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Quantization of surface polaritons

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We derive the exact quantization of surface polarions on ionic crystals. We show there are two different methods: (1) classical theory and (2) quantum theory. They give different results and both results are different than what is used currently. We argue the quantum theory is the correct choice. We also derive the interaction potential between a charged particle that interacts with these surface polaritons and also interacts with the bulk polaritons.

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I. INTRODUCTION

Surface polaritons are excitations that are a mixture of electromagnetic waves (photons) and polarization modes of the crystal.[1] Two common types are surface plasmons on a metal and surface optical phonons on a polar insulator. The latter are called Fuchs-Kliewer modes.[2,3] Here we discuss the quantization of the Fuchs-Kliewer surface polariton. There are several methods in the literature.[1,4] The classical method is well known[1] and is rederived in Sec. V. The derivation of the quantum method is the subject of this paper. We show that the classical and quantum methods are both plausible but are in fact different. We argue that the quantum method is correct. Using this distinct method of quantization, we are able to derive the interaction between a charged particle and these surface polaritons. There are several different terms in the interaction. Most previous theories have included only one term.

Previous theories of surface polaritons are classical and derive that the surface polaritons are given by[1]

$$\kappa^2 = \frac{\omega^2}{c^2}\frac{\varepsilon(\omega)}{\varepsilon(\omega)+1}, \tag{1}$$

where $\varepsilon(\omega)$ is the dielectric function of the material and $\boldsymbol{\kappa}=(k_x,k_y,0)$ is the wave vector along the surface. Recently we derived and solved the quantum mechanical equations for the Fuchs-Kliewer mode.[5] We follow the method of Hopfield,[6] who first quantized bulk polariton modes in 1958. He introduced quantum operators for both the photon field, and the phonon (or exciton) field, and solved the coupled oscillator problem. He found for bulk polaritons the dispersion $k^2=(\omega^2/c^2)\varepsilon(\omega)$ which is also the equation found classically. Here $\mathbf{k}=(k_x,k_y,k_z)$ is the three-dimensional wave vector of the polariton. One difference between the classical and quantum derivations is that the classical derivation assumes the dielectric function $\varepsilon(\mathbf{k},\omega)$ is entirely local $\varepsilon(\omega)$ and can be applied at atomic distances. We do not make this assumption.

A charged particle outside of a solid surface interacts with the surface polaritons of the solid. Our solution using quantum mechanics has a different interaction than the one found using classical physics.[7–17] They use

$$H=\sum_{\boldsymbol{\kappa}}\left[\hbar\omega(\kappa)\left(C^\dagger_{\boldsymbol{\kappa}}C_{\boldsymbol{\kappa}}+\frac{1}{2}\right)+M(\kappa)e^{i\vec{\kappa}\cdot\vec{\rho}+\kappa z}(C_{\boldsymbol{\kappa}}+C^\dagger_{-\boldsymbol{\kappa}})\right], \tag{2}$$

where the charge is outside of the surface at $(\vec{\rho},z<0)$. The raising and lowering operators are those of the surface polariton. Completing the square gives the ground-state energy

$$H=\sum_{\boldsymbol{\kappa}}\left[\hbar\omega(\kappa)\left(\tilde{C}^\dagger_{\boldsymbol{\kappa}}\tilde{C}_{\boldsymbol{\kappa}}+\frac{1}{2}\right)-\frac{M(\kappa)^2}{\hbar\omega(\kappa)}e^{2\kappa z}\right], \tag{3}$$

$$\tilde{C}_{\boldsymbol{\kappa}}=C_{\boldsymbol{\kappa}}+\frac{M}{\hbar\omega}e^{i\vec{\kappa}\cdot\vec{\rho}+z\kappa}. \tag{4}$$

By selecting

$$\frac{M^2}{\hbar\omega(\kappa)}=\frac{\pi e^2}{A\kappa}\left(\frac{\varepsilon-1}{\varepsilon+1}\right), \tag{5}$$

$$V_I(z)=-\sum_{\boldsymbol{\kappa}}\frac{M(\kappa)^2}{\hbar\omega(\kappa)}e^{2\kappa z}=-\frac{e^2}{4z}\left(\frac{\varepsilon-1}{\varepsilon+1}\right) \tag{6}$$

which is the classical interaction energy for a charge e outside of a solid with dielectric constant ε. The above theory is the present standard which is widely used, even today.[18–21] However, when we actually quantize the Hamiltonian for surface polaritons, we do not get the above function for $M(\kappa)$. This is shown by the following derivation. Another problem with the above theory is that the surface polariton dispersion does not extend to zero wave vector. It begins at the cut-off wave vector $\kappa_i=\omega_T/c$, where ω_T is the transverse optical phonon frequency and c is the speed of light. Using this cut-off in the above integral gives

$$\int_{\kappa_i}^{\infty}d\kappa e^{2\kappa z}=\frac{e^{-2|z|\kappa_i}}{2|z|\kappa_i}. \tag{7}$$

The potential decays exponentially, and cannot be the classical image potential. This point was first made by Ekardt.[22] He showed that radiation modes also contribute to the image potential.

