Minimization of Eqs. (26) to which we add T gives (for $\beta \gg L$)

$$E_0 = -\frac{2\alpha L}{\pi} \left[1 - \frac{2a^2 L^2}{3} \right] + 3\beta_{\min}^2, \quad (27)$$

with

$$\beta_{\min}^4 \approx \frac{2\alpha L^3}{9\pi} - \frac{4a^2\alpha L^5}{15\pi}.$$

Equation (27), without the Zak correction, is the same as that found by Sumi and Toyozawa¹¹ in the same limit. The first term is the strong-coupling limit of E_0 calculated with a Debye cutoff. It is the same as that found by Lee and Pines¹⁰ in the same limits. The second term of (27) comes from the Zak correction to the continuum approximation. It is of the same order of magnitude as the first term, L being proportional to a^{-1} .

For $L \gg \beta$, β minimizes to

$$\beta_{\min} = \left[\frac{2}{\pi} \right]^{1/2} \frac{\alpha}{3} - \frac{4\sqrt{2}a^2\alpha^3}{9\pi^{3/2}}, \quad (28a)$$

and L is much larger than α . We find, from (21), using (25) for T_2 and a procedure described by Schultz,⁹

$$E_0 = -\frac{\alpha^2}{3\pi} + \frac{2\alpha}{\pi L} + \frac{4a^2\alpha L}{\pi} + \frac{8a^2\alpha^4}{27\pi^2} - 3 \ln 2. \quad (28b)$$

The first term is the usual strong-coupling polaron ground-state energy. The second term is the correction coming from the Debye cutoff to the first term. The two last terms come from the Zak correction to the Fröhlich Hamiltonian. The second and third terms have the same dependence on α and L and are of the same order of magnitude. They are identical to the corresponding terms for weak coupling [Eq. (24)]. The second term is the same as that found by Schultz⁹ for all values of α : it results from a Debye cutoff done on the electron-phonon interaction.

A few remarks can be made about the above results. First, in weak coupling and in strong coupling when $L \gg \beta$ (or α), the corrections to the continuum approximation are exactly the same: a term in L^{-1} coming from the Debye cutoff and a second term in $a^2 L$ coming from the Zak corrections. Because a is proportional to L^{-1} , these two terms are of the same order of magnitude and are proportional to a length that characterizes the discreteness of the lattice. In the remaining limit [strong coupling ($\alpha \gg 1$) with $L \ll \beta$ or α], the effect of the cutoff is more dramatic: the strong-coupling behavior in α^2 disappears. The resulting ground-state energy is proportional to α , a behavior typical of weak coupling. This suggests that an important Debye cutoff can reduce enough of the electronic recoil correlations to eliminate the strong-coupling regime. The polaron radius then be-

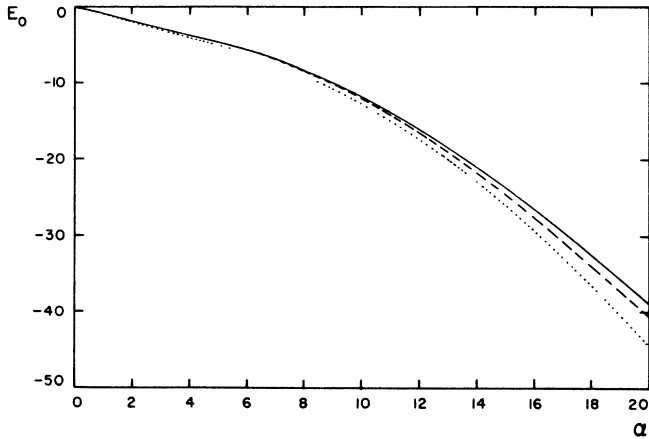


FIG. 1. Ground-state energy of the polaron as a function of α , for $L=10$ and $S=0.2777$. The solid curve is for E_0^Z , the dashed line for E_0^D , and the dotted line for E_0^C .

comes so small that phonons of very short wavelength would be necessary to describe the lattice distortion around the electron. If these components are absent because of an important cutoff ($L \ll \beta$), the strong-coupling regime can no longer exist. In that case, the Fröhlich Hamiltonian is no longer valid. This shows that the asymptotic strong-coupling behavior of the Fröhlich Hamiltonian can never apply to a real crystal. This is because, for a real crystal, L is always finite and, for the asymptotic case, we can always find a value of α for which $L \ll \beta$.

