Corrections to the continuum approximation for the free and bound polarons: The first-relaxed-excited-state energy

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Corrections to the continuum approximation are calculated for the first-relaxed-excited-state energy of the free and bound large polarons. Two types of corrections are considered. First, a Debye cutoff L is made to eliminate phonons with wavelengths smaller than the unit cell. In addition, corrections to the effective-mass approximation are obtained up to second order in a parameter that measures the unit-cell dimension relative to the polaron quantum radius. With use of the Green's-function formalism of Matz and Burkey, an estimate of the first-relaxed-excited-state energy is obtained in the Fock approximation. A Gaussian variational spectrum (parametrized by β) is used in order to approximate the polaron wave function. In weak coupling, the corrections are found to be positive and small; they decrease the self-energy of the polaron as well as its binding energy to the defect. In strong coupling, the corrections become larger and two limits are interesting: $L \gg \beta$ and $L \ll \beta$, with polaron radius larger or smaller than the dimension of the unit cell, respectively. In the first case, the corrections remain small and have the same form as in the weak-coupling limit. In the large-β limit, however, the continuum approximation is no longer adequate and the corrections indicate that another approach should be used. Our numerical calculations confirm these analytic asymptotic results. Nevertheless, for real polar crystals, the Fröhlich Hamiltonian is quite good for evaluating the first-relaxed-excited-state energy. The corrections are much smaller than those obtained for the ground-state energy.

I. INTRODUCTION

The presence of an electron in a polar crystal induces a deformation of the lattice in its neighborhood. This distortion forms a potential well in which the electron is trapped for those crystals having strong electron-phonon interaction. The polaron (the electron with its associated lattice distortion) has an internal structure when the potential well is deep enough to sustain at least one excited state.[1] When an infrared transition from the ground state to the first excited state occurs, the lattice distortion stays in the polaron ground-state configuration, the lattice relaxation being too slow. This is a so-called Franck-Condon transition. After the transition, the crystal relaxes to a new configuration to accomodate the electron in the first excited state. This leads to a relaxed excited state.[1]

Calculations of the first-relaxed-excited-state energy of the free polaron have been made in the strong-coupling limit using the adiabatic approximation and canonical transformations.[2,3,4] The Feynman-Hellwarth-Iddings-Platzman (FHIP) approximation[5] and Green's functions[6] have also been used and are valid for all coupling strengths for which such an excited state exists. All these calculations were performed in the continuum approximation. The latter consists in treating the crystal as a continuous deformable medium, the band structure at low energy being approximated by a quadratic isotropic energy characterized by an effective mass and the individual charges being approximated by dielectric constants.

When a charged defect is added to the system, the polaron may become bound to it. In that case the electron "sees" a potential well which is deeper, because the charge of the defect also induces a distortion of the lattice. Calculations of the first-relaxed-excited-state energy of the bound polaron have been made in weak electron-phonon coupling, using a variational approach[7] and perturbation theory.[8,9] In strong coupling, the adiabatic approximation has been used.[10] Finally, a unitary transformation approach[11] and a Green's-function approach[12] have been developed which are valid for any coupling strength. All these calculations were also performed in the continuum approximation.

Recently, corrections to the continuum approximation for the ground-state energy of the free polaron[13] and of the bound polaron[14] have been considered. These corrections include a Debye cutoff to eliminate phonons with wavelength smaller than the unit cell. They also include corrections to the effective-mass approximation up to order a^2, a being a parameter that measures the unit-cell dimension relative to the polaron quantum radius. The corrections were found to be more important in the case of the ground-state energy of the bound polaron than for the free polaron since the wave function is more localized in that case and since the screening of the defect by phonons is strongly modified if the continuum approximation is relaxed. These corrections are expected to be smaller for an excited state since the extent of the wave function is larger. In this paper we present calculations of the first-relaxed-excited-state energies of the free and of the bound polarons, including the same type of corrections as for the ground-state energy. They are calculated in the

Fock approximation using the Green's-function formalism of Matz and Burkey[15] which is valid for all coupling strengths, the Gaussian-model spectrum being used as variational spectrum.

The organization of the paper is as follows: In Sec II, analytical results for the first-relaxed-excited-state energy of the free polaron are obtained, including asymptotic limits. Section III is devoted to the analytical results for the first-relaxed-excited-state energy of the bound polaron. In Sec. IV, numerical results are presented for both cases. The corrections for chosen polar crystals are also given. The last section consists in a discussion of the results and in our conclusion relative to the validity of the continuum approximation for the first-relaxed-excited-state energy of the large polaron.

II. THE FREE POLARON

In this section, analytical expressions for the first-relaxed-excited-state energy of the free polaron are presented. They include corrections to the continuum approximation. Our starting point is the free-polaron Hamiltonian, presented below, with these corrections included. It has been derived in a previous paper,[13] in the tight-binding approximation, for a cubic structure with inversion symmetry. It is obtained using the kq representation of Zak[16] and includes two types of correction to the continuum approximation. First, a spherical Debye cutoff, $L=\pi/a^*$, is imposed to eliminate phonons with wavelength smaller than the lattice parameter a^*. Secondly, corrections to the effective-mass approximation (that we called Zak corrections) are included, up to second order in a parameter a that measures the unit-cell dimension relative to the polaron quantum radius. That Hamiltonian, written in dimensionless units ($2m^*=\hbar\omega_0=\hbar=1$) is given by the following expression:

$$H=\nabla_{\mathbf{r}}^2+\sum_{|l|\le L} b_l^\dagger b_l+\sum_{|l|\le L}(B_l e^{il\cdot\mathbf{r}}b_l+B_l^* e^{-il\cdot\mathbf{r}}b_l^\dagger)\ , \tag{1}$$

where

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

$$\alpha=\frac{e^2}{2\hbar\omega_0\tau_0}(\epsilon_\infty^{-1}-\epsilon_0^{-1})\ , \tag{3}$$

$$\tau_0=\left[\frac{\hbar}{2m^*\omega_0}\right]^{1/2} \tag{4}$$

and

$$a^2=\frac{\langle r^2\rangle}{6}\ . \tag{5}$$

In these equations, $\mathbf{r}$ and m^* are, respectively, the position and the effective band mass of the electron, and ω_0 is the long-wavelength longitudinal-optical- (LO-) phonon frequency. $b_l^\dagger$ and b_l are the second quantization operators for phonons of wave vector l. α represents the electron-phonon coupling constant and τ_0 the polaron quantum radius which is the natural unit of length in the problem. ϵ_0 and ϵ_∞ are the static and the high-frequency dielectric constants, respectively, and Ω stands for the system volume. The parameter a is the root mean square of the electron-orbit radius for the atomic level leading to the conduction band (divided by $\sqrt{6}$) when the tight-binding approximation is made.