II. QUANTUM THEORY OF SURFACE POLARITONS

Here we summarize our theory of surface polaritons.[5]

A. Hamiltonian

We start with a Hamiltonian that contains the photons, the phonons, and the phonon-photon interaction, We employ the Coulomb gauge.[23]

$$H = H_{0t} + H_{0n}. \tag{8}$$

The first term is the photon Hamiltonian H_{0t} which is written as a harmonic oscillator using the usual raising $(a^{\dagger}_{\mathbf{k}\lambda})$ and lowering $(a_{\mathbf{k}\lambda})$ operators

$$H_{0t} = \frac{1}{2}\sum_{\mathbf{k}\lambda} (\Pi_{\mathbf{k}\lambda}\Pi_{-\mathbf{k}\lambda} + \omega_k^2 \mathcal{A}_{\mathbf{k}\lambda}\mathcal{A}_{-\mathbf{k}\lambda}), \tag{9}$$

$$\mathcal{A}_{\mathbf{k}\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}(a_{\mathbf{k}\lambda} + a^{\dagger}_{-\mathbf{k}\lambda}), \quad \omega_{\mathbf{k}} = ck, \tag{10}$$

$$\Pi_{\mathbf{k}\lambda} = -i\sqrt{\frac{\hbar\omega_k}{2}}(a_{\mathbf{k}\lambda} - a^{\dagger}_{-\mathbf{k}\lambda}), \tag{11}$$

$$\frac{1}{c}A_{\mu}(\mathbf{r}) = \sqrt{\frac{4\pi}{\Omega}}\sum_{\mathbf{k}\lambda} \mathcal{A}_{\mathbf{k}\lambda}\xi_{\mu}(\mathbf{k}\lambda)e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{12}$$

where Ω is the volume of the system, and the three-dimensional photon wave vector is $\mathbf{k}=(\vec{\kappa},k_z)$.

Similarly, the phonon Hamiltonian is

$$H_{0n} = \frac{1}{2M}\sum_{j\mu}\left[P_{j\mu} - \frac{e}{c}A_{\mu}(\mathbf{R}_j)\right]^2 + \frac{M\omega_0^2}{2}\sum_{j\mu} Q_{j\mu}^2 + \frac{e^2}{2}\sum_{jj'\mu\nu} Q_{j\mu}\phi_{\mu\nu}(\mathbf{R}_j - \mathbf{R}_{j'})Q_{j'\nu}, \tag{13}$$

where $\phi_{\mu\nu}(\mathbf{R})$ is the instantaneous dipole-dipole interaction, j denotes the lattice cite (at $\mathbf{R}_j$), (μ,ν) are vector components, and ω_0 is the vibrational frequency of the optical phonon in the absence of photons. We convert the variables to a slab geometry, where the two dimensional wave vector $\boldsymbol{\kappa}=(k_x,k_y,0)$ is in the plane of the slab. The integer l denotes the layer, starting from the surface of the solid ($l=0,1,2,\ldots$). The phonon variables become $Q_{\boldsymbol{\kappa},l,\mu}, P_{\boldsymbol{\kappa},l,\mu}$. There is also a variable for the photon field at the lattice site and ω_i is the ion plasma frequency

$$\mathcal{D}_{\boldsymbol{\kappa},l,\mu} = \sqrt{\frac{a}{L}}\sum_{k_z,\lambda} \xi_{\mu}(\mathbf{k}\lambda)\mathcal{A}_{\mathbf{k}\lambda}e^{ik_z al}, \tag{14}$$

$$\omega_i^2 = \frac{4\pi e^2}{\Omega_0 M}. \tag{15}$$

The volume of the system is $\Omega = N_{xy}LA_0$, where A_0 is the area per unit cell in the layer, N_{xy} is the number of molecules in each layer, and L is the length in the z direction. We also introduce the volume of a unit cell $\Omega_0 = A_0 a$.

