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Interaction of Slow Electrons with the Surface of a Model Dielectric: Theory of Surface Polarons*

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We discuss the interaction of a slow electron with the surface of a semi-infinite dielectric with dielectric constant that differs from unity by virtue of the presence of an infrared-active TO phonon. We obtain an expression for the effective interaction energy between the electron and the surface which reduces to the expression obtained from image-potential theory when the electron is far from the surface, either inside or outside the crystal. When the electron is near the surface, the effective potential differs from the image potential and becomes nonlocal. The form of the image potential is obtained by adapting to the present problem a method used by Lee, Low, and Pines in bulk polaron theory. We have applied the theory to the study of the binding of electrons to the crystal surface produced by the coupling of the electron to surface optical phonons and bulk LO phonons. We consider both the case where the electron is outside the crystal and trapped on the surface (the exterior-surface polaron) and the case where it is on the inside (the interior-surface polaron).

I. INTRODUCTION

In a recent series of experiments, Ibach has explored the inelastic scattering of low-energy electrons by surface optical phonons from surfaces of the semiconducting crystals ZnO and silicon.[1] These experiments have provided detailed information about the nature of the interaction between low-energy electrons and surface optical phonons. In the case of the ionic crystal ZnO, the data have been interpreted in a complete and quantitative fashion by Lucas and Sunjic.[2] These authors have derived an expression for the probability that the incident electron excites n surface optical phonons by means of a theory which utilizes a classical description of the electron motion. In earlier papers,[3] we have developed a model of the interaction of low-energy electrons with surface optical phonons in ionic crystals and in silicon. We have also demonstrated how the results obtained by Lucas and Sunjic for scattering of low-energy electrons from ionic-crystal surfaces follow from a purely quantum-mechanical treatment of the electron motion, and how the expression for the scattering cross section is modified when the electron scatters from a coherently generated surface wave.

One striking feature of the data on ZnO is the great strength of the interaction between the electron and the electric field generated by the surface optical phonon. For example, when electrons with an incident energy of ≈7 eV are incident on the ZnO surface, the intensity of the one-phonon loss peak is about one-half the intensity of the specular beam produced by electrons scattered elastically from the surface.

The purpose of the present paper is to explore the possibility that in the presence of this strong interaction between electrons and surface optical phonons, an electron either inside or outside the surface may be trapped at the crystal surface. In an earlier note,[4] we pointed out that the method used by Lee, Low, and Pines[5] may be adapted to the study of such surface-polaron states. In our earlier note, we considered only the case where the electron interacts with the surface optical phonons. When the electron is inside the crystal, it is also necessary to consider the interaction of the electron with the bulk LO-phonon modes as well. One purpose of the present paper is to extend our earlier study to the case where the electron interacts with both the surface and bulk LO waves when it is inside the crystal. For the simple model described below, we find for our model that surface-polaron states (i.e., states where the electron is bound to the crystal surface by means of the electron–surface-optical-phonon coupling) exist when the electron is inside the crystal and coupling to the bulk waves is included in the theory. As we conjectured in our earlier note, inclusion of the electron–bulk-LO-phonon interaction reduces the surface-polaron binding energy considerably. In fact, when the polaron coupling constant α exceeds a certain critical value, the surface-polaron state fails to exist when the electron is inside the crystal.

In this paper, we first examine the nature of the interaction of the electron with the crystal surface, for the case where the surface optical phonons and bulk LO phonons are the only electric-dipole active excitations to which the electron is coupled. Far from the crystal surface, when the electron is either inside or outside the crystal, the interaction potential is found to be the image potential, as elementary considerations demand. However, when the electron approaches the crystal surface, and comes within a distance the order of the bulk-polaron radius from it, the effective interaction is strongly modified, in a manner described below. The effective interaction becomes nonlocal in character, incidentally. After this examination of the nature of the interaction of the electron with the surface is completed, we then present results of studies of the surface-polaron binding energy when the electron is both outside (the exterior-surface polaron) and inside (the interior-surface polaron) our model crystal. For the exterior-surface polaron, we also present calculations of its effective mass.

While our work was under way, a study of surface-polaron states for the case where the electron is outside the crystal has been reported by Sak.[6] Sak presents two calculations, one valid in the strong-coupling limit where the wave function of the polaron becomes localized in the two dimensions parallel to the surface, and one valid in the weak-coupling limit where the electron is clothed only by a single surface optical phonon. The electron-scattering data on ZnO cited earlier demonstrates very clearly that the interaction between the electron and the surface optical phonons is quite strong in ionic crystals. As a consequence, Sak's weak-coupling theory does not seem applicable to such a system. It is this consideration which originally led us[4] to apply the method of Lee, Low, and Pines[5] to the present problem. This approach is nonperturbative in nature, and allows the wave function of the polaron to contain contributions from multiphonon states. In bulk-polaron theory, the method of Lee, Low, and Pines provides an adequate picture of the energy and wave function of the polaron in the region of intermediate coupling, where the wave function surely contains contributions from multiphonon states, but where the interaction is not sufficiently strong to actually localize the polaron. We presume this method has a similar regime of validity for the surface-polaron problem. A large number of ionic semiconductors are characterized by polaron-coupling constants in the range where the Lee-Low-Pines method is valid.[7] As we proceed with our discussion, we shall compare the results we obtain with results obtained by Sak in his weak-coupling theory.

The outline of this paper is as follows. In Sec. II, we define the model to be employed, and we recall the nature of the interaction between an electron and surface optical phonons and bulk LO phonons in a finite slab. In Sec. III, we present a qualitative and heuristic discussion of the effective interaction between an electron and the crystal surface, for the two cases where the electron is inside or outside the crystal. In Sec. IV, we set up a variational wave function for the coupled electron-phonon system, and we obtain a more precise expression for this effective interaction. We have applied the variational principal to the study of the two sets of bound states mentioned earlier, the case where the electron is outside the crystal and trapped on the surface (the exterior-surface polaron) and the case where it is inside the crystal and trapped on the surface (the interior-surface polaron). We present the results of these calculations in Sec. V.

While our model provides a highly oversimplified picture of the interaction of an electron with the crystal surface, and many important corrections must be included before the results may be applied to real crystals in a quantitatively reliable manner, we feel the results presented here give one a good picture of the main qualitative features of the phonon-mediated contribution to the electron-surface interaction.

II. GENERAL DESCRIPTION OF THE MODEL

The problem we wish to consider is illustrated in Fig. 1. We consider a dielectric slab of thickness L, with surfaces normal to the z axis. An electron is placed near the slab, a distance z from the left-hand surface. The electron may be either inside or outside the slab. We have in mind the limit $|z| \ll L$, so the electron feels the presence of only the left-hand surface. Thus, while we keep L finite for parts of the discussion, we ultimately take the limit $L \rightarrow \infty$ with z held fixed.

The dielectric constant of the slab differs from unity because of the presence of an infrared-active TO phonon. The frequency-dependent dielectric constant of the material from which the slab is constructed is thus given by

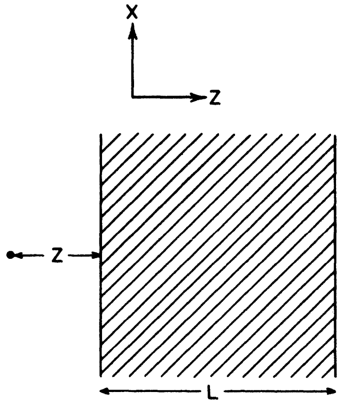

FIG. 1. Model considered in the present paper. We examine the interaction of an electron located a distance z from the surface of a dielectric slab of thickness L. We consider the case $z \ll L$, and the electron may be either inside or outside the slab.

$$\epsilon(\omega) = 1 + \Omega_p^2/(\omega_T^2 - \omega^2), \qquad (2.1)$$

where $\Omega_p^2 = 4\pi n e^{*2}/\mu$ provides a measure of the oscillator strength of the TO phonon, and ω_T is the frequency of the TO mode. In the expression for Ω_p, $n = N/V$ is the number of unit cells per unit volume, μ is the reduced mass of the unit cell, and e^* is the transverse effective charge. We will require the term in the Hamiltonian which describes the interaction between the electron and the long-wavelength modes of the dielectric slab which set up a macroscopic electric field. While the form of this interaction has been derived elsewhere,[8] we shall present here a derivation that is quite short.

If we ignore retardation effects, then the electric field set up by a long-wavelength phonon may be derived from an electrostatic potential $\varphi(\vec{x}, t)$. Because of the fact that translational invariance exists in the x and y directions, we examine waves for which

$$\varphi(x, t) = \Phi(z) e^{i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}} e^{-i\omega t}, \qquad (2.2)$$

where the subscript $\parallel$ denotes the projection of a given vector onto a plane parallel to the surface, or a vector which lies entirely in such a plane.

In the medium, we must have $\nabla\cdot\vec{D} = 0$, and $\nabla\cdot\vec{E} = 0$ outside the slab. Thus, we require

$$\epsilon(\omega)\left(\frac{d^2\Phi}{dz^2} - Q_{\parallel}^2\Phi\right) = 0, \quad 0 < z < L \qquad (2.3a)$$

and

$$\frac{d^2\Phi}{dz^2} - Q_{\parallel}^2\Phi = 0, \quad z < 0, \quad z > L. \qquad (2.3b)$$

Equation (2.3a) requires that either $\epsilon(\omega) = 0$, or Φ be a linear combination of $e^{\pm Q_{\parallel} z}$. The first possibility requires that ω equal the bulk-LO-phonon frequency ω_L, where $\omega_L^2 = \omega_T^2 + \Omega_p^2$, and the second solution describes a surface optical phonon.