From this Hamiltonian, an upper bound to the ground-state energy was previously calculated[13] using the Green's-function formalism of Matz and Burkey.[15] This approximation, in the continuum limit, leads to a transition of the free polaron to a self-trapped polaron for $\alpha\approx 6$. This is usually considered as an artifact of the approximation.[17] However, for the ground-state energy, the numerical values of the energies and their asymptotic behavior correspond well to those of other methods. Here, the same approach is used to obtain an estimate of the first-relaxed-excited-state energy E_1 at zero temperature. This method has been previously applied to the calculation of the first-relaxed-excited-state energy (E_1) of the free polaron in the continuum limit.[6] It allows one to obtain an estimate of E_1 for any value of α for which such a state exists. It cannot be shown, however, that the energy obtained is an upper bound to E_1, even if it coincides with variational results in strong coupling. Also, as discussed in Ref. 6, these energies are obtained for an infinite-lifetime level. This approximation is good in strong coupling[1] but becomes weaker for lower values of α ($\alpha<3$), when the internal structure of the polaron just appears. Using this formalism, we write the energy E_1 in a form valid for all electron-phonon coupling strengths (see Ref. 6):

$$E_1=-\int\phi_1^*(\mathbf{r})\nabla_{\mathbf{r}}^2\phi_1(\mathbf{r})d^3r+\sum_{\substack{l,n\\(|l|<L)}}\int d^3r\int d^3r_1\,|B_l|^2\exp[il\cdot(\mathbf{r}-\mathbf{r}_1)]\frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}_1)}{\varepsilon_1-1-\varepsilon_n}\phi_1^*(\mathbf{r})\phi_1(\mathbf{r}_1)\ , \tag{6}$$

where the $\{\phi_n(\mathbf{r})\}$ form a complete variational model spectrum, the ε_n's being its eigenvalues. Here the Gaussian-model spectrum will be used with variational parameter β. The model Hamiltonian is thus

$$H_m=\hat{p}^2+\beta^4r^2\ . \tag{7}$$

The first relaxed excited state will be approximated by a $2p$ state and ϕ_1 and ε_1 will refer, in Eq. (6), to a Gaussian $2p$ state. A similar approach was previously used in the case of the continuum approximation.[6] In the present case, in contrast to the procedure followed in Ref. 6, the summation on l is limited to $|l|<L$ and the electron-

phonon interaction potential V_l is renormalized to B_l. Note the presence of a singularity in Eq. (6) when $\varepsilon_1-1=\varepsilon_0$ (when $2\beta^2=1$). This singularity is present because the first relaxed excited state was assumed of infinite lifetime. In fact it is the case for asymptotic strong coupling. In intermediate coupling, the first relaxed excited state can have a short lifetime and its energy is then less accurate.[6] In weak coupling, no minimum is obtained with a negative energy; a relaxed excited state then does not exist.

Equation (6) with the Gaussian spectrum leads to

$$E_{2p}=\tfrac{5}{2}\beta^2+T_1^{2p}+T_2^{2p}\ , \tag{8}$$

where

$$T_1^{2p}=-\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha\beta}{6}\int_0^\infty e^{(2\beta^2-1)t}\left[\frac{6-5z^2}{z}\phi(yz)-\phi(y)\right]dt+\frac{\alpha L}{3\pi}\int_0^\infty e^{(2\beta^2-1)t}(z^2e^{-y^2z^2}-e^{-y^2})dt$$
$$+\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha\beta}{6(2\beta^2-1)}\left[\phi(y)-\frac{2}{\sqrt{\pi}}ye^{-y^2}\right], \tag{9}$$

$$T_2^{2p}=\left[\frac{2}{\pi}\right]^{1/2}a^2\alpha\beta^3\int_0^\infty e^{(2\beta^2-1)t}\left[\frac{2-z^2}{z^3}\phi(yz)-\phi(y)\right]dt$$
$$-\frac{2}{\pi}a^2\alpha\beta^2L\int_0^\infty e^{(2\beta^2-1)t}\left[\left[\frac{2-z^2}{z^2}+\tfrac{2}{3}y^2z^2\right]e^{-y^2z^2}-(1+\tfrac{2}{3}y^2)e^{-y^2}\right]dt$$
$$-\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha a^2\beta^3}{(2\beta^2-1)}\left[\phi(y)-\frac{2}{\sqrt{\pi}}y(1+\tfrac{2}{3}y^2)e^{-y^2}\right], \tag{10}$$

with

$$z=(1-e^{-2\beta^2t})^{1/2} \tag{11}$$

and

$$y=\frac{L}{\sqrt{2}\beta}\ . \tag{12}$$

This energy (E_{2p}) has to be minimized with respect to β. In these equations, $\phi(x)$ is the error function. In Eq. (8), the first term is the kinetic energy of the electron. T_1^{2p} corresponds to the Fock term and includes the Debye cutoff correction. T_2^{2p} represents the Zak correction, in a^2, associated with the Fock approximation.

When $a=0$ and $L\to\infty$, Eqs. (8)–(10) reduce to

$$E_{2p}\sim\frac{5\beta^2}{2}-\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha\beta}{6}\int_0^\infty e^{(2\beta^2-1)t}\left[\frac{6-5z^2}{z}-1\right]dt+\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha\beta}{6}\frac{1}{2\beta^2-1} \tag{13}$$

which is the result obtained in Ref. 6 in the continuum approximation.

For asymptotic limits the minimization of Eq. (8) can be effected analytically. First, when $\alpha\to0$, $\beta\to0$ and the resulting energy is in fact the ground-state energy in weak coupling:

$$E_0\sim-\alpha+\frac{2\alpha}{\pi L}+\frac{4a^2\alpha L}{\pi}\ . \tag{14}$$

This result is obtained for large values of L. No other minimum of negative energy can be found for $\beta>1/\sqrt{2}$. As a consequence, no excited state exists in weak coupling.

When α is large, the energy is minimized for a large value of β. If $\beta\ll L$, the minimization gives

$$\beta=\frac{11}{60}\left[\frac{2}{\pi}\right]^{1/2}\alpha-\frac{121}{1200}\left[\frac{2}{\pi}\right]^{1/2}\frac{a^2\alpha^3}{\pi} \tag{15}$$

and the first-relaxed-excited-state energy reduces to

$$E_{2p}\sim\frac{121\alpha^2}{720\pi}+\frac{2\alpha}{\pi L}+\frac{4a^2\alpha L}{\pi}\ . \tag{16}$$

The first term is the continuum-approximation result and it can be found from the adiabatic approximation.[6] The second term is the Debye-cutoff correction and the last term is the Zak correction. Both corrections are positive; they reduce the self-energy of the polaron. They are asymptotically the same, to that order, as those found for the ground state (see Ref. 13) in strong coupling as well as in weak coupling. Note that these corrections are small and the strong-coupling continuum polaron behavior in α^2 is the dominant contribution. For $\beta\approx L$, the corrections for the first-relaxed-excited-state energy would be smaller than those of the ground state, as will be seen in the next section.