The lattice transform, in the layer geometry, of the instantaneous dipole-dipole interaction is

$$S_{\mu\nu} = \begin{cases} l = l' & \frac{1}{3}d_{\mu\nu} \\ l \neq l' & \frac{a}{2\kappa}e^{-\kappa a|l-l'|}[q_{\mu}^{-}q_{\nu}^{-}\Theta(l-l') + q_{\mu}^{+}q_{\nu}^{+}\Theta(l'-l)], \end{cases} \tag{16}$$

$$d_{\mu\nu} = \delta_{\mu\nu}(1-3\delta_{\mu z}), \quad q_{\mu}^{\pm} = i\kappa_{\mu} \pm \kappa\delta_{\mu z}, \tag{17}$$

where a is the lattice constant in the $\hat{z}$ direction. The vector $\boldsymbol{\kappa}$ is in the (x,y) plane, so that κ_{μ} is nonzero whenever $\mu=(x,y)$. We also need the two-dimensional Fourier transform of the retarded dipole-dipole interaction[7]

$$T_{\mu\nu}(\boldsymbol{\kappa},l-l') = \begin{cases} l = l' & \frac{1}{3}d_{\mu\nu} \\ l \neq l' & \frac{a}{2p}e^{-pa|l-l'|}\left[\delta_{\mu\nu}\frac{\omega^2}{c^2} + \eta_{\mu}^{-}\eta_{\nu}^{-}\Theta(l-l') + \eta_{\mu}^{+}\eta_{\nu}^{+}\Theta(l'-l)\right] \end{cases}$$

$$p = \sqrt{\kappa^2 - \omega^2/c^2}, \quad \eta_{\mu}^{\pm} = i\kappa_{\mu} \pm p\delta_{\mu z}. \tag{18}$$

The two Fourier transforms are equal if $c \to \infty$.

The phonon system has a transverse phonon (ω_T), a longitudinal phonon (ω_L), and a surface phonon (ω_S) given by

$$\omega_T^2 = \omega_0^2 - \frac{1}{3}\omega_i^2, \quad \omega_L^2 = \omega_0^2 + \frac{2}{3}\omega_i^2, \quad \omega_S^2 = \omega_0^2 + \frac{1}{6}\omega_i^2. \tag{19}$$

The dielectric function is

$$\varepsilon(\omega) = 1 + \frac{\omega_i^2}{\omega_T^2 - \omega^2} = \frac{\omega_L^2 - \omega^2}{\omega_T^2 - \omega^2}. \tag{20}$$

Using this dielectric function in Eq. (1), the classical theory of the surface polariton has the dispersion

$$\omega^2(\kappa) = \frac{1}{2}[\omega_L^2 + 2c^2\kappa^2 - \sqrt{(\omega_L^2 + 2c^2\kappa^2)^2 - 8c^2\kappa^2\omega_S^2}]. \tag{21}$$

The classical and quantum solutions has an eigenfunction of the form $\exp(-\gamma al)$ where $\gamma = \sqrt{\kappa^2 - \omega^2\varepsilon(\omega)/c^2}$. Using the dispersion relation in Eq. (1), one can show for surface polaritons

$$p^2\gamma^2 = \kappa^4 - \frac{\omega^2}{c^2}\left[\kappa^2(\varepsilon+1) - \frac{\omega^2}{c^2}\varepsilon\right] = \kappa^4, \tag{22}$$

$$p\gamma = \kappa^2 \tag{23}$$

which is useful later.

The above equations are solved using the equations of motion. After some algebra,[5] the eigenvalue equation for the ion displacement

$$\omega^2 Q_{\boldsymbol{\kappa},l,\mu} = \left[\omega_0^2 - \frac{1}{3}\omega_i^2 d_{\mu\mu} \right] Q_{\boldsymbol{\kappa},l,\mu} - \omega_i^2 \sum_{l' \neq l,\nu} T_{\mu\nu}(l-l') Q_{\boldsymbol{\kappa},l',\nu}. \tag{24}$$

The only interaction between layers is the retarded interaction $T_{\mu\nu}$, which is due to the photons.