V. NUMERICAL RESULTS

In this section, we present numerical calculations for the ground-state energy of the polaron, as calculated from Eqs. (21). These results will be presented for three levels of approximation: the ground-state energy as obtained from the continuum Hamiltonian (E_0^C), its value

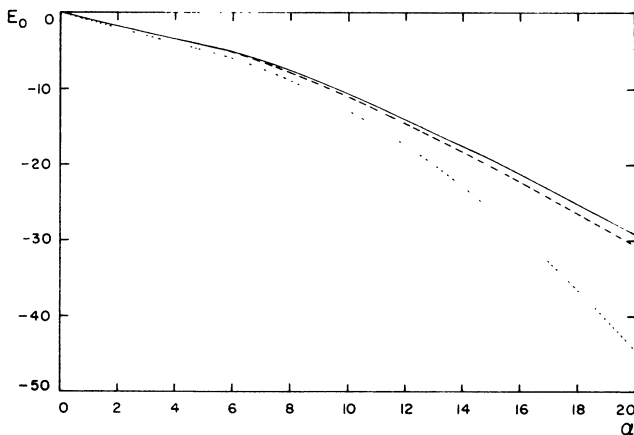


FIG. 2. Ground-state energy of the polaron as a function of α , for $L=5$ and $S=0.2777$. The solid curve is for E_0^Z , the dashed line for E_0^D , and the dotted line for E_0^C .

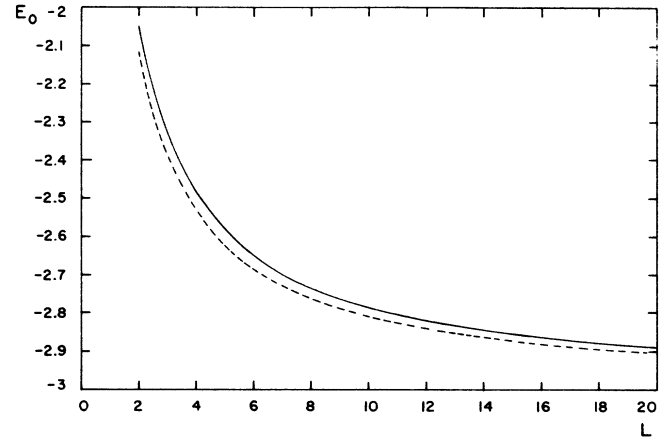


FIG. 3. Ground-state energy of the polaron as a function of L , the Debye cutoff, for $\alpha=3$ and $S=0.2777$. The solid curve is for E_0^Z and the dashed one for E_0^D .

calculated with the Debye cutoff (E_0^D), and finally its value including the Debye cutoff and the Zak second-order correction (E_0^Z). Also, the numerical values of these corrections will be given in the case of real crystals in order to test the validity of the continuum approximation and of the Fröhlich Hamiltonian.

In order to do these calculations, we need a relation between a and L . From Eq. (12) and the definition of L as being π/a^* , we find

$$a = \frac{S}{L}, \quad (29)$$

where S is a geometric factor depending on the crystal structure. From the above definitions, it is calculated to be 0.2777 for the zinc-blende structure, 0.5554 for the cesium chloride structure, and 0.3206 for the sodium chloride structure. These values have been obtained assuming an ionic radius equal to half the distance between two nearest-neighbor ions.