When α is large but $\beta\gg L$, Eq. (8) minimizes to

$$\beta^2=\left[\frac{2\alpha L^3}{9\pi}\left[1-\frac{6a^2L^2}{5}\right]\right]^{1/2} \tag{17}$$

and the energy is

$$E_{2p}\sim-\frac{2\alpha L}{\pi}+\frac{4\alpha a^2L^3}{3\pi}+5\beta^2=E_0+\beta^2\ . \tag{18}$$

This result is very similar to that for the ground-state energy. We obtain here the same value of β and the energy differs only by an additional β^2 term. As a consequence, the ground-state and the first-relaxed-excited-state energies approach each other in this regime (as opposed to the $L\gg\beta$ limit), their separation in energy being proportional to $\sqrt{\alpha}$. The quadratic dependence of the energy on α disappears and is replaced by a linear dependence. This indicates that the continuum approximation is not applicable in these conditions. In fact, in strong coupling, $1/\beta$ is proportional to the polaron wave-function extension and $\beta\gg L$ means that the polaron is localized in a region smaller than the unit cell. The small-polaron theory constitutes a better approach in this limit.

III. THE BOUND POLARON

In this section, analytical results for the first-relaxed-excited-state energy of the bound polaron are presented. Our starting point is the bound-polaron Hamiltonian, presented below, including corrections to the continuum approximation, as obtained in a previous paper.[14] It contains terms describing an electron of charge $-e$, a defect of effective charge qe, and a phonon field, all interacting together. The static distortion of the lattice induced by the defect is taken into account by a unitary transformation which is an adaptation of that of Platzman.[18] This Hamiltonian, written in dimensionless units ($2m^*=\hbar\omega_0=\hbar=1$), is the following (it has been obtained under the same conditions as in Sec. II):

$$H_B=H_0+H_I\ , \tag{19}$$

where

$$H_0=-\nabla_{\mathbf{r}}^2+\sum_{\substack{l\\|l|<L}}b_l^\dagger b_l-\frac{2q}{r}\left[\mathcal{R}_\infty^{1/2}-\frac{2\alpha\,\mathrm{Si}(Lr)}{\pi}\right]+8\pi qa^2[\mathcal{R}_\infty^{1/2}\delta(\mathbf{r})-\alpha\Delta_L(\mathbf{r})]\ , \tag{20}$$

$$H_I=\sum_{\substack{l\\|l|<L}}(B_l e^{il\cdot\mathbf{r}}b_l+B_l^* e^{-il\cdot\mathbf{r}}b_l^\dagger)\ , \tag{21}$$

and

$$\mathcal{R}_\infty^{1/2}=\frac{e^2}{2\hbar\omega_0\tau_0\epsilon_\infty}\ , \tag{22}$$

$$\Delta_L(\mathbf{r})=\frac{1}{2\pi^2}\left[\frac{\sin(Lr)-Lr\cos(Lr)}{r^3}\right]\ . \tag{23}$$

Note that $\lim_{L\to\infty}\Delta_L(\mathbf{r})=\delta(\mathbf{r})$.[19] In these equations $\mathcal{R}_\infty$ is the dimensionless Rydberg without screening of the defect and $\mathrm{Si}(x)$ denotes the sine integral. We also define $\mathcal{R}_0$: the Rydberg of the defect as screened by the electron-phonon interaction. It is the same as $\mathcal{R}_\infty$, calculated with ϵ_0 instead of ϵ_∞. The first two terms of H_0 [Eq. (20)] are the usual free-particle energies. The third term represents the Coulombic potential energy of the electron in the field of the screened defect, the Debye cutoff reducing the screening induced by the LO phonons. The last term in Eq. (20) constitutes the corrections to the effective-mass approximation associated with the screened Coulombic energy. H_I is the electron-phonon interaction term including the two types of corrections. As stated in Ref. 14, this Hamiltonian differs significantly from that of Platzman,[18] principally due to the cutoff which reduces the screening of the defect.

From the Hamiltonian (19) an estimate of the first-relaxed-excited-state energy can be obtained using the Green's-function formalism of Matz and Burkey in the Fock approximation.[12] Note that for the bound polaron, in contrast to the free-polaron case, no transition occurs to a self-trapped state [discussion preceding Eq. (6)]. The resulting energy for the bound polaron in a $2p$ state is

$$E_{2p}=-\int\phi_{2p}^*(\mathbf{r})H_0\phi_{2p}(\mathbf{r})d^3r+\sum_{\substack{l,n\\(|l|<L)}}\int d^3r\int d^3r_1\,|B_l|^2\exp[il\cdot(\mathbf{r}-\mathbf{r}_1)]\frac{\phi_n(\mathbf{r})\phi_n^*(\mathbf{r}_1)}{\varepsilon_{2p}-1-\varepsilon_n}\phi_{2p}^*(\mathbf{r})\phi_{2p}(\mathbf{r}_1)\ . \tag{24}$$

This expression is similar to that obtained for the free polaron, Eq. (6). The only difference is the presence, in the first term of H_0 (instead of $-\nabla_{\mathbf{r}}^2$) which includes the interaction with the defect. It is also similar to the expression obtained for the excited states of the bound polaron in Ref. 12, the difference being the corrections to the continuum approximation in the present case. We will use the same Gaussian variational model spectrum for the bound polaron as for the free polaron. This is not the best spectrum to use when $\alpha^2\ll\mathcal{R}_0$, but in the case of $\alpha^2\gg\mathcal{R}_0$ the Gaussian spectrum gives the lowest energies.

