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Theory of Surface Polarons*

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We attempt to determine the binding energy and the wave function of the ground state of an electron that is attracted to the surface of an ionic crystal by its image potential and is repelled from the interior of the solid. For ionic crystals, such as LiF, the electrostatic theory is inadequate and the solid must be treated as a dynamical system. For shallow levels, the correction to the electrostatic approximation is small and behaves asymptotically as z^{-3}, where z is the distance from the surface. The mass of a shallow electron is not enhanced. For deep levels the ground-state energy is calculated by a variational procedure in the limits of both weak and strong electron-phonon coupling. For the ground-state energy of an electron trapped on the LiF surface we find the value -0.29 eV. The mass of the deeply bound electron is enhanced.

I. INTRODUCTION

Let us consider an insulator which has a bottom of the conduction band above the vacuum level (Fig. 1). An electron outside the insulator induces positive charges on the surface and is attracted to it by the force whose potential is[1]

$$V_{\mathrm{im}}(z)=\frac{e^2}{4}\,\frac{\epsilon_s-1}{\epsilon_s+1}\,\frac{1}{z}\,, \tag{1}$$

where ϵ_s is the static dielectric constant and z is the distance of the electron from the surface which is considered to be a plane. For sufficiently low energy the electron cannot penetrate inside the insulator.

Cole and Cohen[2,3] worked out a theory of the surface states which are induced by the potential (1) and applied it to atomic and molecular insulators

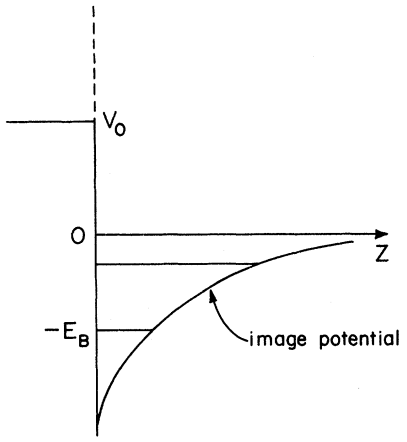

FIG. 1. Image potential of the electron outside an insulator.

such as He, Ne, H_2, and D_2, both solid and liquid. In these materials $\epsilon_s - 1$ is small so that the surface states have small binding energies ranging from 0.39 meV for liquid He^3 to 21.9 meV for solid D_2. The polarization is electronic and is associated with the excitation of virtual electron-hole pairs across the energy gap of several electron volts. Therefore the conditions for the validity of the electrostatic approximation (1) are satisfied in the work of Cole and Cohen.

In this paper we shall study the problem of the surface states in a situation for which the energy of the surface-bound electron is not negligible in comparison to the energy of the polarization quantum (e.g., LiF). Here the polarization has two components, an electronic one and one associated with the displacement of the ions. To estimate the ratio of the binding energy and the longitudinal-optical-phonon energy we use for LiF[4] $\epsilon_s = 8.65$ (at 77 °K) and $\hbar\omega_L = 0.08$ eV for the optical-phonon energy. The ground-state level of the electron in the potential (1) is -0.5 eV, provided the wave function vanishes at the surface (hydrogenic approximation[2,3]). The conclusion is that the electron moves too fast for the ions to follow its motion and the electrostatic approximation is not adequate for LiF. Obviously, we are dealing here with a surface polaron. We need a theory which treats the dielectric as a dynamical system. In Sec. II the Hamiltonian for the surface polaron is derived. As in the case of the bulk polaron in an external field, various situations are possible depending on the values of ϵ_s, ϵ_∞ (optical dielectric constant), and $\hbar\omega_L$. In Sec. III we study the weak electron-phonon coupling for both shallow and deep surface states. The subject of Sec. IV is the strong electron-phonon coupling. The theory is applied to LiF for which numerical values of the ground-state binding energy and of the characteristic dimensions of the wave function are calculated.