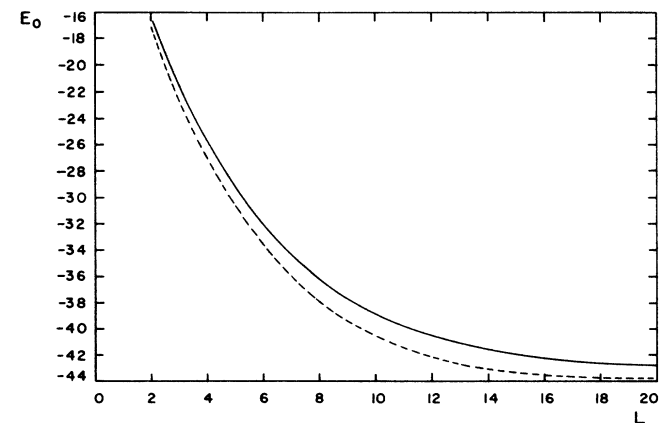


FIG. 4. Ground-state energy of the polaron as a function of L , the Debye cutoff, for $\alpha=20$ and $S=0.2777$. The solid curve is for E_0^Z and the dashed one for E_0^D .

The numerical calculations have been done on Eqs. (21). They have been checked with the asymptotic expansions of Sec. IV and were found to agree to more than six digits. The result is shown in Figs. 1–4. In Fig. 1, we have plotted E_0^C , E_0^D , and E_0^Z as a function of α for α between 0 and 20, for $S=0.2777$ and for $L=10$. In Fig. 2, the equivalent graph is presented for $L=5$. From these figures, we observe that the effect of the Debye cutoff on T_1 and of the Zak correction is to reduce the self-energy of the polaron. We also note that the effect of the Debye cutoff is more important than the effect of the Zak correction. This is due to our choice of parameters: $L=5$ or 10 and $S=0.2777$. This choice is, however, typical of real crystals for which S is always smaller than 1, reducing the contribution of T_2 , this term being proportional to a^2 . We also observe that the effect of the Debye correction is much more important for $L=5$ than for $L=10$. Note also that, for these curves, we are in the $L \gg \beta$ limit. As a consequence, the $L \ll \beta$ limit can never be reached for existing crystals.

In Figs. 3 and 4, we plot E_0^D and E_0^Z as a function of the value of the Debye cutoff L , for $\alpha=3$ and 20 , respectively. Features similar to those of the first two figures are seen: small value of the Zak correction and a decrease in the self-energy of the polaron. For large L , the value of E_0^C is asymptotically obtained. In Fig. 3, β minimizes always to zero and L is always larger than β . In Fig. 4, β minimizes asymptotically around 5 and both limits ($\beta \gg L$ and $L \gg \beta$) are present on the curve. In both curves, we see that the effect of the discreteness of the lattice is important only for L smaller than ~ 10 .

In Fig. 5, we have plotted β_{\min} , the value of β that minimizes the ground-state energy, as a function of α , for $L=5, 10$, and without cutoff. This quantity (β) characterizes the inverse radius of the polaron in the strong-coupling regime. The Zak correction is not included because, for parameters of interest, it does not change significantly the value of β_{\min} . In this figure, we see that the effects of the corrections to the continuum are more

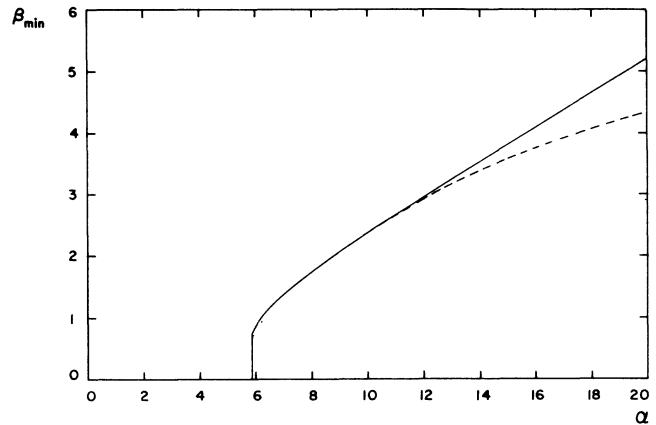


FIG. 5. β_{\min} as a function of α as obtained from the minimization of $T+T_1$, without T_2 . The solid curve is obtained without cutoff, the dashed one with $L=10$, and the dotted one with $L=5$.

important than in the case of the ground-state energy. They can be as high as 50% for the same parameters as before and are apparent for much larger values of L . β_{\min} is seen to increase linearly with α , for large α , when the cutoff is absent, while for $L=5$ it is not the case. Also on this graph, we see that the $\beta \gg L$ limit can be reached only for very small values of L (around $L=1$ for $\alpha=20$).