Using a $2p$ excited state of the model spectrum, we obtain the following energy for the bound polaron:

$$E_{2p}=\frac{5\beta^2}{2}-\frac{8q\beta}{3\sqrt{\pi}}\left[\mathcal{R}_\infty^{1/2}-\alpha\phi\left[\frac{L}{2\beta}\right]\right]+\frac{4q\alpha L}{3\pi}e^{-L^2/4\beta^2}(1-a^2L^2)+T_1^{2p}+T_2^{2p}\ . \tag{25}$$

This expression has to be minimized with respect to β. The first term represents the kinetic energy of the electron. The second and the third terms correspond to the Coulomb energy of the electron on the defect, including the screening and the associated corrections. The last two terms are defined by Eqs. (9) and (10) and result from the Fock approximation with its corrections as ex-

plained in Sec. II. Note that in Eq. (25), as in Eqs. (8)–(10), a singularity is present at $\beta=1/\sqrt{2}$. In the present case, a minimum for $\beta<1/\sqrt{2}$ indicates an excited state of the defect while for $\beta>1/\sqrt{2}$ an excited state of the polaron-defect complex is obtained.[12]

From Eq. (25) the continuum-approximation limit is obtained by imposing $a=0$ and $L\to\infty$:

$$E_{2p}\sim\frac{5\beta^2}{2}-\frac{8q\beta\mathcal{R}_0^{1/2}}{3\sqrt{\pi}}+\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha\beta}{6}\frac{1}{2\beta^2-1}-\left[\frac{2}{\pi}\right]^{1/2}\frac{\alpha\beta}{6}\int_0^\infty e^{(2\beta^2-1)t}\left[\frac{6-5z^2}{z}-1\right]dt\ , \tag{26}$$

where

$$\mathcal{R}_0^{1/2}=\frac{e^2}{2\hbar\omega_0\tau_0\epsilon_0}\ . \tag{27}$$

This is the result previously obtained in Ref. 12 in the continuum approximation. Note that in this reference the Rydberg is defined using the static dielectric constant ($\mathcal{R}_0$ is the Rydberg of a fully screened defect). The most important difference between Eq. (25), which contains the corrections to the continuum approximation, and Eq. (26), which does not include them, is the reduction of the screening of the defect by polar LO phonons resulting from the Debye cutoff.

The minimization of Eq. (25) can be effected analytically for asymptotic limits. When α and $\mathcal{R}_\infty$ are small, the variational parameter β is small.

$$\beta=\frac{8q\mathcal{R}_0^{1/2}}{15\sqrt{\pi}(1-\alpha_m/6)}\ . \tag{28}$$

and the resulting energy is

$$E_{2p}\sim-\alpha_E-\frac{32q^2\mathcal{R}_0}{45\pi(1-\alpha_m/6)}\ , \tag{29}$$

where

$$\alpha_E=\frac{2\alpha}{\pi}\tan^{-1}(L)-\frac{4a^2\alpha}{L}[L-\tan^{-1}(L)] \tag{30}$$

and

$$\alpha_m=\frac{2\alpha}{\pi}\left[\tan^{-1}(L)+\frac{L}{1+L^2}-\frac{2L}{(1+L^2)^2}\right]-\frac{4a^2\alpha}{\pi}\left[3\tan^{-1}(L)-\frac{5L}{1+L^2}+\frac{2L}{(1+L^2)^2}\right]\ . \tag{31}$$

This expression represents a polaron in its ground state, with a self-energy of $-\alpha_E$, and an effective mass, $m^{**}=m^*/(1-\alpha_m/6)$, bound to the defect in its first excited state. The factor $32/45\pi$ in Eq. (29) comes from the use of the Gaussian spectrum instead of the hydrogenic spectrum which would have given $\frac{1}{4}$. α_E and α_m are the same as those obtained for the free polaron.[13]

In the limit of strong coupling, when α or $\mathcal{R}_\infty$ is large, the energy is minimum for a large value of β and two cases have to be considered: $L\gg\beta$ and $L\ll\beta$. When $L\gg\beta$, E_{2p} is minimum for

$$\beta=\frac{11}{60}\left[\frac{2}{\pi}\right]^{1/2}\left[\alpha+\frac{16\sqrt{2}q\mathcal{R}_0^{1/2}}{11}\right] \tag{32}$$

and we obtain

$$E_{2p}=-\frac{121\xi^2}{720\pi}+\frac{1331a^2\alpha\xi^3}{21600\pi^2}+\frac{2\alpha}{\pi L}+\frac{4a^2\alpha L}{\pi}\ , \tag{33}$$

where

$$\xi=\alpha+\frac{16\sqrt{2}q\mathcal{R}_0^{1/2}}{11}\ . \tag{34}$$

Without the corrections, this expression is identical to that found by Lépine.[12] The last two terms of Eq. (33) are the same as those found for the ground-state energy of the bound polaron and for the free polaron. For $\alpha\gg\mathcal{R}_0$, Eq. (33) reduces to

$$E_{2p}\sim-\frac{121\alpha^2}{720\pi}-\frac{22\sqrt{2}q\alpha\mathcal{R}_0^{1/2}}{45\pi}+\frac{2\alpha}{\pi L}+\frac{4a^2\alpha L}{\pi}+\frac{1331a^2\alpha^4}{21\,600\pi^2}\ . \tag{35}$$

The first two terms of Eq. (35) are the usual strong-coupling terms for large α in the continuum approximation.[12] The three other terms are the corrections to the continuum approximation. These are all positive; they reduce the self-energy of the polaron and its binding energy to the defect. For $\alpha\ll\mathcal{R}_0$, Eq. (33) gives

$$E_{2p}\sim-\frac{32q^2\mathcal{R}_0}{45\pi}-\frac{22\sqrt{2}q\alpha\mathcal{R}_0^{1/2}}{45\pi}+\frac{256\sqrt{2}q^3a^2\alpha\mathcal{R}_0^{3/2}}{675\pi^2}\ . \tag{36}$$

The first two terms are the usual strong-coupling terms for large $\mathcal{R}_0$ with Gaussian wave function in the continuum approximation.[12] The last term is the leading correction to the continuum approximation. No polaron effective-mass behavior is obtained.

The limit $L\ll\beta$ corresponds to the case where the polaron radius [$\sim 2/(\sqrt{\pi}\beta)$ in strong coupling] is much smaller than the unit-cell dimension (π/L). In this case, we expect our approach to the effective-mass correction (the Zak correction) to be inapplicable.[13] Nevertheless, the Debye-cutoff correction can still be applied and the minimization gives

$$\beta=\frac{8q\mathcal{R}_\infty^{1/2}}{15\sqrt{\pi}} \tag{37}$$

and

$$E_{2p}\sim-\frac{32q^2\mathcal{R}_\infty}{45\pi}+\frac{2\alpha L}{\pi}(2q-1)-\frac{125\alpha L^3}{64q^2\mathcal{R}_\infty}(q-1)\ . \tag{38}$$

The corrections are now very important. The first term corresponds to the Coulomb potential energy of an electron in a $2p$ state of an unscreened defect (calculated with a Gaussian wave function); it involves the high-frequency Rydberg $\mathcal{R}_\infty$. This indicates that the Debye cutoff has significantly reduced the screening of the defect. Also, the polaron effective mass does not appear in this expression. The second term gives the remaining reduced screening of the defect and of the electron charges. It is the same as that found for the ground-state energy E_0 of the bound polaron in the same limit.[14] As a consequence of the reduction of the screening when L decreases, the binding energy to the defect becomes larger. This has the effect of increasing the difference in energy between E_0 and E_{2p}, in contrast to the case of the free polaron in the same limit. In conclusion, when the cutoff is important ($L \ll \beta$), the polaron bound to a defect looks very much as an electron bound to an unscreened defect. The effects of the electron-phonon interaction are then rather small, the short-wavelength phonons being absent. However, as in this case corrections to the effective-mass approximation should be important, a small-polaron approach has to be used instead of a band approach. The continuum approximation is no longer a good starting point.