II. HAMILTONIAN

The Hamiltonian has three parts: electronic, one describing the dielectric in the absence of the electron, and electron dielectric interaction. The electronic part has the form

$$H_{el} = \frac{p^2}{2m} - \frac{e^2 E_\infty}{4}\frac{1}{z}\ , \quad z>0\ ; \tag{2}$$

here $E_\infty = (\epsilon_\infty - 1)/(\epsilon_\infty + 1)$. The dielectric fills the half-space $z<0$. It is assumed that the electronic part of the polarization can follow the electron adiabatically and therefore formula (1) is applicable to it. In LiF the forbidden gap is 13 eV, while the binding energy will be shown to be around 0.3 eV. We also assume that the potential difference V_0 between the vacuum level and the bottom of the conduction band is much larger than the binding energy. For LiF, the photoemission experiments and the band-structure calculations[5] show that $V_0 \approx 2$–4 eV. Therefore, the electron spends very little time inside the dielectric and we may simplify the problem by replacing the step V_0 by an impenetrable wall. This approximation is discussed in detail by Cole.[3]

The dielectric is treated as a continuum and its Hamiltonian can be written as a sum of independent oscillators corresponding to its eigenmodes. It is well known from the work of Ritchie[6] and Stern and Ferrell[7] that the surface of a metal can support a new kind of excitation—a surface plasmon. Similarly, there exist surface optical phonons which propagate along the surface of a dielectric. The theory of the surface phonons has been worked out by Fuchs and Kliewer.[8] Following their work we have for the polarization associated with the surface modes

$$\vec{p}_s = p_s^{(0)}(i\kappa_x e^{\kappa z}, i\kappa_y e^{\kappa z}, \kappa e^{\kappa z}) e^{i\vec{\kappa}\cdot\vec{\rho}}\ , \tag{3}$$

where $\vec{\kappa}$ is a two-dimensional wave vector perpendicular to the z axis. If the surface has a shape of a large square ($L\times L$) and periodic boundary conditions are imposed, then the allowed values of $\vec{\kappa}$ are $(2\pi n/L, 2\pi m/L)$ with n, m integers. $\vec{\rho}$ is a position vector of a point on the surface. The frequency ω_s of these modes is given by the following formula:

$$\omega_s^2 = \tfrac{1}{2}(\omega_L^2 + \omega_T^2), \tag{4}$$

where ω_L and ω_T are the frequencies of the bulk longitudinal and transverse phonons (see Fig. 2). The bulk phonons also belong to the excitation spectrum of the dielectric but it has been shown by Sunjic and Lucas[9] and by Mahan,[10] that the bulk optical-longitudinal phonons give rise to zero electric field outside the dielectric and therefore do

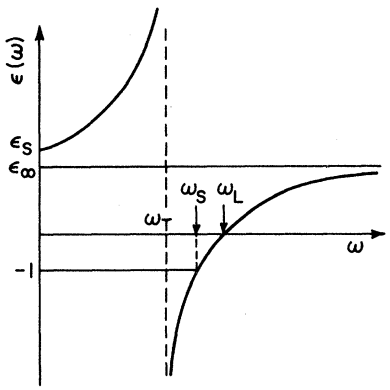

FIG. 2. Phenomenological model of the dielectric is fully characterized by the values of three parameters ϵ_∞, ϵ_s, and ω_T.

not couple to the electron which does not penetrate inside. The transverse modes have zero polarization charges both in the volume ($\mathrm{div}\vec{P}=0$) and on the surface ($P_n=0$) and do not give rise to an electric field. Thus, the phonon part of the Hamiltonian can be written as

$$H_{\mathrm{ph}}=\hbar\omega_s\textstyle\sum_{\vec{k}} a_{\vec{k}}^{\dagger}a_{\vec{k}}\,, \tag{5}$$

keeping only the surface phonons. $a_{\vec{k}}^{\dagger}$ and $a_{\vec{k}}$ are the creation and destruction operators for the surface phonons, obeying the usual commutation relations $[a_{\vec{k}},\ a_{\vec{k}'}^{\dagger}]=\delta_{\vec{k}\vec{k}'}$, etc.