We have also calculated the corrections to the continuum approximation for a few polar crystals. In Table I, we present E_0^C and E_0^Z and the percentage of correction to the continuum approximation, together with α , L , and S for GaAs, CdTe, AgCl, AgBr, TiCl, KCl, RbCl, LiF, and NaCl. Most of the parameters used in these calculations come from Kartheuser.¹⁷ In the last two cases, we used the electron bare mass in the calculations, since the band mass is unknown. From these data, we observe that, for these crystals, the corrections to the continuum

TABLE I. Ground-state energy of the free polaron in polar crystals. In this table, α is the electron-phonon coupling constant, L the Debye cutoff, and S the geometric factor defined in (29). E_0^C and E_0^Z are the polaron ground-state energy as calculated from the continuum approximation and from its corrections, respectively. In the last column, we put the percentage of correction brought by the corrections discussed. The values of the parameters have been taken mostly from Kartheuser (Ref. 17).

Crystal	α	L	S	E_0^C (meV)	E_0^Z (meV)	$100(\Delta E_0/E_0^C)$ (%)
GaAs	0.068	22.12	0.2777	-2.499	-2.417	3.3
CdTe	0.315	21.74	0.2777	-6.561	-6.342	3.4
AgBr	1.56	17.55	0.3206	-26.63	-25.48	4.3
AgCl	1.94	13.37	0.3206	-44.66	-42.15	5.6
TiCl	2.56	19.45	0.5554	-52.58	-49.88	5.1
KCl	3.44	9.05	0.3206	-91.99	-84.42	8.2
RbCl	3.81	9.44	0.3206	-85.04	-78.33	7.9
NaCl ^a	4.86	5.94	0.3206	-163.1	-143.0	12.3
LiF ^a	5.13	5.31	0.3206	-424.6	-366.5	13.7

^aFor these crystals, the band mass being unknown, the bare mass has been used.

approximation never exceed 14% (the largest correction is 13.7% for LiF and it has been calculated using the bare mass). Also, L is always larger than 5, while α is always smaller than 5.2. As a result, real crystals always satisfy to the condition $L \gg \beta$. In fact, for a free polaron, β minimizes to zero for all the crystals studied above.

As a conclusion, the corrections to the continuum approximation for the ground-state energy of the polaron are seen to be relatively small for the polar crystals described above. They never exceed 14%. However, their effect on β_{\min} , a parameter characterizing the internal structure of the polaron, is much more important. Also, we have seen that these crystals are all in the regime with $L \gg \beta$. This means that the electronic recoil correlations are not eliminated by the cutoff. Consequently, in these crystals, particularly those with the strongest electron-phonon coupling constants, polarons with internal structure can exist, even in the framework of a discrete formulation.

VI. CONCLUSION

In this paper, we have investigated how corrections to the continuum approximation of the Fröhlich Hamiltonian describing the dielectric polaron affects the properties of its ground-state energy. These corrections include a Debye cutoff (of wave vector L) and a renormalization of the electron-phonon interaction coming from corrections to the effective-mass approximation. The starting point has been the small-polaron Hamiltonian of Emin,⁷ with an arbitrary electron-phonon interaction. This Hamiltonian has then been formulated in the kq representation of Zak.⁵ The resulting Hamiltonian is equivalent to the small-polaron Hamiltonian of Emin if a short-range interaction is chosen. Also, the Fröhlich Hamiltonian can be derived from it if an expansion for a slowly varying potential is done, using the continuum limit as a starting point. The resulting Hamiltonian has the same form as the Fröhlich Hamiltonian, but with the summation over the phonon wave vectors limited to the first Brillouin zone and the electron-phonon interaction potential V_l renormalized to $V_l(1-a^2l^2)$, a being a constant of the order of the atomic radius. If the continuum limit is taken ($a \rightarrow 0$ and $L \rightarrow \infty$), it tends towards the usual Fröhlich Hamiltonian.