IV. NUMERICAL RESULTS

In this section the first-relaxed-excited-state energies calculated numerically are presented. They are obtained from Eq. (8) for the free polaron and from Eq. (25) for the bound polaron. To take into account the Zak correction, we approximate the parameter a, which is defined in Eq. (5) by

$$a = \frac{S}{L} , \tag{39}$$

where S is a geometric factor depending on the crystal structure.[13] It is calculated by assuming ionic radii equal to half the nearest-neighbor distance. In what follows we present the energy curves obtained for the free and the bound polaron. We also discuss application of our results to polar crystals.

We present, in Figs. 1 and 2, the ground-state energy E_0 and the first-relaxed-excited-state energy E_{2p} of the free polaron, first, as a function of the electron-phonon coupling constant α, and, second, as a function of the Debye cutoff L. In Fig. 1(a), these energies are presented for three levels of approximation: E^C gives the continuum-approximation results, E^D includes the Debye-cutoff correction calculated for $L=10$, and E^Z takes into account both the Debye-cutoff correction, and the Zak correction (correction to the effective-mass approximation) calculated for $L=10$ and $S=0.2777$ (zinc-blende structure). We observe that the corrections to the continuum approximation for the first-relaxed-excited-state energy are smaller than those for the ground-state energy. This is expected since the first-excited-state wave function is more delocalized than the ground-state wave function. Also the corrections are positive; they decrease the self-energy of the polaron. This behavior can be understood because the cutoff reduces the number of short-wavelength phonons interacting with the electron.

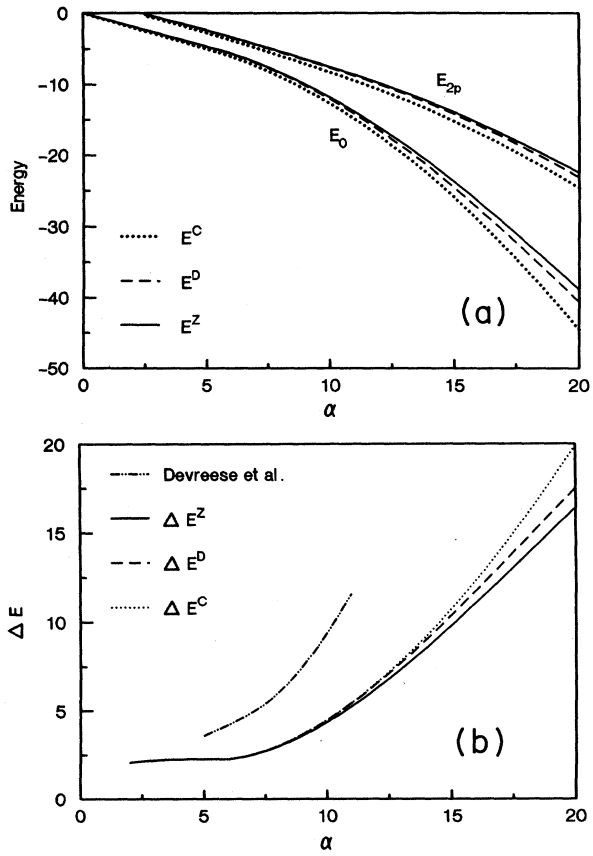

FIG. 1. (a) Ground-state energy E_0 and first-relaxed-excited-state energy E_{2p} of the free polaron as a function of the electron-phonon coupling constant α. E^C is the continuum-approximation result, E^D is calculated with a Debye cutoff $L=10$, and E^Z includes both the Debye-cutoff ($L=10$) and the Zak correction calculated with $S=0.2777$. (b) Transition energy, $\Delta E = E_{2p} - E_0$, as a function of α. ΔE^C is calculated in the continuum approximation, ΔE^D includes the effect of the Debye cutoff with $L=10$, and ΔE^Z takes into account both the Debye-cutoff and the Zak correction obtained for $L=10$ and $S=0.2777$. The results of Devreese *et al.* (Ref. 20) are also presented.

In Fig. 1(b), we have plotted the transition energies ($\Delta E = E_{2p} - E_0$) as a function of α for the same three levels of approximation. Also we have plotted on this graph this transition energy as obtained from the Feynman-Hellworth-Iddings-Platzman (FHIP) approach.[5,20] In the asymptotic limit of large α's, our approach and that of FHIP are expected to converge to the same value. However, for the intermediate α's (between 5 and 11) for which the FHIP energies are available, our results for ΔE are much lower than those coming from the FHIP approximation. This discrepancy is difficult to evaluate, since in both cases, the energies themselves are not variational even if they have been obtained from variational methods and since our results are less reliable for smaller values of α. Note, however, that in this range of α the corrections to the continuum approximation are very

small, much smaller than the difference between our results and those of the FHIP approach.

The effect of the Debye cutoff on the energies E^D and E^Z is presented in Fig. 2. These are calculated for $\alpha=20$ and $S=0.2777$. The continuum approximation corresponds to the limit $L\to\infty$. For this strong-coupling case, the corrections to the continuum approximation are important for L smaller than 10. When L decreases, the corrections increase rapidly. The decrease of L also induces a reduction of the difference between the ground-state and the first-relaxed-excited-state energy. This comes from a reduction of the electron-recoil correlation due to the cutoff which destroys the strong-coupling behavior in α^2, as can be seen in Eq. (18), which is applicable for small L.

The five other figures describe the behavior of the bound polaron. The ground-state energy E_0, and the first-relaxed-excited-state energy E_{2p}, are plotted as a function of the Debye cutoff L in Fig. 3. E^D is calculated with the Debye-cutoff correction only while E^Z includes, in addition, the Zak correction ($S=0.2777$). These curves are given for $\alpha=1$ and $\mathcal{R}_\infty=2$. The effective charge of the defect q is fixed to be unity. The presence of the defect does not significantly change the behavior of the corrections to the continuum approximation; they are still positive, and small for $L>10$. The excited-state energy is well approximated by its weak-coupling asymptotic limit, Eq. (29). This corresponds to a polaron in its ground state bound to an excited state of the defect. In this case, the screening of the defect by the phonons has for effect the renormalization of $\mathcal{R}_\infty$ to $\mathcal{R}_0$.