The interaction between the electron and the polarization field is

$$H_{\mathrm{int}}=-e\int \vec{p}_s(\vec{r}\,')\cdot\frac{(\vec{r}\,'-\vec{r})}{|\vec{r}\,'-\vec{r}|^3}\,dV'\,, \tag{6}$$

where $\vec{r}$ is the position vector of the electron. In terms of the creation and destruction operators the interaction can be written in the form[9,11]

$$H_{\mathrm{int}}=2\pi i\left(\frac{\hbar e^2}{2\delta S\omega_s}\right)^{1/2}\sum_{\vec{k}}\frac{e^{-\kappa z}}{\sqrt{\kappa}}\,(e^{-i\vec{k}\cdot\vec{\rho}}a_{\vec{k}}^{\dagger}-e^{i\vec{k}\cdot\vec{\rho}}a_{\vec{k}}) \tag{7}$$

where $S=L^2$ is the normalization area, z is the distance of the electron from the surface, and δ is given by

$$2\pi/\delta\omega_s^2=E_s-E_\infty\,, \tag{8}$$

where $E_s=(\epsilon_s-1)/(\epsilon_s+1)$. The total Hamiltonian H is the sum $H_{\mathrm{el}}+H_{\mathrm{ph}}+H_{\mathrm{int}}$.

We define the coupling constant in analogy to the bulk polaron[12]:

$$\alpha_s=e^2(E_s-E_\infty)(m/2\hbar^3\omega_s)^{1/2}\,. \tag{9}$$

III. WEAK ELECTRON-PHONON COUPLING

In the weak-coupling limit[13] (first order in α_s), we restrict the Hilbert space to include only the zero- and one-phonon states. We write the state vector corresponding to the total momentum $\vec{k}$ parallel to the surface in the form

$$|\psi\rangle=\varphi(z)e^{i\vec{k}\cdot\vec{\rho}}|O\rangle+\textstyle\sum_{\vec{\kappa}} c_{\vec{\kappa}}(z)e^{i(\vec{k}-\vec{\kappa})\cdot\vec{\rho}}a_{\vec{\kappa}}^{\dagger}|O\rangle\,, \tag{10}$$

where $|O\rangle$ is the phonon "vacuum" and the functions $\varphi(z)$ and $c_{\vec{\kappa}}(z)$ are to be determined. Since the probability for the electron to be on the surface is zero, we have the boundary conditions

$$\varphi(z=0)=0\,,\quad c_{\vec{\kappa}}(z=0)=0\,. \tag{11}$$

Putting the expression (10) into the Schrödinger equation, and equating the zero- and one-phonon components on both sides, we get a system of coupled equations for $\varphi(z)$ and $c_{\vec{\kappa}}(z)$:

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(z)}{dz^2}-\frac{e^2E_\infty}{4z}\varphi(z)-iV\sum_{\vec{\kappa}}\frac{e^{-\kappa z}}{\sqrt{\kappa}}\,c_{\vec{\kappa}}(z)$$

$$=\left(E-\frac{\hbar^2k^2}{2m}\right)\varphi(z)\,, \tag{12}$$

$$iV\frac{e^{-\kappa z}}{\sqrt{\kappa}}\,\varphi(z)-\left(\frac{\hbar^2}{2m}\frac{d^2}{dz^2}+\frac{e^2E_\infty}{4z}\right)c_{\vec{\kappa}}(z)=-\frac{\hbar^2\gamma^2}{2m}\,c_{\vec{\kappa}}(z)\,, \tag{13}$$

where

$$V=2\pi(\hbar e^2/2\delta S\omega_s)^{1/2}\,,$$

$$\gamma^2=(\vec{k}-\vec{\kappa})^2-\frac{2m}{\hbar^2}\,(E-\hbar\omega_s)\,.$$

E is an eigenvalue of H which for a given $\vec{k}$ has a discrete spectrum.

Instead of the system of the coupled Eqs. (12) and (13), we can get a closed equation for φ by solving Eq. (13) for $c_{\vec{\kappa}}$ in terms of φ and substituting into Eq. (12). The calculation goes according to the method of the variation of constants.[14] The resulting equation for φ has the form

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dz^2}-\frac{e^2E_\infty}{4z}\varphi-\frac{mV^2}{\hbar^2}\sum_{\vec{\kappa}}\frac{e^{-\kappa z}}{\kappa}\,\frac{\Gamma(1-K)}{\gamma}$$

$$\times\left(W_{K,1/2}(2\gamma z)\int_0^z e^{-\kappa\zeta}M_{K,1/2}(2\gamma\zeta)\varphi(\zeta)\,d\zeta\right.$$

$$\left.+M_{K,1/2}(2\gamma z)\int_z^\infty e^{-\kappa\zeta}W_{K,1/2}(2\gamma\zeta)\varphi(\zeta)\,d\zeta\right)$$

$$=\left(E-\frac{\hbar^2k^2}{2m}\right)\varphi\,, \tag{14}$$

where $K=me^2E_\infty/4\hbar^2\gamma$ and $W_{K,1/2}$ and $M_{K,1/2}$ are Whittaker functions.[15] Equation (14) is too difficult to solve exactly but approximate solutions can be obtained in the cases of shallow and deep bound states.