For the bulk-LO-phonon solution, we have

$$\Phi(z) = \Phi_1 \sin(Q_z z) + \Phi_2 \cos(Q_z z), \qquad (2.4)$$

and outside the crystal, $\Phi(z)$ satisfies Eq. (2.3b). Thus, outside the crystal, for $z < 0$, we must have $\Phi(z) = \Phi_3 e^{+Q_{\parallel} z}$, since the field cannot increase exponentially as $z \to -\infty$.

Next consider the boundary conditions at $z = 0$. Normal components of $\vec{D}$ must be conserved, and $D_z = 0$ inside the slab since $\epsilon(\omega_L) = 0$. Thus, $D_z = 0$ just outside. This condition requires $\Phi_3 \equiv 0$, so the electrostatic potential is identically zero outside the slab. This means that just outside the slab, $E_x = 0$. Conservation of tangential components of $\vec{E}$ then requires $\Phi_2 = 0$, so that $\Phi(z) = 0$ at $z = 0$. Similar reasoning shows that $\Phi(z) = 0$ at $z = L$ also, so $k_z = n\pi/L$, $n = 1, 2, 3, \ldots$.

Thus, we conclude that for the bulk LO phonons in the slab, the electrostatic potential is given by

$$\varphi(\vec{x}) = \Phi_1 e^{i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}} \sin(Q_z z), \quad Q_z = n\pi/L \qquad (2.5)$$

where n ranges over the positive integers.

The interaction between an electron and a given bulk LO phonon is given by $-e\varphi(\vec{x})$. Thus, the second-quantized form of the interaction between an electron and bulk LO phonon may be written

$$H_{e\text{-LO}} = \Theta(z)\Theta(L - z) \sum_{\vec{Q}_{\parallel} Q_z} \frac{eB(Q)}{V^{1/2}} e^{i\vec{Q}_{\parallel}\cdot\vec{x}_{\parallel}} \times \sin(Q_z z)(b_Q + b_{-Q}^{\dagger}), \qquad (2.6)$$

where $\Theta(z) = 1$ if $z > 0$, and $\Theta(z) = 0$ for $z < 0$, and the form of the coefficient $B(Q)$ remains to be determined. Notice that the sum over Q_z ranges only over the values $Q_z > 0$.

A simple argument which leads to the value of $B(Q)$ may be constructed. Since $\vec{D} = 0$ when an LO phonon is excited,

$$\vec{D} = \vec{E} + 4\pi n e^* \vec{u} = 0,$$

where $\vec{u}$ is the relative displacement of the two sublattices of the ionic slab. Thus, for $0 < z < L$,

$$\vec{u} = \frac{1}{4\pi n e^*} \nabla\varphi \qquad (2.7a)$$

$$= \sum_{\vec{Q}_{\parallel} Q_z} \frac{B(Q)\, Q}{4\sqrt{2}\,\pi n e^* V^{1/2}} \vec{e}_Q(\vec{x})\,(b_Q + b_{-Q}^{\dagger}). \qquad (2.7b)$$

In Eq. (2.7b), $Q = (Q_{\parallel}^2 + Q_z^2)^{1/2}$, and we have introduced the vector

$$\vec{e}_{\vec{Q}}(\vec{x}) = \frac{\sqrt{2}}{Q}\left[\hat{z}\, Q_z \cos(Q_z z) + i\vec{Q}_{\parallel} \sin(Q_z z)\right],$$

which has the property that

$$\int (d^3x/V)\, |\vec{e}(\vec{x})|^2 = 1. \qquad (2.7c)$$

We may also write for $\vec{u}$ the expression

$$\vec{u} = \sum_{\vec{Q}} \left(\frac{\hbar}{2\mu\omega_L}\right)^{1/2} \vec{e}_Q(\vec{l})\,(b_Q + b_{-Q}^{\dagger}) \qquad (2.8)$$

where $\vec{l}$ refers to the position of a unit cell, and the eigenvector $\vec{e}_Q(\vec{l})$ is normalized so that

$$\sum_{\vec{l}} |\vec{e}_Q(\vec{l})|^2 = 1. \qquad (2.8a)$$

In the long-wavelength limit of interest in this work, we may regard $\vec{l}$ as a continuous variable. Equations (2.8a) and (2.7c) then become equivalent, and $B(Q)$ may be obtained by comparing Eqs. (2.7b) and (2.8):

$$B(Q) = \frac{4\sqrt{2}\,\pi n^{1/2} e^*}{Q}\left(\frac{\hbar}{2\mu\omega_L}\right)^{1/2}. \qquad (2.9)$$

The form of the term in the Hamiltonian that describes the interaction between the electron and the surface optical phonon may be deduced in a similar manner. If the electron is near the surface at $z=0$, and $L\rightarrow\infty$, then we need consider only the interaction between the electron and the surface waves which propagate along the surface $z=0$. The coupling to surface waves which propagate along the surface $z=L$ may be ignored. For the surface waves which propagate along the left-hand surface in Fig. 1, we have $\Phi(z)=\Phi_0 e^{-Q_\parallel|z|}$ from Eqs. (2.3a) and (2.3b). When one examines the constraint imposed on the solution by the requirement that the normal component of $\vec{D}$ is conserved, one finds the surface-wave frequency ω_s is given by the well-known condition

$$\epsilon(\omega_s)=-1,$$

or for our model,

$$\omega_s=\omega_T[\tfrac{1}{2}(1+\epsilon_s)]^{1/2},$$

where ϵ_s is the static dielectric constant of the slab.

If $a_{Q_\parallel}$ and $a^\dagger_{Q_\parallel}$ are the annihilation and creation operators for a surface optical phonon of wave vectors $\vec{Q}_\parallel$, then the term in the Hamiltonian that describes the interaction between the electrons and these modes has the form

$$H_{e\text{-}s}=\sum_{\vec{Q}_\parallel}\frac{eC(Q_\parallel)}{A^{1/2}}\,e^{-Q_\parallel|z|}\,e^{i\vec{Q}_\parallel\cdot\vec{x}_\parallel}(a_{Q_\parallel}+a^\dagger_{-Q_\parallel}), \tag{2.10}$$

where A is the area of one surface. An explicit form for the coefficient $C(Q_\parallel)$ may be deduced by an argument similar in form to the one presented above. In fact, we have presented this argument in an earlier paper.[3] One finds

$$C(Q_\parallel)=2\pi n^{1/2}e^*\left(\frac{\hbar}{2\omega_s\mu}\right)^{1/2}\frac{1}{Q_\parallel^{1/2}}. \tag{2.11}$$

We complete this section by enumerating the remaining terms in the model Hamiltonian. We shall not take detailed account of band-structure effects. The bottom of the conduction band is generally located a few volts below the vacuum level, and when the electron moves in the crystal in states near the bottom of the conduction band, its wave function leaks out into the vacuum a bit. We describe this effect by simply introducing a step potential at $z=0$, with step height V_0. Thus, when we consider motion of the electron inside the crystal, we shall introduce the term

$$V(z)=V_0\Theta(z)$$

into the Hamiltonian.

When the electron is inside the crystal, and in states near the bottom of the conduction band, it moves with the effective mass m^*. In the vacuum outside the crystal, the mass of the electron is the free-electron mass m. For the operator which describes the kinetic energy of the electron, we use the form

$$T=-\frac{\hbar^2}{2m^*}\,\vec{\nabla}\cdot\Theta(z)\vec{\nabla}-\frac{\hbar^2}{2m}\,\vec{\nabla}\cdot\Theta(-z)\vec{\nabla}. \tag{2.12}$$

This operator has the property that for $z>0$, $T=-\hbar^2\nabla^2/2m^*$ and $T=-\hbar^2\nabla^2/2m$ for $z<0$. The Θ functions are positioned between the factors of $\vec{\nabla}$ in order to ensure that T is properly Hermitian.

Finally, we add to the Hamiltonian the energy of the bulk LO phonons and the surface phonons:

$$H_p=\hbar\omega_s\sum_{\vec{Q}_\parallel}a^\dagger_{Q_\parallel}a_{Q_\parallel}+\hbar\omega_L\sum_{\vec{Q}_\parallel Q_z}b^\dagger_Q b_Q. \tag{2.13}$$

In summary, the model crystal employed in this work is described by the Hamiltonian

$$H=T+V(z)+H_{e\text{-}s}+H_{e\text{-}\mathrm{LO}}+H_p. \tag{2.14}$$

III. INTERACTION OF AN ELECTRON WITH THE SURFACE: A HEURISTIC DISCUSSION

In this section, we discuss the principal qualitative features of the interaction of an electron with the crystal surface. The discussion presented here is intended to be qualitative in nature, in order to provide a feeling for those features of the interaction important in the subsequent section of the paper. In Sec. IV, we shall present a more complete theoretical study of this interaction.

Imagine we place a point charge e a distance z from the crystal surface, outside the crystal as indicated in Fig. 1; then $z<0$. From the discussion of Sec. II, it is clear that the electron will interact with only the surface optical phonons. We calculate the shift in energy of the electron produced by the interaction $H_{e\text{-}s}$ displayed in Eq. (2.10). The first correction to the energy of the electron arises in the second order of perturbation theory. In the process described by this second-order correction, the electron emits a virtual surface optical phonon of wave vector $\vec{Q}_\parallel$, and then reabsorbs it. We presume the electron always remains fixed at the point z. The energy of the intermediate state is thus higher than that of the initial state by the amount $\hbar\omega_s$, the energy of the surface optical phonon in the intermediate state. Thus, the energy shift $\Delta E(z)$ is given by

$$\Delta E_s(z)=-\frac{1}{A}\sum_{\vec{Q}_\parallel}\frac{e^2|C(Q_\parallel)|^2}{\hbar\omega_s}\,e^{-2Q_\parallel|z|}. \tag{3.1}$$

If the expression for $C(Q_\parallel)$ given in Sec. II is inserted into Eq. (3.1), the sum over $\vec{Q}_\parallel$ may be converted to an integral, and the integration carried out. The result may be written in the form

$$\Delta E_s(z)=-\frac{e^2}{2}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right)\frac{1}{2|z|}. \tag{3.2}$$

This result is a familiar one from elementary electrostatics. It is simply the amount of work required to bring the electron from $z=\infty$ to the finite distance z from the surface, where the force of attraction is provided by the image charge.