In Fig. 4, we plot the same quantities as in Fig. 3, for strong coupling: $\alpha=10$ and $\mathcal{R}_\infty=150$. The arrows indicate the value of L for which $L=2\beta$, β being the value of the variational parameter at the minimum energy. This graph is quite different from the previous figures. In the present case, the corrections are very important for the ground state. They become negative for small L, in contrast to the behavior manifested in the preceding graphs.

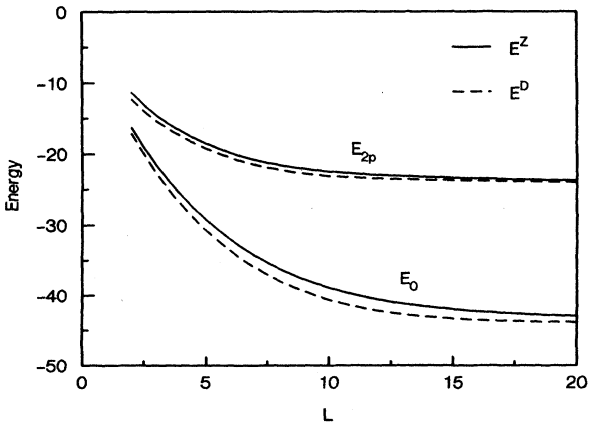

FIG. 2. Ground-state energy E_0 and first-relaxed-excited-state energy E_{2p} of the free polaron as a function of the Debye cutoff L, for $\alpha=20$. E^D is calculated with the Debye cutoff, and E^Z includes both the Debye-cutoff and the Zak correction calculated with $S=0.2777$.

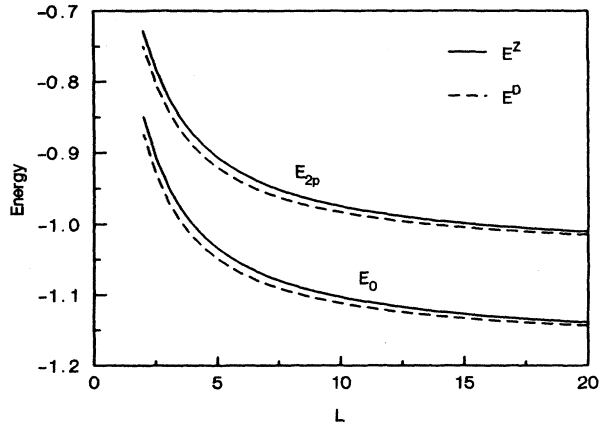

FIG. 3. Ground-state energy E_0 and first-relaxed-excited-state energy E_{2p} of the bound polaron as a function of the Debye cutoff L, for $\alpha=1$, $\mathcal{R}_\infty=2$, and $q=1$. E^D is the energy calculated with the Debye-cutoff correction alone, and E^Z includes both the Debye-cutoff and the Zak correction calculated with $S=0.2777$.

For the excited state, the same behavior is obtained but the corrections are smaller. Note that for $L<2\beta$, the Zak correction is no longer applicable, since it was assumed small from the start. The curve E^D_{2p}, which takes into account the Debye cutoff only, can be well approximated by the strong-coupling asymptotic result, Eq. (38), for the $L<2\beta$ region, the slope being $2\alpha(2q-1)/\pi$. This region corresponds to the regime where the screening of the defect by the phonons is reduced due to the application of an important Debye cutoff which eliminates phonons with wavelength smaller than the polaron radius. This results in a large increase of the binding energy of the defect. Note that there is a sharp change in slope for the curves E_{2p} at the point indicated by the arrow. At that point, the variational parameter β which minimizes

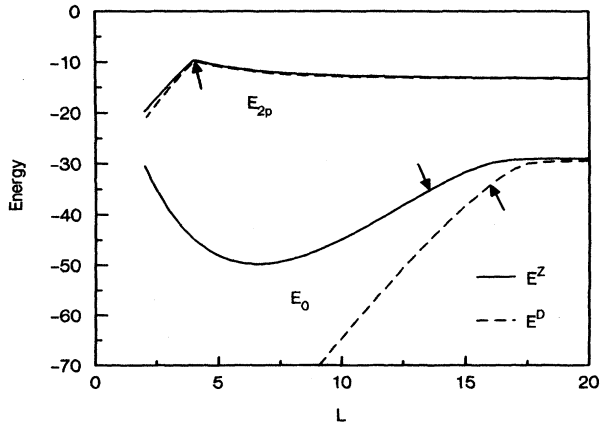

FIG. 4. Ground-state energy E_0 and first-relaxed-excited-state energy E_{2p} of the bound polaron as a function of the Debye cutoff L, for $\alpha=10$, $\mathcal{R}_\infty=150$ and $q=1$. E^D is the energy calculated with the Debye-cutoff correction alone, and E^Z includes both the Debye-cutoff and the Zak correction calculated with $S=0.2777$. The arrows on the curves indicate the values at which $2\beta=L$.

the energy jumps from 1.2 for $L>4$ to 3.6 for $L<4$. This behavior corresponds to an abrupt change in the screening of the defect; for $L\leq 4$, this screening decreases abruptly. The same behavior occurs for E_0^D but the transition is less abrupt and occurs for larger values of L ($L\approx 15$). This figure illustrates clearly the fact that the corrections to the continuum approximation are much smaller for the excited state than for the ground state, the electron wave function being less localized.

In Fig. 5, the ground-state energy and the first-relaxed-excited-state energy of the bound polaron are presented as a function of the effective charge of the defect q. E^C gives the continuum-approximation result, E^D includes the Debye cutoff with $L=10$ and E^Z takes into account the Debye cutoff and the Zak correction calculated with $S=0.2777$. This graph is obtained for $\alpha=1$ and $\mathcal{R}_\infty=2$, an intermediate-coupling situation with a polaron in its ground state bound to a defect in its excited state. The energy E_{2p} is well approximated by Eq. (29). Relatively small corrections are observed in this regime. We note that when the defect disappears ($q=0$), the first-relaxed-excited-state energy collapses to the ground-state energy since, in weak coupling, the polaron has no internal structure.

In Fig. 6, E_0 and E_{2p} are plotted as a function of q, for $\alpha=10$ and $\mathcal{R}_\infty=150$. E^C, E^D, and E^Z have the same meaning as in the preceding figures. The Debye cutoff is calculated with $L=10$, and the Zak correction, with $S=0.2777$. These parameters correspond to strong coupling and the arrows indicate the points for which $L=2\beta$. It is clear from this graph that the corrections to the continuum approximation are much more important for the ground-state energy than for the first-relaxed-excited-state energy. This is related to the larger spatial extension of the first-relaxed-excited-state wave function. As $L>2\beta$ for all values of q on the graph, E_{2p} can be approximated by the strong-coupling $L\gg\beta$ limit: Eq. (33).