A. Shallow States

If the binding energy of the electron E_B and its kinetic energy along the surface are considerably smaller than the surface phonon energy then we expect the electrostatic theory based on Eq. (1) to give an adequate description of the system. Even if the condition $E_B\ll\hbar\omega_s$ is not satisfied for the ground state it will be valid for sufficiently high excited states. The question arises: What are the corrections to the potential (1)?

Because of the exponential dependence of the electron-phonon matrix element, Eq. (7), only the phonons with the wave vector $\kappa\lesssim z_0^{-1}$ will effectively interact with the electron; z_0 is the average distance of the electron from the surface. Thus, for a shallow state, $\kappa\ll\gamma\approx(2m\omega_s/\hbar)^{1/2}$. We also assume that the momentum of the electron along the surface is small: $k\ll\gamma$. We are interested in the corrections to the electrostatic image potential for distances z of the order of z_0. Then

the arguments of the Whittaker functions in Eq. (14) are large and we may use the asymptotic expressions[15]

$$M_{K,1/2}(2\gamma z)\approx\frac{1}{\Gamma(1-K)}\,e^{\gamma z}(2\gamma z)^{-K}\left(1+\frac{me^2E_\infty}{8\hbar^2\gamma^2}\,\frac{1}{z}\right), \tag{15}$$

$$W_{K,1/2}(2\gamma z)\approx e^{-\gamma z}(2\gamma z)^{K}\left(1+\frac{me^2E_\infty}{8\hbar^2\gamma^2}\,\frac{1}{z}\right), \tag{16}$$

where the fact that $K\ll 1$ for shallow states was also used. The integrals in Eq. (14) have exponentials $e^{\gamma z}$ and $e^{-\gamma z}$. Therefore they can be approximated by the following asymptotic expressions:

$$\int_0^z f(\zeta)e^{\gamma\zeta}\,d\zeta\approx(1/\gamma)\,[f(z)-(1/\gamma)f'(z)+(1/\gamma^2)f''(z)]\,e^{\gamma z}, \tag{17}$$

$$\int_z^\infty f(\zeta)e^{-\gamma\zeta}\,d\zeta\approx(1/\gamma)\,[f(z)+(1/\gamma)f'(z)+(1/\gamma^2)f''(z)]\,e^{-\gamma z}. \tag{18}$$

Using the asymptotic approximations in Eq. (14) the summation takes the form $\sum_{\vec\kappa}e^{-2\kappa z}\times$ (slowly varying function of κ). The slowly varying function is expanded into a Taylor series. Keeping only the terms leading to corrections of the order $E_B^2/\hbar\omega_s$ or lower in the effective wave equation, we get

$$-\frac{\hbar^2}{2m}\varphi''-\frac{e^2E_\infty}{4z}\varphi+\frac{2mV^2}{\hbar^2}\left[-\frac{\hbar S}{8m\omega_s\pi}\,\frac{\varphi}{z}+\frac{S}{8\pi m\omega_s^2}\left(\frac{\hbar^2k^2}{2m}-E\right)\frac{\varphi}{z}+\frac{\hbar^2S}{16\pi m^2\omega_s^2}\left(-\frac{\varphi''}{z}+\frac{\varphi'}{z^2}-\frac{2me^2E_\infty}{\hbar^2z^2}\varphi\right)\right]=\left(E-\frac{\hbar^2k^2}{2m}\right)\varphi\,. \tag{19}$$

The first term in the square brackets combines with the image potential of the electronic polarization to give the electrostatic image potential. The second term contains the energy and in order to put the equation into a form of an eigenvalue problem we bring it to the right-hand side and multiply the equation by $1-(E_s-E_\infty)e^2/4\hbar\omega z$. As a result we get

$$\left(\frac{p_z^2}{2m}-\frac{e^2E_s}{4z}+i\,\frac{(E_s-E_\infty)e^2}{8m\omega_s}\,\frac{1}{z^2}\,p_z\right)\varphi=\left(E-\frac{\hbar^2k^2}{2m}\right)\varphi\,. \tag{20}$$