Our discussion is oversimplified in one regard. The electron actually has a finite mass m. Thus, if the electron is initially at rest, it will recoil, with momentum $\hbar\vec{Q}_{\parallel}$ in the intermediate state. Thus, we should add the recoil energy $\hbar^2 Q_{\parallel}^2/2m$ to the energy denominator in Eq. (3.1). One has

$$\Delta E_s(z) = -\frac{1}{A}\sum_{\vec{Q}_{\parallel}} \frac{e^2\,|C(\vec{Q}_{\parallel})|^2}{\hbar\omega_s+\hbar^2 Q_{\parallel}^2/2m}\, e^{-2Q_{\parallel}|z|} \tag{3.3a}$$

$$= -\frac{ne^{*2}e^2}{\omega_s\mu}\int\frac{d^2Q_{\parallel}}{Q_{\parallel}}\,\frac{e^{-2Q_{\parallel}|z|}}{\omega_s+\hbar Q_{\parallel}^2/2m}\,. \tag{3.3b}$$

For large values of $|z|$, because of the exponential factor in the numerator of Eq. (3.3b), only small values of $Q_{\parallel}$ are important in the integral, the recoil term in the denominator may be ignored, and Eq. (3.3b) gives the result in Eq. (3.2) for $\Delta E_s(z)$. However, when $|z| \sim z_s = (\hbar/2m\omega_s)^{1/2}$, a length the order of the radius of a bulk polaron formed from an electron of mass m, the behavior of $\Delta E_s(z)$ is profoundly modified by the recoil effects. In particular, the interaction energy in Eq. (3.2) diverges as $z\to 0$, while the expression in Eq. (3.3b) remains finite. Thus, the recoil effects round off the divergence interaction energy deduced from electrostatic considerations, and as a consequence greatly modify the form of the interaction energy for $z<z_c$. Direct integration of Eq. (3.3b) gives

$$\Delta E_s(z=0) = -e^2\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right)\frac{\pi}{4z_s}\,, \tag{3.4}$$

where again

$$z_s = (\hbar/2m\omega_s)^{1/2}\,.$$

This rounding off of the divergence in the interaction energy was implicit in our earlier work,[4] and Sak[6] also noted that the effective interaction between the electron and the surface also differed from the electrostatic value, when $z \lesssim z_s$. Ray and Mahan[9] have considered the motion of an electron of velocity $\vec{V}$ outside the crystal, and within the framework of a calculation that describes the electron motion classically, these authors have obtained an effective potential with a form very similar to that in Eq. (3.3a) when the electron moves normal to the surface. In fact, our Eq. (3.3b) becomes identical to the expression obtained by Mahan and Ray, if one replaces the velocity V of the electron (for the case where the electron moves normal to the surface) by the quantity $V_c=(\hbar\omega_s/2m)^{1/2}$. We presume our expression describes the interaction energy in the limit that the electron moves slowly, with velocity $V<V_c$, while the expression of Mahan and Ray applies when V is large compared to V_c.

Next consider the case where the electron is inside the crystal, again a distance z from the surface. The electron now interacts with the bulk LO phonons as well as with the surface optical phonons. The contribution to the interaction energy from the virtual emission and reabsorption of surface optical phonons depends only on $|z|$, as one can see from Eq. (2.10). Thus, when the electron is inside the crystal, the contribution to the interaction energy from emission and absorption of virtual surface optical phonons is still given by Eq. (3.3b), provided z is replaced by its absolute value. To obtain the total interaction energy, we must add to this the contribution from emission and reabsorption of bulk LO phonons. Before we proceed with the calculation, one important feature of this contribution is evident from the form of the interaction in Eq. (2.6). Because of the factor of $\sin Q_z z$ which appears in this expression, the contribution to the interaction energy from the bulk phonons vanishes at the surface, and by continuity is small near the surface. Thus, when the electron is very near the surface, but inside the crystal, it will be *attracted* to the surface, just as when it is outside. This result is completely opposite to that obtained from electrostatic considerations. In the theory of electrostatics, when the electron is inside the crystal, its image charge is of the same sign as the electron, so the electron is repelled from the surface. Our microscopic theory will show that although one realizes the repulsive image potential when z is greater than a certain length z_0 and the contribution to $\Delta E(z)$ from both bulk and surface optical phonons is considered, as $z\to 0$, an attractive potential well develops. This potential well is responsible for the binding energy we find for the interior-surface polaron described in Sec. I of the present paper. We now proceed with the calculation.

The second-order shift in energy of an electron placed at the position z inside the crystal due to emission and reabsorption of a bulk LO phonon is

$$\Delta E_B(z) = -\frac{e^2}{V}\sum_{\vec{Q}_{\parallel}Q_z}\frac{B(Q)^2\sin^2(Q_z z)}{\hbar\omega_L+\hbar^2Q^2/2m}\,. \tag{3.5}$$

The sums are replaced by integrations according to the prescriptions

$$\sum_{\vec{Q}_{\parallel}} = \frac{A}{4\pi^2}\int d^2Q_{\parallel}\,,\quad \sum_{Q_z}\to\frac{L}{\pi}\int_0^{\infty} dQ_z\,.$$

Since the integrand is an even function of Q_z, the integration over Q_z may be extended from $-\infty$ to $+\infty$ with insertion of a factor of $\frac{1}{2}$. After the explicit form of $B(Q)$ is inserted into this form, the results may be arranged to read

$$\Delta E_B(z) = -\frac{4ne^2e^{*2}m}{\pi\mu\omega_L\hbar}\int\frac{d^3Q\,\sin^2(Q_z z)}{Q^2(Q^2+2m\omega_L/\hbar)}\,.$$

We separate $\Delta E_B(z)$ into a portion independent of z, and one that will be seen to vanish as $z \to \infty$ through use of the identity

$$\sin^2(Q_z z) = \tfrac{1}{2} - \tfrac{1}{2}\cos 2Q_z z .$$

First consider the part of $\Delta E_B(z)$ that is independent of z. We call this portion ΔE_∞. The integration is readily evaluated to yield

$$\Delta E_\infty = -\frac{4\pi n e^2 e^{*2}}{\mu \omega_L}\left(\frac{m}{2\hbar\omega_L}\right)^{1/2} . \tag{3.6}$$

This result may be cast in a more familiar form by introducing the polaron coupling constant α, which for our model with background dielectric constant unity is given by

$$\alpha = e^2\left(1-\frac{1}{\epsilon_s}\right)\left(\frac{m}{2\omega_L\hbar^3}\right)^{1/2} . \tag{3.6a}$$

One then finds

$$\Delta E_\infty = -\alpha\hbar\omega_L ,$$

the well-known expression for the binding energy of the bulk polaron, produced by both second-order perturbation theory and the intermediate-coupling theory of Lee, Low, and Pines.[7]

It is a short exercise to evaluate the contribution to $\Delta E_B(z)$ that depends on z. To express this result in a convenient form, introduce the length

$$z_0 = (\hbar/2m\omega_L)^{1/2} ,$$

the bulk polaron radius in the theory of Lee, Low, and Pines. Then for $\Delta E_B(z)$, we find

$$\Delta E_B(z) = -\alpha\hbar\omega_L + \frac{e^2}{4z}\left(\frac{\epsilon_s - 1}{\epsilon_s}\right)(1 - e^{-2z/z_0}) . \tag{3.7}$$

When $z \gg z_0$, the expression for $\Delta E_B(z)$ becomes

$$AE_B(z) = -\alpha\hbar\omega_L + \frac{e^2}{4z}\left(\frac{\epsilon_s - 1}{\epsilon_s}\right) .$$

The total energy shift provided by the coupling of the electron to the optical phonons follows upon adding $\Delta E_s(z)$ to $\Delta E_B(z)$, noting that the former is a symmetric function of z about $z = 0$, as noted earlier. When $z \gg z_0$, we have

$$\begin{aligned}\Delta E_{\text{tot}}(z) &= \Delta E_s(z) + \Delta E_B(z)\\ &= -\alpha\hbar\omega_L + \frac{e^2}{4z}\left(\frac{\epsilon_s - 1}{\epsilon_s + 1}\right)\frac{1}{\epsilon_s} .\end{aligned} \tag{3.8}$$

The second term in Eq. (3.8) is the expression provided by elementary electrostatics for the interaction between the bulk polaron and its image charge.

In the above discussion, we have ignored the difference between the free-electron mass and the band-structure effective mass m^*. Of course, when the electron is in the crystal, m must be everywhere replaced by m^*. It is not obvious at this point what mass should be used when the electron is near the surface, so its wave function extends into the vacuum outside. An answer to this equation will emerge in Sec. IV.

As remarked earlier, as $z \to 0$, $\Delta E_B(z) \to 0$. This also may be checked from the explicit form given above. Thus, there is a minimum in $\Delta E_{\text{tot}}(z)$ at $z = 0$. We shall see in Sec. IV that an electron may form a bound state inside the crystal near the surface with energy lower than the bulk polaron energy, $\alpha\hbar\omega_L$. It is necessary to use the full nonlocal form to obtain an accurate expression for the binding energy, however.