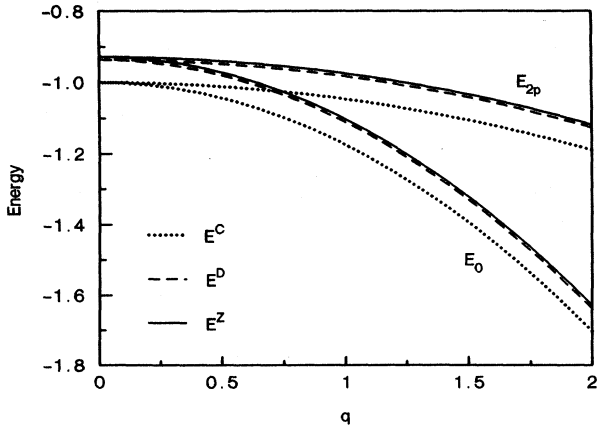

FIG. 5. Ground-state energy E_0 and first-relaxed-excited-state energy E_{2p} of the bound polaron as a function of the effective charge of the defect q, for $\alpha=1$ and $\mathcal{R}_\infty=2$. E^C is the continuum-approximation result, E^D is calculated with a Debye cutoff $L=10$, and E^Z includes both the Debye-cutoff ($L=10$) and the Zak correction calculated with $S=0.2777$.

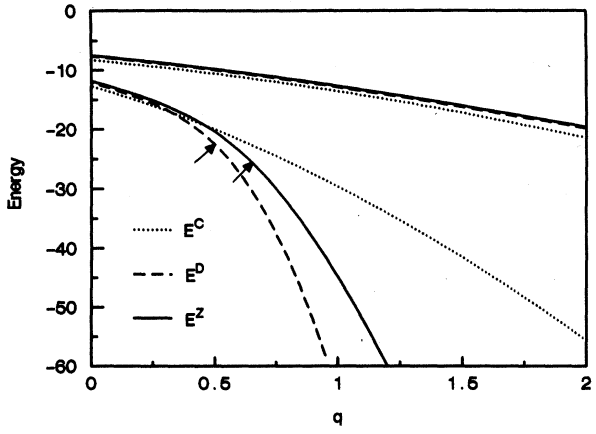

FIG. 6. Ground-state energy E_0 and first-relaxed-excited-state energy E_{2p} of the bound polaron as a function of the effective charge of the defect q, for $\alpha=10$ and $\mathcal{R}_\infty=150$. The three lower curves give E_0 and the three upper curves, which are superimposed, give E_{2p}. E^C is the continuum-approximation result, E^D is calculated with a Debye cutoff $L=10$, and E^Z includes both the Debye-cutoff ($L=10$) and the Zak correction calculated with $S=0.2777$. The arrows on the curves indicate the values at which $2\beta=L$.

For the ground state, the major part of the curves are in the $L<2\beta$ regime.

In Fig. 7, we present the phase diagram of the bound polaron in the $\alpha-\mathcal{R}_0$ plane. It is calculated for $L=5$, and $q=1$, without the Zak correction (the Zak correction has no significant effect on these curves). For parameters in the lower left part of the graph, an effective-mass state of an excited defect is found. In the upper right part of the graph, an excited state of the polaron-defect complex is observed. This is to be compared to the behavior in the continuum approximation which is shown on this graph by a dashed line.[12] The effect of the corrections is to slightly increase the area of the region of existence of the effective-mass state.

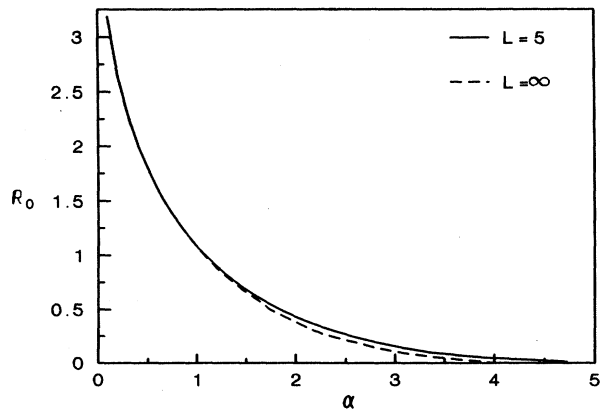

FIG. 7. Phase diagram of the bound polaron in the $\alpha-\mathcal{R}_0$ plane. An effective-mass state exists below the lines. The solid line is calculated using a Debye cutoff with $L=5$, without the Zak correction. The dashed line is obtained without corrections to the continuum approximation.

TABLE I. First-relaxed-excited-state energy of the bound polaron in polar crystals. $\mathcal{R}_\infty$ is the unscreened electron-defect coupling constant. E_{2p}^C, E_{2p}^D, and E_{2p}^Z are the energies calculated in the continuum approximation, using the Debye-cutoff correction and including the Debye-cutoff and Zak corrections, respectively. ΔE_{2p} is the difference $E_{2p}^Z - E_{2p}^C$ and E_0^Z in the ground-state energy obtained with the corrections. These results were calculated mostly using the parameters taken from Kartheuser (Ref. 1, p. 715). We also present E_{expt}, the transition energy ($1s \rightarrow 2p$) obtained experimentally, as well as E_t^{Ad}, the theoretical results for that transition obtained by Adamowski (Ref. 21).

	α	$\mathcal{R}_\infty$	E_{2p}^C (meV)	E_{2p}^D (meV)	E_{2p}^Z (meV)	ΔE_{2p} (meV)	$E_{2p}^Z - E_0^Z$ (cm^{-1})	E_{expt} (cm^{-1})	E_t^{Ad} (cm^{-1})
GaAs	0.068	0.205	−3.745	−3.673	−3.662	0.083	27.57	35[a]	
CdTe	0.316	1.14	−9.412	−9.219	−9.192	0.220	62.71	87[b]	89.5
ZnSe	0.432	2.19	−21.45	−20.89	−20.81	0.64	180.8	158[c]	158
CdS	0.527	1.99	−27.61	−26.67	−26.54	1.07	163.5	196[d]	198
TlCl	2.56	8.74	−53.96	−52.24	−51.26	2.70	27.95		
AgBr	1.56	7.82	−19.62	−18.61	−18.42	1.20	303.5	168[e]	209
AgCl	1.94	11.1	−39.08	−36.94	−36.52	2.56	485.1	272[e]	399
CdF_2	3.19	21.26	−148.6	−135.0	−133.1	15.5	1365	524[f]	669
KCl	3.44	45.6	−175.7	−169.1	−167.4	8.3	2554		
RbCl	3.83	54.4	−170.0	−164.0	−162.4	7.6	2540		
NaCl[g]	4.86	73.4	−318.9	−289.4	−285.1	33.8	5551		
LiF[g]	5.13	44.1	−413.8	−375.8	−365.8	48.0	5240		

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[f]See Ref. 21.
[g]For these crystals, the band mass being unknown, the free-electron mass has been used.