B. Solutions

We summarize the solutions to Eq. (24). Surface modes have a dependence upon layer index of $\exp[-\alpha l a]$, where a is a lattice constant, and α is a function of $(\boldsymbol{\kappa},\omega)$. The theory seems to have three possible choices of α: κ, p, γ. Bulk modes have an oscillatory layer dependence such as $\sin(k_z a l + \alpha)$. The five solutions are (1) the surface polariton mode is also called the Fuchs-Kliewer mode[2,3]

$$Q_{\boldsymbol{\kappa},l,\mu} = Q_{SP}\bar{\eta}_\mu e^{-\gamma a l}. \tag{25}$$

(2) The longitudinal surface mode has a frequency $\omega = \omega_L$

$$Q_{\boldsymbol{\kappa},l,\mu} = Q_{SL}[\bar{q}_\mu e^{-\kappa l} - \bar{\eta}_\mu e^{-pal}]. \tag{26}$$

(3) The bulk longitudinal mode also has a frequency $\omega = \omega_L$

$$Q_{\mathbf{k},l,\mu} = Q_{BL}[i\kappa_\mu \sin(k_z a l), k_z \cos(k_z a l)]. \tag{27}$$

(4) There are two bulk transverse modes. Both are solutions to the equation $c^2k^2 = \omega^2\varepsilon(\omega)$. The first is

$$Q_{\mathbf{k},l,\mu} = Q_{BT1} t_\mu \sin(k_z a l + \phi), \quad t_\mu = (k_y, -k_x, 0), \tag{28}$$

$$\tan(\phi) = \frac{k_z}{p}. \tag{29}$$

(5) The other bulk transverse mode is

$$Q_{\mathbf{k},l,\mu} = Q_{BT2}[i\kappa_\mu k_z \sin(k_z a l + \alpha), -\kappa^2 \cos(k_z a l + \alpha)], \tag{30}$$

$$\alpha = \phi + \tan^{-1}\left(\frac{\kappa^2}{k_z p}\right), \quad \tan(\alpha) = \frac{pk^2}{k_z(p^2 - \kappa^2)} < 0. \tag{31}$$

All five modes are mutually orthogonal except the two longitudinal modes. Since they have identical eigenvalues, they do not have to be orthogonal. They can be made orthogonal by the standard method.

III. QUANTIZATION OF MODES

We consider the quantization of these solutions. We need to know the value of other quantum variables for these modes: variables such as $\dot{\mathcal{D}}_{\boldsymbol{\kappa},l,\mu}$.

A. Longitudinal mode

The easiest case is the longitudinal mode, which is done first. It has no mixing with photons.

$$\dot{\mathcal{D}}_{\boldsymbol{\kappa},l,\mu} = 0, \quad \frac{\dot{P}_{\boldsymbol{\kappa},l,\mu}}{M} = -\omega_L^2 Q_{\boldsymbol{\kappa},l,\mu}. \tag{32}$$

This result is valid for the surface mode $Q_{\boldsymbol{\kappa},l,\mu}$. It is simple to quantize. The surface longitudinal mode is expressed in terms of boson raising ($C^\dagger_{SL,\boldsymbol{\kappa}}$) and lowering ($C_{SL,\boldsymbol{\kappa}}$) operators

$$Q_{\boldsymbol{\kappa},l,\mu} = \sqrt{\frac{\hbar}{2M\omega_L}}[C_{SL,\boldsymbol{\kappa}} + C^\dagger_{SL,\boldsymbol{\kappa}}]\phi^{(SL)}_{\boldsymbol{\kappa},l,\mu}, \tag{33}$$

$$\phi^{(SL)}_{\boldsymbol{\kappa},l,\mu} = N_{SL}(\kappa)[\bar{q}_\mu e^{-\kappa a l} - \bar{\eta}_\mu e^{-pal}], \tag{34}$$

$$N_{SL}(\kappa) = \frac{\sqrt{2pa}}{|\kappa - p|}, \tag{35}$$

$$P_{\boldsymbol{\kappa},l,\mu} = -i\sqrt{\frac{\hbar\omega_L M}{2}}[C_{SL,\kappa} - C^\dagger_{SL,\kappa}]\phi^{(SL)}_{\kappa,l,\mu}. \tag{36}$$

The longitudinal mode does not produce a field outside of the surface and does not mix with photon. A similar procedure can be done for the bulk longitudinal mode, Eq. (27).