IV. APPLICATION OF METHOD OF LEE, LOW, AND PINES TO STUDY OF ELECTRON MOTION NEAR SURFACE

In this section, we derive the basic equation that will be employed in our study of surface-polaron states. We begin by writing out the Hamiltonian of the electron-phonon system in explicit form:

$$\begin{aligned} H = {}& \frac{1}{2m^*} f(z) P_\parallel^2 + \frac{1}{2m^*} P_z f(z) P_z + V(z) + \sum_{\vec{Q}_\parallel} \frac{eC(Q_\parallel)}{A^{1/2}} (a_{Q_\parallel} + a^\dagger_{-Q_\parallel}) e^{i\vec{Q}_\parallel\cdot\vec{r}_\parallel} e^{-Q_\parallel |z|} \\ & + \sum_{\vec{Q}_\parallel Q_z} \Theta(z) \frac{eB(Q)}{V^{1/2}} [b_Q + b^\dagger_{-Q}] e^{i\vec{Q}_\parallel\cdot\vec{r}_\parallel} \sin Q_z z + \hbar\omega_s \sum_{Q_\parallel} a^\dagger_{Q_\parallel} a_{Q_\parallel} + \hbar\omega_L \sum_{\vec{Q}_\parallel Q_z} b^\dagger_Q b_Q . \end{aligned} \tag{4.1}$$

In this expression,

$$f(z) = \Theta(z) + (m^*/m)\Theta(-z) . \tag{4.2}$$

We begin by introducing a canonical transformation S which removes the coordinate $\vec{r}_\parallel$ from the Hamiltonian:

$$S = S_B S_s , \tag{4.3}$$

where

$$S_s = \exp\left(-i\vec{r}_\parallel \cdot \sum_{\vec{Q}_\parallel} \vec{Q}_\parallel a^\dagger_{Q_\parallel} a_{Q_\parallel}\right) , \tag{4.3a}$$

$$S_B = \exp\left(-i\vec{r}_\parallel \cdot \sum_{\vec{Q}_\parallel Q_z} \vec{Q}_\parallel b^\dagger_Q b_Q\right) . \tag{4.3b}$$

The transformed Hamiltonian H' is then related to H in the standard manner:

$$H' = SHS^{-1} = S_s^{-1} S_B^{-1} H S_B S_s \, .$$

Notice that

$$S a_{Q_\parallel} S^{-1} = e^{-i\vec{Q}_\parallel \cdot \vec{r}_\parallel} a_{Q_\parallel} \, , \tag{4.4a}$$

$$S a^\dagger_{Q_\parallel} S^{-1} = e^{+i\vec{Q}_\parallel \cdot \vec{r}_\parallel} a^\dagger_{Q_\parallel} \, , \tag{4.4b}$$

with a similar relation for b_Q and $b^\dagger_Q$, and also

$$S\vec{P}_\parallel S^{-1} = \vec{P}_\parallel - \hbar \sum_{Q_\parallel} \vec{Q}_\parallel a^\dagger_{Q_\parallel} a_{Q_\parallel} - \hbar \sum_{\vec{Q}_\parallel Q_z} \vec{Q}_\parallel b^\dagger_Q b_Q \, .$$

From Eqs. (4.4a) and (4.4b), along with the corresponding results for b_Q and $b^\dagger_{-Q}$, it is clear that the coordinate $\vec{r}_\parallel$ does not appear in H'. The wave function of the coupled electron-phonon system can then be written in the new representation in the form

$$\psi(\vec{r}_\parallel z;\ \{a_{Q_\parallel}\}\{b_{Q_\parallel}\}) = e^{i\vec{k}_\parallel \cdot \vec{r}_\parallel}\, \Phi(z;\ \{a_{Q_\parallel}\},\ \{b_{Q_\parallel}\}) \, . \tag{4.5}$$

Then

$$H'\psi = e^{i\vec{k}_\parallel \cdot \vec{r}_\parallel} h \Phi \, ,$$

where the effective Hamiltonian that describes the states characterized by the wave vector $\vec{k}_\parallel$ is given by

$$h = \frac{\hbar^2 f(z)}{2m^*}\left(\vec{k}_\parallel - \sum_{\vec{Q}_\parallel} \vec{Q}_\parallel a^\dagger_Q a_{Q_\parallel} - \sum_{\vec{Q}_\parallel Q_z} \vec{Q}_\parallel b^\dagger_Q b_Q\right)^2 + \frac{1}{2m^*} P_z f(z) P_z + V(z)$$
$$+ \sum_{\vec{Q}_\parallel} \frac{eC(Q_\parallel)}{A^{1/2}} (a_{Q_\parallel} + a^\dagger_{-Q_\parallel}) e^{-Q_\parallel |z|} + \sum_{\vec{Q}_\parallel Q_z} \Theta(z) \frac{eB(Q)}{V^{1/2}} \sin(Q_z z)(b_Q + b^\dagger_{-Q}) + \hbar\omega_s \sum_{Q_\parallel} a^\dagger_{Q_\parallel} a_{Q_\parallel} + \hbar\omega_L \sum_{\vec{Q}_\parallel Q_z} b^\dagger_Q b_Q \, .$$

To proceed, we make an ansatz about the form of Φ introduced in Eq. (4.5). We generalize the treatment of Lee, Low, and Pines by utilizing the ansatz

$$\Phi = \varphi(z)\, U_s U_B \mid 0\rangle \, , \tag{4.6a}$$

where the state $\mid 0\rangle$ is the phonon vacuum state, $\varphi(z)$ is normalized so that $\int dz \mid \varphi(z)\mid^2 = 1$,

$$U_s = \exp\left(\sum_{\vec{Q}_\parallel} (f_{Q_\parallel} a_{Q_\parallel} - f^*_{Q_\parallel} a^\dagger_{Q_\parallel})\right) \, , \tag{4.6b}$$

and

$$U_B = \exp\left(\sum_{\vec{Q}_\parallel Q_z} (g_Q e^{iQ_z z} b_Q - g^*_Q e^{-iQ_z z} b^\dagger_Q)\right) . \tag{4.6c}$$

In Eq. (4.6a) the function $\varphi(z)$ and the parameters $f_{Q_\parallel}$ and g_Q are treated as variational parameters, to be determined by the requirement that the energy of the system be minimized. The operators U_s and U_B describe displacements of the lattice oscillators in response to the presence of the electron cloud represented by $\varphi(z)$. If the electron moves well inside the bulk of the crystal so that the excitation of the surface waves may be ignored, then upon choosing $\varphi(z) = e^{ik_z z}$ one may show that the wave function in Eq. (4.4a) has the same form as that of Lee, Low, and Pines.

The next step is to compute the expectation value $\langle \Phi \mid h \mid \Phi\rangle$. This quantity is equal to $E(\vec{k}_\parallel)$, the energy of the surface polaron when its wave vector parallel to the surface is $\vec{k}_\parallel$, since the function $\mid \Phi\rangle$ defined in Eq. (4.4a) is normalized to unity. Since we wish to study bound surface-polaron states in the present paper, we confine our attention to the case where $\varphi(z)$ is real. The expectation value $E(\vec{k}_\parallel)$ is readily computed by means of the following identities:

$$\langle 0 \mid U_s^\dagger a_{Q_\parallel} U_s \mid 0\rangle = -f^*_{Q_\parallel} \, , \tag{4.7a}$$

$$\langle 0 \mid U_s^\dagger a^\dagger_{Q_\parallel} U_s \mid 0\rangle = -f_{Q_\parallel} \, , \tag{4.7b}$$

$$\langle 0 \mid U_B^\dagger b_{\vec{Q}} U_s \mid 0\rangle = -g^*_Q e^{-iQ_z z} \, , \tag{4.7c}$$

$$\langle 0 \mid U_B^\dagger b^\dagger_Q U_B \mid 0\rangle = -g_Q e^{+iQ_z z} \, , \tag{4.7d}$$

$$\langle 0 \mid U_s^\dagger a^\dagger_{Q_\parallel} a_{Q_\parallel} U_s \mid 0\rangle = \mid f_{Q_\parallel}\mid^2 , \tag{4.7e}$$

$$\langle 0 \mid U_B^\dagger b^\dagger_Q b_Q U_B \mid 0\rangle = \mid g_Q \mid^2 , \tag{4.7f}$$

$$\langle 0 \mid U_s^\dagger a^\dagger_{Q_\parallel} a_{Q_\parallel} a^\dagger_{Q'_\parallel} a_{Q'_\parallel} U_s \mid 0\rangle$$
$$= \mid f_{Q_\parallel}\mid^2 (\delta_{Q_\parallel, Q'_\parallel} + \mid f_{Q'_\parallel}\mid^2) , \tag{4.7g}$$

$$\langle 0 \mid U_B^\dagger b^\dagger_Q b_Q b^\dagger_{Q'} b_{Q'} U_B \mid 0\rangle$$
$$= \mid g_Q \mid^2 (\delta_{Q,Q'} + \mid g_{Q'}\mid^2) , \tag{4.7h}$$

and finally when $\varphi(z)$ is real, we have

$$\frac{1}{2m^*}\int dz\, \varphi(z) \langle 0 \mid U_B^\dagger P_z f(z) P_z U_B \mid 0\rangle\, \varphi(z)$$
$$= \frac{1}{2m^*} \langle \varphi \mid P_z f(z) P_z \mid \varphi\rangle$$
$$+ \frac{\lambda}{2m^*}\left[\sum_{\vec{Q}} Q_z^2 \mid g_Q \mid^2 + \left(\sum_Q Q_z \mid g_Q\mid^2\right)^2\right] . \tag{4.7i}$$

In Eq. (4.7i), we have introduced the quantity

$$\lambda = \int dz\, f(z) \mid \varphi(z)\mid^2 \tag{4.8}$$

and also

$$\langle \varphi \mid P_z f(z) P_z \mid \varphi\rangle = -\hbar^2 \int dz\, \varphi(z) \frac{\partial}{\partial z} f(z) \frac{\partial}{\partial z} \varphi(z) . \tag{4.9}$$

The derivations of the identities displayed in Eqs. (4.7) are quite straightforward, except for the one in Eq. (4.7i). As a consequence, the derivation of this identity is given in the Appendix.