In the process of obtaining Eq. (20) a term was dropped which contains $(E_s-E_\infty)^2$, which makes it proportional to α_s^2. Equation (20) has a form of a wave equation but its "Hamiltonian" is non-Hermitian. We introduce the renormalized amplitude F

$$\varphi=\left(1-\frac{(E_s-E_\infty)e^2}{8\hbar\omega_s z}\right)F\,. \tag{21}$$

In terms of F, Eq. (20) takes the form

$$\left(\frac{p_z^2}{2m}-\frac{e^2E_s}{4z}+\frac{\hbar(E_s-E_\infty)e^2}{8m\omega_s}\,\frac{1}{z^3}\right)F=\left(E-\frac{\hbar^2k^2}{2m}\right)F\,. \tag{22}$$

As we expected, the effective potential is essentially the static image potential plus a correction of the relative order $\alpha_s r_{pol}/z_0$, where $r_{pol}=(\hbar/m\omega_s)^{1/2}\ll z_0$, the average distance of the electron from the surface. It must be emphasized that we neglected terms of relative order α_s^2 so that the condition of the validity of Eq. (22) is not only the smallness of α_s (weak coupling) and $r_{pol}/z_0\ll 1$ (shallow states), but also $\alpha_s\ll r_{pol}/z_0$.

The image charge is a point charge in the static limit. When the dielectric is treated as a dynamical system, the image charge will no longer be strictly a point and deviations which occur are described by the correction term in Eq. (22). This term vanishes in the static limit $\omega_s\to\infty$. The use of asymptotic expansions renders Eq. (22) inapplicable for $z\lesssim r_{pol}$. Although this region is small in comparison with the dimensions of the wave function, the singularity $1/z^3$ is so strong that the term cannot be treated by perturbation theory.

B. Deep States

When the binding energy is larger than the surface-phonon quantum, the electron moves too fast in the z direction for the ions to follow its motion. The situation is better described by saying that the ions adjust their positions to an average field of the electron (averaged in the z direction only, however). We are still treating the weak coupling case and use the ansatz[16]

$$|\psi\rangle=\varphi(z)\,(e^{i\vec k\cdot\vec\rho}+\textstyle\sum_{\vec\kappa}c_{\vec\kappa}^{(0)}\,e^{i(\vec k-\vec\kappa)\cdot\vec\rho}\,a_{\vec\kappa}^\dagger|0\rangle)\,. \tag{23}$$

$\varphi(z)$ and $c_{\vec\kappa}^{(0)}$ are to be determined variationally. For a given φ we can define an effective Hamiltonian

$$H_{eff}[\varphi]=\int_0^\infty dz\,\varphi^*(z)\,H\varphi(z)=\int_0^\infty dz\,\varphi^*\left(-\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial z^2}-\frac{e^2E_\infty}{4z}\right)\varphi-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)+\hbar\omega_s\sum_{\vec k}a_{\vec k}^\dagger a_{\vec k}$$

$$+2\pi i\left(\frac{\hbar e^2}{2\delta S\omega_s}\right)^{1/2}\sum_{\vec k}\frac{1}{\sqrt{\kappa}}\int_0^\infty dz\,\varphi^*(z)\,e^{-\kappa z}\varphi(z)\,(e^{-i\vec k\cdot\vec\rho}\,a_{\vec k}^\dagger-e^{i\vec k\cdot\vec\rho}\,a_{\vec k})\,. \tag{24}$$