From this new Hamiltonian, the ground-state energy of the polaron has been calculated, using second-order perturbation theory which is valid for small electron-phonon coupling and the Fock approximation which gives an upper bound to the ground-state energy for any strength of coupling. We find that two limits are important. First, in weak coupling and also in strong coupling when α is not too large, L , the cutoff wave number, is much larger than β . In this case, the continuum polaron behavior is preserved with corrections proportional to α/L reducing the self-energy of the polaron. Second, in strong coupling and when $L \ll \beta$, the corrections are more important and the strong-coupling behavior in α^2 is destroyed. However, for large polarons in existing polar

crystals, L is always larger than β and only small corrections to the continuum limit are predicted. The largest value of these corrections for the ground-state energy is 13.7% in the case of LiF.

Recently, cyclotron resonance was done on both silver bromide and chloride.¹⁸ In that experiment, a beautiful agreement concerning the dependence of the cyclotron mass on the magnetic field was found with the path-integral theory based on the continuum approximation. Unfortunately, for the silver halides, the corrections to the continuum approximation are not large enough to be seen. The error for the ground-state energy is estimated to be of the order of 5% (see above). This experiment measures the difference in energy between the ground-state energy of the polaron in a magnetic field and its first Landau excited state. Because the radius of the Landau orbit is much larger than the lattice spacing, even for the largest magnetic field that was used, the corrections to the continuum approximation for the first two Landau levels are expected to be also of the order of 5%. The curvature of the dependence of the effective mass on the magnetic field is only slightly affected by these corrections, even if the energies themselves can be shifted substantially. This conclusion is consistent with the previous discussion: the corrections to the continuum approximation of the free polaron are small for real crystals. They can become important in high fields only if the localization due to these fields is important enough to be smaller than a unit cell. It is not the case for the above experiment: the magnetic field is not high enough.

In the previous sections, we have considered the effects of the corrections to the effective-mass approximation in the Fröhlich Hamiltonian. These corrections have been calculated in the continuum limit. The results that have been obtained are thus applicable to large polarons. Also, a Debye cutoff has been included in the phonon wave vectors. This takes account of the discrete character of the lattice. There is another point that has not been treated here: we have used in the present calculations the electron-phonon interaction potential derived by Fröhlich¹² in the continuum approximation. This is evident from the use of the dielectric constants to describe the lattice polarization. This is correct as far as we consider a long-range potential as it is the case for a dielectric polaron in a polar crystal: this potential is in l^{-1} and is more important near $l=0$ (for long wavelengths). However, if a polaron with a radius of the order of a lattice parameter is considered, corrections to this potential for interactions with nearest neighbors have to be considered. One would then speak of a polaron in a regime intermediate between large and small polarons.

We have seen that the corrections to the continuum approximation for the ground-state energy, in the large-polaron limit, are rather small in the case of existing polar crystals. These corrections are expected to be larger for a polaron in a large external field (polaron bound to a defect or in a magnetic field). It is the case because these fields have the effect to localize the polaron wave function. On the other hand, they are expected to be smaller in the case of excited state, since the wave function is then more extended. They are expected to be larger for

surface or interface polarons, again because of a localization of the wave function. Also of interest is the case of intermediate polarons: polarons in a configuration for which neither the small polaron nor the large polaron is valid, as is the case in the perovskites.^{3,4} These points will be treated in future publications.

ACKNOWLEDGMENTS

This research has been supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and by Le Ministère de l'Éducation du Québec [le Fonds Pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR)].

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