With these identities, one can readily compute $E(\vec{k}_\parallel)$, and express the result in terms of quantities introduced above, along with the matrix elements

$$M(Q_\parallel)=\langle \varphi \,|\, e^{-Q_\parallel |z|} \,|\, \varphi\rangle \ ,$$

and also

$$W(Q_z)=\langle \varphi \,|\, \Theta(z) e^{-iQ_z z} \sin Q_z z \,|\, \varphi\rangle \ .$$

One finds that

$$E(k_\parallel)=\left\langle \varphi \left| \frac{P_z f(z) P_z}{2m^*} \right| \varphi \right\rangle + \langle \varphi \,|\, V(z) \,|\, \varphi\rangle - \sum_{\vec{Q}} \frac{eC(Q_\parallel)M(Q_\parallel)}{A^{1/2}} (f_{Q_\parallel}+f^*_{Q_\parallel}) - \sum_{\vec{Q}} \frac{eB(Q)}{V^{1/2}} [W(Q_z)g_Q + W^*(Q_z)g^*_Q]$$
$$+ \sum_{\vec{Q}_\parallel} \left(\hbar\omega_s + \frac{\lambda\hbar^2 Q_\parallel^2}{2m^*}\right) |f_{Q_\parallel}|^2 + \sum_{\vec{Q}} \left(\hbar\omega_L + \frac{\lambda\hbar^2 Q^2}{2m^*}\right) |g_Q|^2 + \frac{\lambda\hbar^2}{2m^*}\left(\vec{k}_\parallel - \sum_{\vec{Q}_\parallel} \vec{Q}_\parallel |f_{Q_\parallel}|^2 - \sum_{\vec{Q}} \vec{Q}\, |g_Q|^2\right)^2 .$$

The amplitudes $f_{Q_\parallel}$ and g_Q are determined by the variational condition that

$$\delta E(\vec{k}_\parallel)/\delta f_{Q_\parallel} = \delta E(\vec{k}_\parallel)/\delta g_Q = 0.$$

One may express $f_{Q_\parallel}$ and g_Q in terms of the two quantities η and ξ defined by the statements

$$\eta\vec{k}_\parallel = \sum_{\vec{Q}_\parallel} \vec{Q}_\parallel |f_{Q_\parallel}|^2 + \sum_{\vec{Q}} \vec{Q}_\parallel |g_Q|^2 \tag{4.10}$$

and

$$\xi = \sum_{\vec{Q}} Q_z |g_Q|^2 \ . \tag{4.11}$$

Both of these quantities are functions of $\vec{k}_\parallel$, but approach limiting values independent of $\vec{k}_\parallel$ in the limit of $\vec{k}_\parallel \to 0$.

One finds that

$$f_{Q_\parallel} = \frac{1}{A^{1/2}} \frac{eC(Q_\parallel)M(Q_\parallel)}{\hbar\omega_s + \lambda\hbar^2 Q_\parallel^2/2m^* + (\lambda\hbar^2/m^*)(\eta-1)\vec{k}_\parallel\cdot\vec{Q}_\parallel} \tag{4.12}$$

and also

$$g_Q = \frac{1}{V^{1/2}} \frac{eB(Q)\,W(Q_z)}{\hbar\omega_L + \lambda\hbar^2 Q^2/2m^* + (\lambda\hbar^2/m^*)\xi Q_z + (\lambda\hbar^2/m^*)(\eta-1)\vec{k}_\parallel\cdot\vec{Q}_\parallel} \ . \tag{4.13}$$

These expressions for $f_{Q_\parallel}$ and g_Q may be substituted back into $E(k_\parallel)$ to obtain an expression for the surface-polaron energy in terms of only $\varphi(z)$. The final step is to choose $\varphi(z)$ to minimize $E(\vec{k}_\parallel)$. Notice that the parameters ξ and η which appear in Eqs. (4.12) and (4.13) are functionals of $\varphi(z)$.

The general expression for $E(\vec{k}_\parallel)$ is cumbersome, and of little general interest. We display explicitly only $E(0)$, the energy at $\vec{k}_\parallel = 0$. After some algebra, one finds

$$E(0) = \left\langle \varphi \left| \frac{P_z f(z) P_z}{2m^*} \right| \varphi \right\rangle + \langle \varphi \,|\, V(z) \,|\, \varphi\rangle - \frac{1}{A} \sum_{\vec{Q}_\parallel} \frac{C^2(Q_\parallel)M^2(Q_\parallel)}{\hbar\omega_s + \lambda\hbar^2 Q_\parallel^2/2m^*}$$
$$- \frac{1}{V} \sum_{\vec{Q}} \frac{B^2(Q)\,|\,W(Q_z)\,|^2}{\hbar\omega_L + \lambda\hbar^2 Q^2/2m^* + \lambda\hbar^2 \xi Q_z/2m^*} - \frac{\lambda\hbar^2\xi^2}{2m^*} \ . \tag{4.14}$$

This expression has been employed in the calculations described in Sec. V. We conclude the present section with a few remarks about the general features of the result in Eq. (4.14), and its relation to the heuristic discussion of the effective interaction between the electron and the surface presented in Sec. III.

Consider the case where the electron is entirely outside the crystal, i.e., $\varphi(z) \equiv 0$ for $z > 0$, inside the slab. Then $W(Q_z)$ and the parameter $\xi = 0$, $\langle \varphi \,|\, V(z) \,|\, \varphi\rangle = 0$, and the parameter $\lambda = m^*/m$. The expression in Eq. (4.14) is then clearly the expectation value of the kinetic energy, along with a potential energy that results from the coupling of the electrons to the surface optical phonons. The potential-energy term is closely related in structure to the result displayed in Eq. (3.3a). In fact, if we suppose the electron is localized near $z = z_0$, and take $\varphi(z) = \delta(z - z_0)$ as a consequence, then $M(Q_\parallel) = e^{-Q_\parallel |z_0|}$, so the potential-energy term in Eq. (4.14) becomes identically equal to the expression for $\Delta E_s(z)$ given in Eq. (3.3a). For general $\varphi(z)$, the effective potential is clearly nonlocal in character, very much like the exchange potential in the Hartree-Fock equations. Thus, while the expression in Eq. (3.3a) for $\Delta E_s(z)$ provides a useful guide to the qualitiative behavior of the effective potential near the surface, the nonlocal character of the effective electron-surface interaction becomes important in the region where $\Delta E_s(z)$ deviates from its limiting form provided by the image potential.

When the electron wave function lies partially or wholly within the crystal, then excitation of both surface and bulk LO phonons occurs, as we have seen in Sec. III. In the limit of weak coupling, the presence of the parameter ξ may be ignored, since ξ is proportional to an average of $B^2(Q)$. The expression for $E(0)$ then involves a contribution to the potential energy from the coupling to bulk LO phonons with a form very similar to the one displayed in Eq. (3.5). If we again assume that the electron is localized in its z coordinate, and take for $\varphi(z)$ the function $\delta(z-z_0)$, where now $z_0>0$ and lies within the crystal, then $|W(Q_z)|^2$ equals $\sin^2(Q_z z_0)$, the parameter λ equals unity, and the two terms in the potential energy become identically equal to the ones displayed in Sec. III, except the recoil mass equals the band mass m^* of the electron.

Again, if a general form is chosen for $\varphi(z)$, then the contribution to the effective potential energy from the bulk phonons is nonlocal in character, as one can see from Eq. (4.14). If the wave function $\varphi(z)$ lies partially within and partially outside the crystal, then the effective mass of the recoiling electron is given by m^*/λ, a value that lies between the band mass m^* and the free-electron mass.

We have applied the theory described in this section to a study of the binding of electrons to the crystal surface by the effective potential in Eq. (4.14), for the case where the electron lies outside the crystal (the exterior-surface polaron), and when it is inside (the interior-surface polaron). The results of these calculations, and a comparison of our work with that of Sak[6] is presented in Sec. V.

V. APPLICATION OF THEORY TO STUDY OF SURFACE-POLARON STATES

In this section, we apply the theoretical structure developed in Sec. IV to the study of surface-polaron states, i.e., bound states of the electron to the crystal surface, where the binding energy arises from the interaction of the electron with the crystal surface provided by coupling to the surface and bulk optical phonons.

We consider two distinct cases. In the first instance, we suppose the electron lies outside the crystal, and in the second, we suppose the electron lies inside. The first case will be referred to as the exterior-surface-polaron state, and the second, the interior-surface-polaron state.

A. Exterior-Surface Polaron

An electron outside the crystal is drawn to the surface by the attractive image potential. It can form a bound state in which it is trapped to the surface of the crystal by the attractive image potential. It should be remarked that this bound state will be stable only if a certain condition is met. In particular, the energy of the surface-polaron state must lie in a region forbidden to electrons in the bulk of the crystal, since otherwise the bound state is unstable with respect to leakage of the electron charge into the crystal. We shall see that the binding energies we calculate are small compared to typical values of electronic bandwidths and band gaps encountered in the solid state. Thus this condition can be satisfied if the inner potential is such that an electron at rest far from the crystal has an energy which lies in between two energy bands in the crystal. In this situation, as one enters the crystal, the wave function of the electron will decay to zero exponentially fast in a distance the order of a few angstroms. We shall assume this is the case, and treat the effect of the crystal surface in a phenomenological manner by treating it as a repulsive barrier of height V_0, with the parameter V_0 adjusted so that the decay length of the electron wave function assumes a reasonable value. If the above criterion is not satisfied, the surface-polaron state becomes a virtual level, with a finite lifetime which results from admixture of bulk Bloch states into its wave function.