This is a Hamiltonian of a two-dimensional polaron where the electron-phonon interaction elements are functionals of $\varphi(z)$. Assuming $\varphi(z)$ in the form

$$\varphi(z) = 2(\tfrac{1}{2}\beta)^{3/2} z\, e^{-\beta z/2} \ , \tag{25}$$

we have

$$H_{\text{eff}} = \frac{\hbar^2\beta^2}{8m} - \frac{e^2 E_\infty}{8}\beta + \frac{1}{2m}(p_x^2+p_y^2) + \hbar\omega_s \sum_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} + 2\pi i\left(\frac{\hbar e^2}{2\delta S\omega_s}\right)^{1/2} \sum_{\vec{k}} \frac{1}{\kappa^{1/2}} \frac{\beta^3}{(\kappa+\beta)^3} \times (e^{-i\vec{k}\cdot\vec{\rho}} a_{\vec{k}}^\dagger - e^{i\vec{k}\cdot\vec{\rho}} a_{\vec{k}}) \ . \tag{26}$$

Now we use the condition that the electron-phonon coupling is weak. In analogy to the three-dimensional case, [13] the energy is given by the second-order perturbation formula

$$E(k) = \frac{\hbar^2\beta^2}{8m} - \frac{e^2 E_\infty}{8}\beta + \frac{\hbar^2 k^2}{2m} - \frac{2\pi^2\hbar e^2}{\delta S\omega_s} \times \sum_{\vec{k}} \frac{1}{\kappa} \frac{\beta^6}{(\kappa+\beta)^6} \frac{1}{\hbar\omega_s - \hbar^2\vec{k}\cdot\vec{\kappa}/m + \hbar^2\kappa^2/2m} \ . \tag{27}$$

Strictly speaking we should determine the energy exactly within the zero plus one phonon space. However, to the first order in α_s the result is the same as given by the Rayleigh–Schrödinger perturbation expansion. The energy (27) is then minimized with respect to β. This is best done numerically and an application of Eq. (27) to LiF will be discussed below.

For very deep levels, $\beta \gg 1/r_{\text{pol}}$. The region of the variable κ which contributes significantly to the sum in Eq. (27) is limited to the values $\kappa \lesssim r_{\text{pol}}^{-1}$. Therefore, we may approximate $\kappa+\beta \approx \beta$. Then we expand the right-hand side of Eq. (28) in powers of k. For $k=0$ we have

$$\Delta E(k=0) = -\tfrac{1}{2}\pi\alpha_s\hbar\omega_s \ . \tag{28}$$

The coefficient in front of the quadratic term determines the effective mass

$$m^* = m(1+\tfrac{1}{8}\pi\alpha_s) \ . \tag{29}$$

Let us note that the mass is renormalized only in the case of the deep levels, but not for shallow states. The reason for this can be traced to the exponential dependence of the electron-phonon matrix element. Generally, the mass renormalization depends on the function $\varphi(z)$ and, roughly speaking, is proportional to the time the electron spends in the region near the surface $z \lesssim r_{\text{pol}}$. The formula (29) gives the maximum enhancement (within the weak-coupling scheme) for very deep states. As the energy level becomes shallower, the mass renormalization factor approaches unity and the electron is effectively out of contact with the surface for very shallow levels.

IV. STRONG COUPLING

For large values of the electron-phonon coupling constant, we use in analogy to the three-dimensional polaron problem, [12] the ansatz

$$|\psi\rangle = \Omega(\vec{r})|\phi\rangle \ , \tag{30}$$

where $\Omega(\vec{r})$ depends only on the electron position and $|\varphi\rangle$ only on the field coordinates. We insert expression (30) into the Schrödinger equation, multiply from the left by Ω^*, and integrate over the electron coordinates. The resulting equation for $|\phi\rangle$ has the form

$$\Big[\int d^3\vec{r}\,\Omega^*\left(\frac{p^2}{2m} - \frac{e^2E_\infty}{4z}\right)\Omega + \hbar\omega_s\sum_{\vec{k}} a_{\vec{k}}^\dagger a_{\vec{k}} + 2\pi i\left(\frac{\hbar e^2}{2\delta S\omega_s}\right)^{1/2}\sum_{\vec{k}}\frac{1}{\sqrt{\kappa}}\left(\int |\Omega|^2 e^{-\kappa z}\, e^{-i\vec{k}\cdot\vec{\rho}}\, d^3\vec{r}\, a_{\vec{k}}^\dagger - \int |\Omega|^2 e^{-\kappa z}\, e^{i\vec{k}\cdot\vec{\rho}}\, d^3\vec{r}\, a_{\vec{k}}\right)\Big]|\phi\rangle = E|\phi\rangle \ . \tag{31}$$