As the asymptotic results are generally not applicable to real crystals, the first-relaxed-excited-state energy of the bound polaron in polar crystals is calculated numerically and presented in Table I. For the first five compounds, the excited state corresponds to the excited state of the defect. For the others, it is a polaron-defect-complex excited state. The three levels of approximation E^C (continuum approximation), E^D (with the Debye-cutoff correction), and E^Z (with the Debye-cutoff and the Zak corrections) are given as well as the energy correction obtained for the different compounds. A comparison to the corrections obtained for the ground-state energy of the bound polaron (see Ref. 14) indicates that they are slightly smaller for the first relaxed excited state than for the ground state for the first seven crystals given in the table. For the remaining crystals, the corrections are small in the present case, in contrast to those of the ground-state energy which are important. The transition energy $E_{2p}^Z - E_0^Z$ is given in the same table and compared to the experimental value when available. We also give this transition energy as calculated by Adamowski.[21] In our case, the agreement is not very good, particularly for AgBr, AgCl, and CdF_2, while it is much better for the calculations of Adamowski, especially for the weak-coupling compounds. The discrepancy can be attributed to one or to several of the following causes: the use of a Gaussian spectrum instead of a Coulombic one (error of the order of +20%), the error on the parameters such as the effective band mass used in the calculation, and certainly the neglect of an important part of the central-cell corrections in the calculation of the ground-state energy, as stated in Ref. 14. Also, for the last seven compounds in the table, the first-relaxed-excited-state energy obtained with our formalism is a polaron-defect-complex excited state, while the experimental value corresponds probably to an excited state of the defect, the lifetime of the latter being much larger. Nevertheless, the agreement is quite good for GaAs, CdTe and CdS if the +20% correction due to the use of a Gaussian spectrum is taken into account. These are crystals for which the coupling to the defect is weak so that the radius of the orbit is large. Central-cell corrections are then negligible.

V. CONCLUSION

The problem of the corrections to the continuum approximation for the first-relaxed-excited-state energy of the free and of the bound polarons is investigated. Two types of corrections to the Fröhlich Hamiltonian are considered: the elimination of short-wavelength phonons with the use of a spherical Debye cutoff, L, and the first corrections to the effective-mass approximation, which we call the Zak correction, calculated using the kq representation of Zak.[16] The Zak correction comes from the expansion of slowly varying electron-phonon and defect potentials as a function of a parameter, a, that measures the unit-cell dimension relative to the polaron quantum radius.

From the resulting Hamiltonians, the first-relaxed-excited-state energies of the free and of the bound polarons are calculated with a Gaussian-model spectrum of variational parameter, β, using the Green's-function for-

malism of Matz and Burkey, in the Fock approximation. This treatment is valid for all coupling strengths and the resulting first-relaxed-excited-state energies reduce to the continuum results when $a \rightarrow 0$ and $L \rightarrow \infty$. Two asymptotical analytical limits are treated: $L \gg \beta$ and $L \ll \beta$, $1/\beta$ being proportional to the radius of the polaron in strong coupling. These limits correspond to a polaron radius larger or smaller than the lattice parameters, respectively.

Consider first the case of the free polaron. In the weak-coupling limit there is no excited state since the free polaron has no internal structure. In the strong-coupling limit, and for $L \gg \beta$, the corrections for the first-relaxed-excited-state energy are small and positive: they decrease the self-energy of the polaron. The strong-coupling behavior of the continuum polaron in α^2 is preserved. On the other hand, the limit $L \ll \beta$, in strong coupling, gives important corrections for the free polaron. In that case, the polaron radius is smaller than the unit cell and the α^2 behavior is replaced by a linear variation of the first-relaxed-excited-state energy with α, as is the case for the ground-state energy.

The presence of a defect does not change the order of magnitude of the corrections, when $L \gg \beta$. For the first-relaxed-excited-state energy of the bound polaron, the corrections are also small and positive; they reduce the self-energy of the polaron and its binding energy to the defect. In weak coupling, an effective-mass state is obtained which can be viewed as a polaron in its ground state bound to the defect in its first excited state. In strong coupling, the corrections are larger than in weak coupling, but in the limit $L \gg \beta$ the continuum polaron behavior is preserved. Also, the screening of the defect by the LO phonons is effective and important and the electron-defect coupling constant, $\mathcal{R}_\infty$, is renormalized to $\mathcal{R}_0$. When $L \ll \beta$, the corrections become large and our approach used to calculate the Zak correction is not applicable. Nevertheless, we can still consider the Debye-cutoff correction. Since the cutoff is important, screening of the defect by the phonons is no longer effective and the Rydberg involves the high-frequency dielectric constant, inducing large, negative corrections: the binding energy to the defect is increased.

The numerical results indicate that the regime $L \ll \beta$ is more difficult to attain for the first relaxed excited state than for the ground state. Also the corrections to excited state remain small for typical values of the parameters (less than 10% for typical polar crystals). This is expected since the first-relaxed-excited-state wave function is more extended than the ground-state wave function. The $1s \rightarrow 2p$ transition energy calculated using our formalism is also compared to experimental values for the bound polaron, when available. This comparison is not expected to be quantitative since an important part of the central-cell corrections were neglected from the beginning. The numerical values are given to estimate the order of magnitude of the corrections to the continuum approximation for these crystals. These corrections are found to be negligible for the bound polaron in real crystals. In three cases (GaAs, CdTe, and CdS), we obtain a good agreement with experimental values if correction for the use the Gaussian spectrum is taken into account.

In conclusion, we have shown that for weakly polar crystals, like the III-V compounds and the II-VI compounds, the continuum approximation is well justified, the corrections being of the order of a few percent. The energies obtained for optical transitions on defects are generally good. On the other hand, the case of more polar crystals is less clear (alkali halides, for example). In that case, even if our formalism does not allow us to calculate the Coulombic excited states, we predict important corrections to the continuum approximation. The largest part of these corrections comes from a reduction in the screening of the defect by the phonons. Also in these cases, the radius of the polaron becomes of the order of magnitude of the unit cell and a perturbative approach to the calculation of the corrections to the continuum approximation is questionable. In this case, a small- or intermediate-polaron approach would be in order. We have also shown in this paper that the corrections to the continuum approximation are much smaller for an excited state than for a ground state because of a larger extension of the wave function. It would thus be interesting to compare with experiment the value of the ionization energy of the excited state instead of that of the $E_0 \rightarrow E_{2p}$ transition, should it become available. A better agreement is expected in this case.

ACKNOWLEDGMENTS

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