For the situation described above, where the wave function of the electron decays to zero rapidly as one enters the crystal, the bulk LO phonons will only be excited weakly compared to the surface optical phonons. This is ensured also by the fact that the contribution of a particular bulk LO phonon of wave vector $\vec{Q}$ to the electrostatic potential near the surface vanishes as $\sin Q_z z$, as we have seen. Thus, in this subsection, we ignore all effects that arise from coupling of the electron to bulk LO phonons by setting to zero the matrix element $W(Q_z)$ defined in Sec. IV.

We begin with some remarks about the nature of the contribution to the interaction energy from the third term in Eq. (4.14), the contribution from the surface optical phonons to the energy $E(0)$ of the surface polaron at $k_\parallel=0$. Suppose we first consider the case where the interaction is very weak. Then the electron will be loosely bound to the surface, and its wave function will have a spatial extent large compared to the critical distance $z_s=(\hbar/2m\omega_s)^{1/2}$ introduced in Sec. III.

In this limit the discussion of Sec. III indicates that the term $\lambda\hbar^2Q_\parallel^2/2m^*$ in the denominator of the third term in Eq. (4.14) may be ignored. After the explicit form of $|C(Q_\parallel)|^2$ is inserted into the form that results after this term is ignored, and the sum is converted to an integral, this contribution to the interaction energy becomes

$$V_s = -(\pi n e^{*2}/\mu\omega_s^2)e^2 \int_0^\infty dQ_\parallel M^2(Q_\parallel)\,. \qquad (5.1)$$

In the limit of weak binding, the effect of the small but finite penetration of the electron into the crystal may be ignored. We thus take $\varphi(z)=0$ inside the crystal. If we define $\rho(z)=\varphi^2(z)$, and insert the explicit form of $M^2(Q_\parallel)$ into Eq. (5.1), the integration over $Q_\parallel$ may be carried out in a trivial manner to yield the result

$$V_s = -\frac{e^2}{2}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right)\int_0^\infty dz\,\rho(z)\int_0^\infty \frac{dz'\,\rho(z')}{z+z'}\,. \qquad (5.2)$$

This term has a simple physical interpretation. The function $\rho(z)$ is, to within a factor of e, the charge density of the electron in its bound state. The function

$$e\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right)\int_0^\infty \frac{dz'\,\rho(z')}{z+z'}$$

is the electrostatic potential felt at the point z outside the crystal by virtue of the presence of the image-charge distribution, where the image-charge distribution is, of course, located within the crystal. The interaction energy in Eq. (5.2) is the interaction energy associated with the interaction of the bound distribution of charge (located outside the crystal) with the distributed image charges.

There is one important point to bear in mind that follows from the result in Eq. (5.2). Even in the limit of weak coupling, where the electron-charge cloud is located well outside the critical distance z_s within which the form of the image potential is modified by recoil effects, the image potential cannot in principle be approximated by a simple *local* one-electron potential. The full Hartree form exhibited in Eq. (5.2) must be used, and the potential calculated self-consistently. If one replaces the function $\int_0^\infty dz'\,\rho(z')/(z+z')$ by the result $1/2z$ obtained if one replaces $\rho(z')$ by the localized form $\delta(z-z')$, then the binding energy is considerably overestimated, and the electron wave function is found to be too tightly compressed to the surface.

To illustrate this point, we have carried out a variational calculation of the energy utilizing the function

$$\varphi(z) = 2_\beta^{3/2} z\, e^{-\beta z}, \qquad (5.3)$$

with β the variational parameter. This wave function is a special case of a more general form used by us earlier,[4] and Sak has used it also in his weak-coupling theory. When recoil effects are neglected, the integrals are readily carried out. The energy is minimized when

$$\beta = \frac{1}{5}\frac{me^2}{\hbar^2}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right) = \frac{\alpha}{10 z_s}\left(\frac{2\epsilon_s}{1+\epsilon_s}\right)^{5/4}, \qquad (5.4)$$

and the binding energy (relative to the vacuum level) $E(0)$ at $k_\parallel=0$ is

$$E(0) = -\frac{1}{50}\frac{me^4}{\hbar^2}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right)^2. \qquad (5.5)$$

Suppose we compare these results with those of a calculation which presumes the electron moves in the simple image potential

$$V(z) = -\frac{e(\epsilon_s-1)}{4(\epsilon_s+1)z}\,,$$

with an infinitely repulsive wall located at the crystal surface $z=0$. This is the potential appropriate to a model which has the electron interact only with a point charge located a distance z inside the crystal, rather than the distribution of charge $\rho(z)$ that enters the Hartree potential of Eq. (5.2). The eigenvalues of this latter problem may be obtained exactly, by the standard series-solution method employed in texts on elementary quantum mechanics. One finds the bound-state eigenvalue spectrum has the Rydberg form, with the nth eigenvalue E_n given by

$$E_n = -\frac{me^4}{32\hbar^2}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right)^2\frac{1}{n^2}\,, \quad n=1,2,3,\ldots.$$

The ground-state wave function has precisely the form used in our variational calculation, with β given by

$$\beta = \frac{me^2}{4\hbar^2}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right).$$

A comparison of these two sets of results shows that if the full Hartree potential of Eq. (5.2) is replaced by the simple local image potential

$$V(z) = -\frac{e^2}{4z}\left(\frac{\epsilon_s-1}{\epsilon_s+1}\right),$$

then the binding energy is overestimated by the rather large factor of $\frac{25}{16}$, and the wave function is too tightly bound to the surface. Even in the limit of weak coupling, a self-consistent potential which recognizes that the electron interacts with an extended image-charge distribution must be used. Of course, the quantitative comparison between the two sets of results is sensitive to the form of the variational function chosen for use with the Hartree potential. The results displayed in Eqs. (5.4) and (5.5) are valid only in the limit $\beta z_s < 1$. When the coupling constant α is sufficiently large that this condition is violated, the wave function is localized close enough to the surface that recoil effects must be included in the effective potential. Next we describe calculations we have carried out which include these effects, and allow extension of the results in Eqs. (5.4) and (5.5) to larger values of α. We conclude this subsection with a comparison of our work with the weak-coupling theory of Sak.

To calculate the binding energy of the exterior-surface polaron in the presence of recoil effects, for $\varphi(z)$ we have chosen the form used in our earlier work,

$$\varphi(z)=\begin{cases} Ae^{\gamma z}, & z<0 \text{ (inside crystal)} \\ B(z+z_0)e^{-\beta z}, & z>0 \text{ (outside crystal)}. \end{cases}$$

The constant γ measures the depth of penetration of the electron wave into the crystal. The decay length of the electron wave function is presumably a few angstroms, and is controlled principally by the distance between the vacuum level, and the nearest unfilled band, as discussed above. Thus, in the calculations below, we have regarded γ to be a fixed parameter. Of the four remaining parameters A, B, z_0, and β, three are fixed by the requirement that $\varphi(z)$ be normalized, continuous at the surface, with slopes in the vacuum and in the crystal fit at the surface. One of these parameters remains free, and may be regarded as a variational parameter. We have chosen β as the variational parameter.

First consider the energy of the surface polaron at $\vec{k}_{\parallel}=0$. This energy $E(0)$ measures the binding energy of the surface polaron relative to the energy of the electron when it is infinitely far from the crystal surface. As remarked above, in these calculations, we ignore the contribution to the binding energy from excitation of the bulk phonons by that portion of the electron wave function which penetrates into the crystal. All the calculations have been carried out with the assumption that the band mass $m^*=0.25m$. We also have the static dielectric constant ϵ_s and the polaron coupling constant α as independent parameters. We have fixed ϵ_s at the value 1.4, and we then consider all physical quantities to be functions of α.

In Fig. 2, we present the value of β which minimizes the energy of the surface polaron for $0<\alpha<10$. We plot the dimensionless quantity βz_s, and when this quantity equals unity, then the wave function extends out into the vacuum a distance the order of z_s. The parameter $D=\gamma z_s$, and we have calculated the value of β for $D=10$, and $D=\infty$ (no penetration of the electron wave function into the crystal). When the electron wave penetrates into the crystal, the wave function becomes more compacted to the surface. If recoil effects are ignored, then for $D=\infty$ an analytic expression for β valid for small α is displayed in Eq. (5.4). For $D=\infty$, this expression fits our numerical results for values of α well outside the weak-coupling limit. In fact, for $0<\alpha<5$, the expression in Eq. (5.4) works well. In fact, even for α as large as 10, where in the theory of bulk polarons the wave function of Lee, Low, and Pines provides a poor description of the polaron,[6,7] the simple formula in Eq. (5.4) is in error by only about 15%.

In Fig. 3, we present the binding energy of the surface polaron, in units of $\hbar\omega_s$, for the case $D=10$ and $D=\infty$, with the remaining parameters arranged as described above. In the limit of weak coupling (small α), where recoil effects can be ignored, for $D=\infty$, the results are fit well by Eq. (5.5), which predicts that $E(0)$ will be proportional to α^2. In fact, just as in the case of the parameter β, the simple formula in Eq. (5.5) fits the results quite well for α as large as 5, while the binding energy falls below that predicted by this expression for α greater than 5. If the electron is allowed to penetrate the crystal ($D=10$), then for large α, the binding energy is increased significantly. The physical reason for this is clear, since when the electron wave function penetrates into the crystal, a portion of the electron charge density is placed right at the surface, where the potential set up by a given surface optical phonon is strongest.