From (31) we see that $|\phi\rangle$ can be found in the form of the product

$$|\phi\rangle = \prod_{\vec{k}} |\phi_{\vec{k}}\rangle \ , \tag{32}$$

where $|\phi_{\vec{k}}\rangle$ obeys

$$\hbar\omega_s a_{\vec{k}}^\dagger a_{\vec{k}}|\phi_{\vec{k}}\rangle + 2\pi i\left(\frac{\hbar e^2}{2\delta S\omega_s}\right)^{1/2}\frac{1}{\sqrt{\kappa}} \times\left(\int |\Omega|^2 e^{-\kappa z}\, e^{-i\vec{k}\cdot\vec{\rho}}\, d^3\vec{r}\, a_{\vec{k}}^\dagger - \int |\Omega|^2 e^{-\kappa z}\, e^{i\vec{k}\cdot\vec{\rho}}\, d^3\vec{r}\, a_{\vec{k}}\right)|\phi_{\vec{k}}\rangle = \lambda_{\vec{k}}|\phi_{\vec{k}}\rangle \tag{33}$$

and

$$E = \textstyle\sum_{\vec{k}}\lambda_{\vec{k}} + \int d^3r\,\Omega^*(p^2/2m - E_\infty e^2/4z)\Omega \ . \tag{34}$$

First we minimize $\lambda_{\vec{k}}$ for a fixed Ω. The Hamiltonian of Eq. (33) is easily diagonalized by a canonical transformation, and its lowest eigenvalue is

$$\lambda_{\vec{k}} = -\frac{2\pi^2 e^2}{\omega_s^2\delta S}\frac{1}{\kappa}\int |\Omega|^2 e^{-\kappa z}\, e^{i\vec{k}\cdot\vec{\rho}}\, d^3r \ . \tag{35}$$

At this stage we choose the form of the function Ω

$$\Omega(\vec{r}) = (\beta^3\nu^2/4\pi)^{1/2} z e^{-(\beta/2)z} e^{-(\nu/2)\rho} \ . \tag{36}$$

Equation (34) then becomes

$$E = \frac{\hbar^2\nu^2}{8m} + \frac{\hbar^2\beta^2}{8m} - \frac{\beta e^2 E_\infty}{8} - \frac{e^2(E_s - E_\infty)}{2}\beta \times \int_0^\infty dx \frac{1}{(1+x)^6[1+(\beta^2/\nu^2)x^2]^3} \ . \tag{37}$$

This expression will be minimized numerically in Sec. V.

V. APPLICATION TO LiF

We use the following values to characterize LiF[4]:

$$\epsilon_s = 8.65\,, \qquad \epsilon_\infty = 1.92\,,$$

$$\hbar\omega_L = 0.081 \text{ eV}\,, \qquad \hbar\omega_T = 0.038 \text{ eV}\,.$$

For $\hbar\omega_s$ we use Eq. (4):

$$\hbar\omega_s = 0.063 \text{ eV}\,.$$

The electron–surface-phonon coupling constant is

$$\alpha_s = 7.1\,.$$

To obtain a lower bound for the ground-state binding energy (with zero momentum along the surface), we calculate E_B for the stiff lattice (only electrons contribute to the polarization). It is $E_B^{(\infty)} = 0.081$ eV. The actual binding energy will be bigger so that we have to do with the case of a deep state.

The minimization of the weak-coupling expression (27) gives for the binding energy

$$E_B^{(w)} = 0.29 \text{ eV}\,.$$

For the extension of the wave function in the direction perpendicular to the surface we get

$$2/\beta = 4 \text{ Å}.$$

The strong-coupling theory, Eq. (37) gives

$$E_B^{(s)} = 0.23 \text{ eV}$$

and

$$2/\beta = 4.1 \text{ Å}\,, \quad 2/\nu = 9 \text{ Å}$$

for the extension of the wave function perpendicular and parallel to the surface, respectively.

Similarly to the three-dimensional polaron,[12] the weak-coupling theory is superior to the strong-coupling scheme [at least with the ansatz (36)] for a coupling constant as large as 7.1.

The maximum of the charge distribution is only 4 Å from the surface. This is to be compared with the LiF distance which is 2 Å, so that the treatment of the dielectric as a continuum may not be adequate.

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