Finally, we present calculations of the effective mass of the exterior-surface polaron. If the energy $E(k_{\parallel})$ is expanded in powers of $k_{\parallel}$, then for small $k_{\parallel}$, one has the form

$$E(k_{\parallel})=E(0)+\hbar^2k_{\parallel}^2/2m_p, \tag{5.6}$$

where the polaron effective mass is related to the coefficient of the $k_{\parallel}^2$ term in the manner indicated in Eq. (5.6). From the expressions in Sec. IV we find that if excitation of the bulk LO phonons is ignored, then the effective mass m_p of the surface

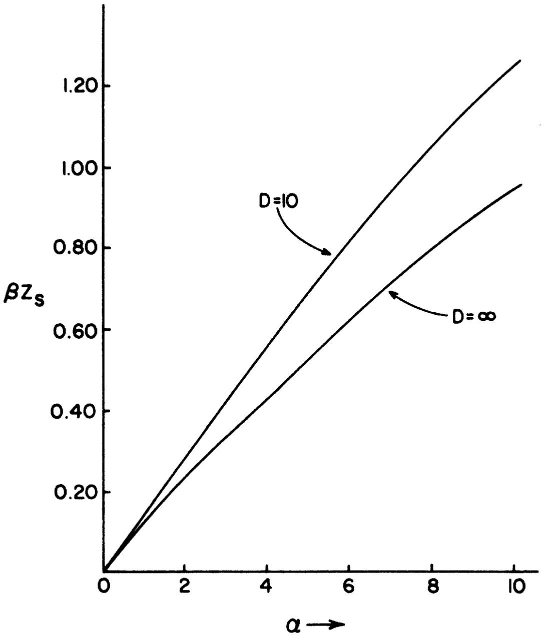

FIG. 2. Value of β which minimizes the energy of the exterior surface polaron, as a function of the polaron coupling constant α. The parameters employed in the calculation are described in the text.

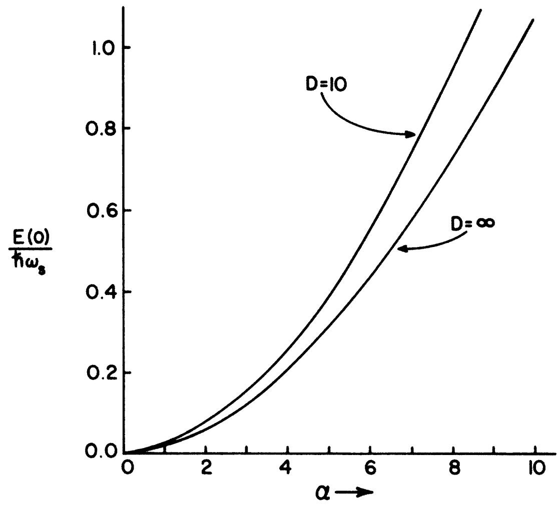

FIG. 3. Binding energy of the exterior surface polaron, as a function of the polaron coupling constant α, for the parameters $D=10$ and $D=\infty$.

polaron is given by

$$m_p = m^*/\lambda + \Delta m, \tag{5.7a}$$

where

$$\Delta m = \frac{e^2\hbar^2}{A} \sum_{Q_\parallel} \frac{Q_\parallel^2 C^2(Q_\parallel) M^2(Q_\parallel)}{(\hbar\omega_s + \lambda\hbar^2 Q_\parallel^2/2m^*)^3} \;. \tag{5.7b}$$

We have computed the polaron effective mass as a function of α, by using the variational function and parameters as described above. For the values of D used in the calculation, λ is well approximated by m^*/m, so that the recoil mass m^*/λ is accurately approximated by the free-electron mass m. The results of the calculation are displayed in Fig. 4.

We conclude this section with some comments on the relationship of our work, and the work of Sak cited earlier. In the paper by Sak, as we mentioned in Sec. I, the theory of the exterior-surface polaron is presented for two limiting cases, the limit of weak coupling where the wave function of the surface polaron consists of a linear combination of a state with zero surface optical phonons, and a state with a single optical phonon excited. He also considers the limit of strong coupling, where the electron–surface-optical-phonon coupling is strong enough to localize the wave function of the electron in the two dimensions parallel to the surface. Our results can be compared with the former case, since our wave function is applicable only for coupling constants small enough to the electron probability density remains extended in the two dimensions parallel to the surface.

If we expand our wave function in powers of $f_{Q_\parallel}$, and compare the one-phonon part with the function utilized by Sak at the beginning of his discussion of the weak-coupling theory, one important difference is apparent. Sak allows $f_{Q_\parallel}$ to vary with z, and eliminates $f_{Q_\parallel}$ from the equation for $\varphi(z)$ to obtain an integral equation for $\varphi(z)$. However, he does not solve this equation, but moves on to use a variational wave function with $f_{Q_\parallel}$ independent of z to obtain all results displayed in his paper, in the portion on the weak-coupling theory. Thus, while it would be very interesting to compare the predictions of our wave function for small α with those deduced from the more general form used by Sak at the beginning of his paper, there are no explicit results for either the binding energy or effective mass displayed by him until he ignores the z dependence of $f_{Q_\parallel}$. To obtain values of the binding energy and effective mass for his general case would require the solution of a rather complex integral equation, unfortunately.

The expression for the energy of the exterior-surface polaron at $\vec{k}_\parallel = 0$ provided by the weak-coupling theory of Sak is identical to our Eq. (4.14), with $W(Q_z)$ assumed zero and excitation of the bulk LO phonons by the surface polaron ignored. Thus, there is a direct analogy between the theory of surface polarons and bulk-polaron theory, since in bulk-polaron theory a calculation which treats the electron–bulk LO-phonon interaction by second-

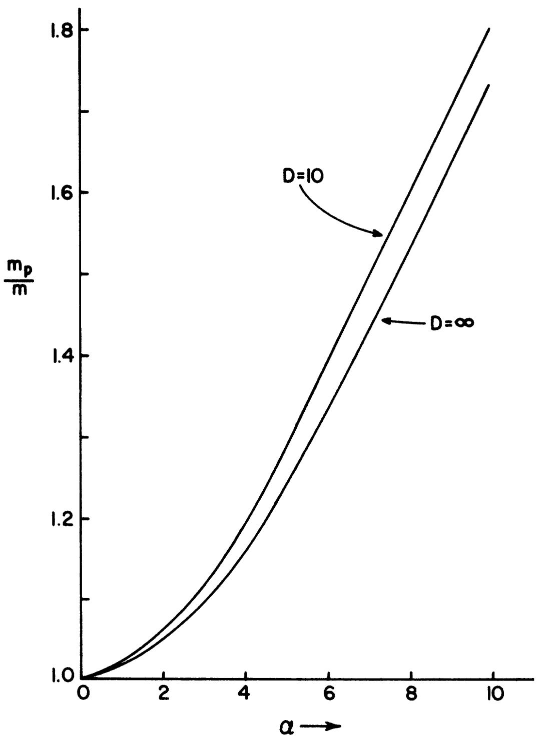

FIG. 4. Effective mass of the exterior surface polaron, as a function of α for $D=10$ and $D=\infty$. The parameters employed in the calculation are described in the text.

order perturbation theory produces the same expression for the polaron binding energy as the theory of Lee, Low, and Pines, even though the wave function of Lee, Low, and Pines includes multiphonon states.[6,7] Sak has not explored the variation of the exterior-surface-polaron binding energy with α in detail, however. He does use a variational wave function identical to ours in the limit $D\rightarrow\infty$ (no penetration of the electron wave function into the crystal) to extract an analytic expression for $E(0)$ valid when $\beta z_s \gg 1$ [see his Eq. (28)]. Our calculation yields a similar result in this limit, however the numerical calculations described above suggest that this limit is not realized for the range of values of α explored here. Thus, we feel this limit will not be realized in practice.

Sak has also included the effect of allowing the background dielectric constant ϵ_∞ to differ from unity. However, he does this by including in the Schrödinger equation for the electron the single-particle local potential $e^2(\epsilon_\infty - 1)/4(\epsilon_\infty + 1)z$, while the argument we presented above suggests that even if recoil effects are ignored for the polarization oscillators responsible for producing $\epsilon_\infty > 1$, the image potential seen by an electron outside the crystal should come not from a point-image charge, but from the distributed image-charge density $e\,|\,\varphi(z)\,|^2$ inside the crystal. Thus Sak's means of introducing a background dielectric constant greater than unity may lead to important quantitative errors. In the example given above, we have seen that Sak's procedure appears in the limit of small α to lead to a polaron wave function too tightly bound to the surface, and an overestimate of the binding energy.

Sak's theory also produces for the polaron effective mass the expression

$$\frac{1}{m_p}=\frac{1}{m}-\frac{\Delta m}{m^2}$$

for $D=\infty$, where Δm is given in Eq. (5.7b). There is again a close relation between the expression provided by the Lee-Low-Pines approach and the perturbative approach.

B. Interior-Surface Polaron

In this subsection, we consider an electron inside the crystal, moving with energy near the bottom of the conduction band. The bottom of the conduction band is presumed to lie below the vacuum level by an energy the order of a few electron volts. The wave function of the electron then is confined to the volume occupied by the crystal, and the wave function decays to zero in an exponential manner as the coordinate of the electron moves into the vacuum outside the crystal.

When the electron is well into the bulk of the crystal, it is clothed by a cloud of virtual bulk LO phonons. Its energy (at $\vec{k}=0$) is lowered below that of the bottom of the conduction band associated with the rigid crystal as a consequence. If this polaron binding energy is computed by means of the procedure introduced by Lee, Low, and Pines, one finds the polaron binding energy is given by the simple expression $\alpha^*\hbar\omega_L$, where α^* is the polaron coupling constant computed with the band structure mass m^*. Now imagine the polaron is brought toward the crystal surface. When it comes close enough to the crystal surface to couple to the surface optical phonons, its energy will be lowered, since it will now acquire a cloud of virtual surface optical phonons. If the energy of the polaron is lowered below that of the bulk polaron, it will remain trapped at the surface in a bound state.

It is not at all clear that such a bound state will exist, however. To speak in physical terms, when the polaron comes within one bulk polaron radius of the surface [the radius of the bulk polaron is the order of $z_p=(\hbar/2m^*\omega_L)^{1/2}$], the cloud of bulk LO phonons which clothe the electron must be distorted or altered in a way that is surely unfavorable from an energetic point of view. Whether or not binding occurs depends on which of the two competing effects is the dominant one. Recall the discussion of Sec. III, where we saw that while the effective potential obtained there was repulsive when the electron is far from the surface, an attractive well existed near the surface. In order to tell whether the attractive well can produce binding, of course, the full form of the nonlocal effective potential must be used.

We have carried out a study of the binding energy of the interior-surface polaron at $\vec{k}_\parallel=0$ by utilizing the full expression given in Eq. (4.14). The bottom of the conduction band was assumed to lie a distance V_0 below the vacuum level, and the surface was represented by a step potential, as in the case in Sec. V A on the exterior-surface polaron. In fact, the variational wave function was presumed to have the same form as that used in the study of the exterior-surface polaron, except that the exponential tail $e^{-\gamma z}$ was now allowed to extend into the vacuum, and the parameter β describes the penetration of the bound state into the vacuum. Once again, γ was regarded to be fixed at a value the order of a few Å^{-1}, and β is the sole variational parameter.

To carry out the calculation, one chooses a value of β, and then computes the parameter ξ defined in Eq. (4.11). The result is then inserted into Eq. (4.14), and the energy is computed. A plot of the energy as a function of β showed the existence of a well-defined minimum in all cases we explored. The binding energy ϵ of the interior-surface polaron is then given by $\epsilon=\hbar\omega_L\alpha^*+E(0)$, where a real bound state exists only if $\epsilon<0$.

In Fig. 5, we plot the binding energy of the in-

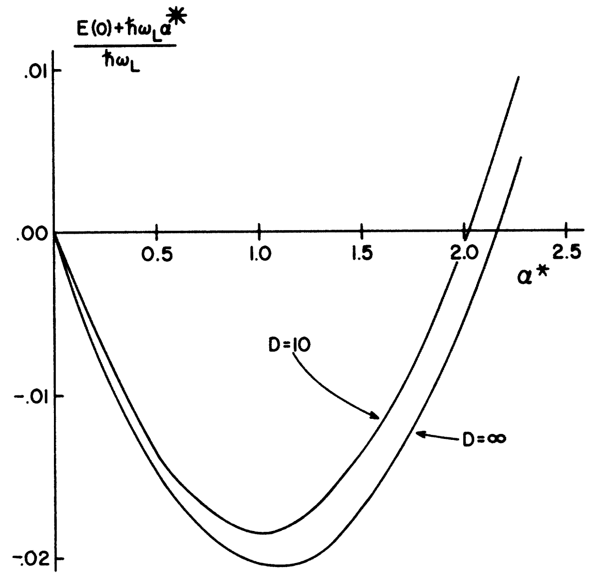

FIG. 5. Energy of the interior-surface polaron, as a function of α^*, for the parameters described in the text. The quantity $[E(0)-\hbar\omega_L\alpha]/\hbar\omega_L$ is the negative of the binding energy.

terior-surface polaron as a function of α^*, the polaron coupling constant defined in Eq. (3.6a) with the mass m replaced by the band-structure effective mass m^*. The parameter D is given by γz_p, and has been chosen as indicated in the figure. The binding energy is seen to be very small indeed. Furthermore, for α^* slightly greater than 2, the bound state ceases to exist, in the sense that the energy associated with our variational wave function lies higher than that of the bulk polaron at $\vec{k}=0$. Thus, while in our earlier note,[4] we conjectured that for large α in particular, inclusion of the bulk LO phonons in the calculation in an explicit manner would lower the binding energy, the effect is much more severe than we supposed.

In Fig. 6(a), the values of β which minimize the energy of the interior-surface polaron are plotted as a function of α^* which produce a bound state, the wave function of the interior-surface polaron extends quite far into the crystal, a distance the order of 100 Å on the nearly flat portion of the curve. In Fig. 6(b), we present the values of the parameter $\xi_m z_p$, where ξ_m is the value of ξ computed for the β which minimized $E(0)$. This parameter increases with α^*, and its presence in the denominator of the term in Eq. (4.14) which gives the contribution from the bulk LO phonons to the binding energy plays an important role in depressing the energy of the interior-surface polaron below that of the bulk polaron.

The binding energies of the interior-surface-polaron calculated in this paper are sufficiently small that these states, if they exist under realistic conditions, can affect the properties of the surface of the crystal only at rather low temperatures, since otherwise they will be thermally ionized.

APPENDIX: DEVIATION OF AN IDENTITY USED IN SEC. IV

In this Appendix we derive the identity displayed in Eq. (4.7i) of the text. Begin by noticing that the identity

$$e^{(A+B)}=e^{A}e^{B}e^{-[A,B]/2}$$

may be utilized to write U_B in the form

$$U_B=\exp\left(\frac{1}{2}\sum_{\vec{Q}}|g_Q|^2\right)\exp\left(+\sum_{\vec{Q}}g_Q\,e^{iQ_z z}b_{\vec{Q}}\right)\times\exp\left(-\sum_{\vec{Q}}g_Q^*e^{-iQ_z z}b_Q^\dagger\right). \quad \text{(A1)}$$

Through the use of this form for U_B, one finds that

$$U_B\frac{\partial}{\partial z}U_B^\dagger=\frac{\partial}{\partial z}+i\sum_{\vec{Q}}Q_z g_Q U_B^\dagger b_Q U_B e^{+iQ_z z}+i\sum_{\vec{Q}}Q_z g_Q^* b_Q^\dagger e^{-iQ_z z}.$$

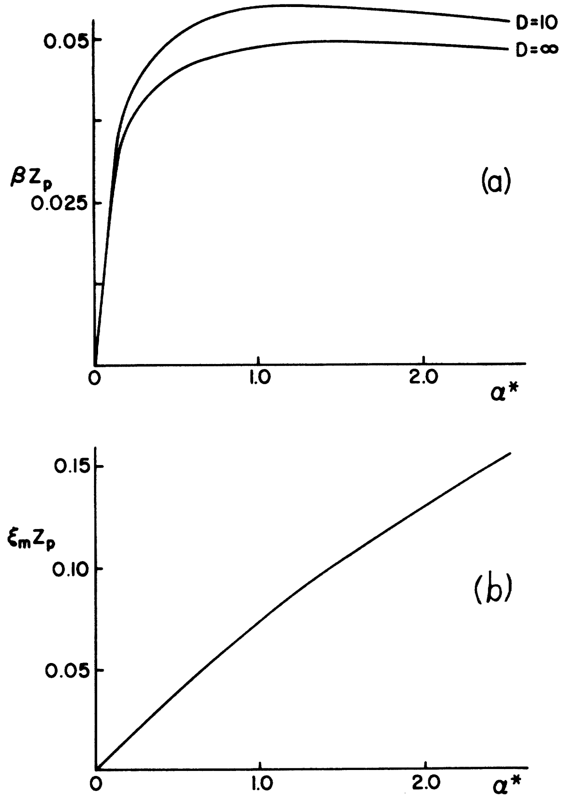

FIG. 6. (a) Quantity βz_p is plotted as a function of α^*, for the parameters described in the text. (b) Parameter $\xi_m z_p$ is plotted as a function of α^*, for the parameters described in the text. The curves for $D=10$ and $D=\infty$ coincide, to within graphical accuracy.

Upon noting that

$$U_B^\dagger b_{\vec{Q}} U_B = b_Q - g_Q^* e^{-iQ_z z},$$

one finds that

$$U_B \frac{\partial}{\partial z} U_B^\dagger = \frac{\partial}{\partial z} - i \sum_{\vec{Q}} Q_z \, |g_Q|^2 + i \sum_{\vec{Q}} Q_z (g_Q b_Q e^{iQ_z z} + g_Q^* b_Q^\dagger e^{-iQ_z z}). \quad \text{(A2)}$$

We wish to compute the expectation value

$$\langle T_\perp \rangle = -\frac{\hbar^2}{2m^*} \int dz \, \varphi^*(z) \left\langle 0 \middle| U_B^\dagger \frac{\partial}{\partial z} f(z) \frac{\partial}{\partial z} f(z) \frac{\partial}{\partial z} U_B \middle| 0 \right\rangle$$

$$= -\frac{\hbar^2}{2m^*} \int dz \, \varphi^*(z) \left\langle 0 \middle| U_B^\dagger \frac{\partial}{\partial z} U_B f(z) U_B^\dagger \frac{\partial}{\partial z} U_B \middle| 0 \right\rangle .$$

Upon utilizing the identity given in Eq. (A2), and evaluating the matrix elements of $b_{\vec{Q}}$ and $b_{\vec{Q}}^\dagger$ that enter the expression, one finds that

$$\langle T_\perp \rangle = -\frac{\hbar^2}{2m^*} \int dz \, \varphi^*(z) \frac{\partial}{\partial z} f(z) \frac{\partial}{\partial z} \varphi(z)$$

$$- i \frac{\hbar_i^2}{2m^*} \sum_{\vec{Q}} Q_z \, |g_Q|^2 \left[\int dz \, \varphi^* \frac{\partial}{\partial z} f \, \varphi + \int dz \, \varphi^* f \frac{\partial \varphi}{\partial z} \right]$$

$$+ \frac{\lambda \hbar^2}{2m^*} \left[\sum_{\vec{Q}} Q_z^2 \, |g_Q|^2 + \left(\sum_{\vec{Q}} Q_z \, |g_Q|^2 \right)^2 \right]. \quad \text{(A3)}$$

After performing a partial integration on the first of the two integrals in the first set of square brackets in Eq. (A3), one finds the two integrals equal

$$\int dz f(z) \left(\varphi^* \frac{\partial \varphi}{\partial z} - \varphi \frac{\partial \varphi^*}{\partial z} \right),$$

which vanishes when φ^* is real, the situation of interest here. The right-hand side of Eq. (A3) then equals the right-hand side of Eq. (4.7i) in the text.

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