B. Quantization of surface polariton

The surface polariton mode has a dispersion given by Eq. (25). The first step is to define raising and lowering operators similar to Eqs. (33) and (36).

$$Q_{\boldsymbol{\kappa},l,\mu} = Q_{SP}\sqrt{\frac{\hbar}{2M\omega_{SP}}}[C_{SP,\boldsymbol{\kappa}} + C^\dagger_{SL,\boldsymbol{\kappa}}]\phi^{(SP)}_{\boldsymbol{\kappa},l,\mu}, \tag{37}$$

$$\dot{Q}_{\boldsymbol{\kappa},l,\mu} = -iQ_{SP}\sqrt{\frac{\hbar\omega_{SP}}{2M}}[C_{SP,\boldsymbol{\kappa}} - C^\dagger_{SP,\boldsymbol{\kappa}}]\phi^{(SP)}_{\boldsymbol{\kappa},l,\mu}. \tag{38}$$

Here $\phi^{(SP)}_{\boldsymbol{\kappa},l,\mu}$ is the normalized form of Eq. (25)

$$\phi^{(SP)}_{\boldsymbol{\kappa},l,\mu} = N_{SP}\bar{\eta}_\mu e^{-\gamma a l}, \tag{39}$$

$$1 = \sum_{l=0}^{\infty} |\phi^{(SP)}_{\boldsymbol{\kappa},l,\mu}|^2, \tag{40}$$

$$N_{SP} = \sqrt{\frac{2\gamma a}{p^2 + \kappa^2}}. \tag{41}$$

The other factor Q_{SP} must be determined by quantizing the entire Hamiltonian.

Every term in the Hamiltonian can be reduced to one of two forms. They each involve a summation over lattice planes l of: (i) QQ or (ii) $\dot{Q}\dot{Q}$. For example, the ion kinetic-energy term is

$$\frac{1}{2M}\sum_j\left[\vec{P}_j-\frac{e}{c}\vec{A}(R_j)\right]^2=\frac{1}{2}\sum_{\boldsymbol{\kappa},l,\mu}\left[\frac{P_{\boldsymbol{\kappa},l,\mu}}{\sqrt{M}}-\omega_i\mathcal{D}_{\boldsymbol{\kappa},l,\mu}\right]\left[\frac{P_{-\boldsymbol{\kappa},l,\mu}}{\sqrt{M}}-\omega_i\mathcal{D}_{-\boldsymbol{\kappa},l,\mu}\right]=\frac{M}{2}\sum_{\boldsymbol{\kappa},l,\mu}\dot{Q}_{\boldsymbol{\kappa},l,\mu}\dot{Q}_{-\boldsymbol{\kappa},l,\mu}. \quad (42)$$

Another example is the photon terms in Eq. (9)

$$\frac{1}{2}\sum_{\mathbf{k}\lambda}\omega_k^2\mathcal{A}_{\mathbf{k}\lambda}\mathcal{A}_{-\mathbf{k},\lambda}=\frac{1}{2}\omega_i^2M\sum_{\boldsymbol{\kappa},l,l'}\sum_{\mu,\nu}\dot{Q}_{\boldsymbol{\kappa},l,\mu}H_{\mu\nu}(l-l')\dot{Q}_{\boldsymbol{\kappa},l',\nu}, \quad (43)$$

$$H_{\mu\nu}(l-l')=\frac{a}{L}\sum_{k_z}\frac{c^2k^2}{(c^2k^2-\omega^2)^2}\left[\delta_{\mu\nu}-\frac{k_\mu k_\nu}{k^2}\right]e^{ik_za(l-l')}. \quad (44)$$

The other term in H_{0t} is found in a similar way

$$\frac{1}{2}\sum_{\mathbf{k}\lambda}\Pi_{\mathbf{k}\lambda}\Pi_{-\mathbf{k}\lambda}=\frac{1}{2}\omega_i^2\omega^4M\sum_{\boldsymbol{\kappa},l,l'}\sum_{\mu,\nu}Q_{\boldsymbol{\kappa},l,\mu}N_{\mu\nu}(l-l')Q_{\boldsymbol{\kappa},l',\nu}, \quad (45)$$

$$N_{\mu\nu}(l-l')=\frac{a}{L}\sum_{k_z}\frac{1}{(c^2k^2-\omega^2)^2}\left[\delta_{\mu\nu}-\frac{k_\mu k_\nu}{k^2}\right]e^{ik_za(l-l')}. \quad (46)$$

Thus we can write the Hamiltonian as a summation over modes (α) and wave vectors $\boldsymbol{\kappa}$

$$H=\frac{1}{4}\sum_{\boldsymbol{\kappa},\alpha}\hbar\omega_\alpha[(C_{\alpha,\boldsymbol{\kappa}}+C^\dagger_{\alpha,-\boldsymbol{\kappa}})(C_{\alpha,\boldsymbol{\kappa}}+C^\dagger_{\alpha,-\boldsymbol{\kappa}})T_\alpha^{(+)}-(C_{\alpha,\boldsymbol{\kappa}}-C^\dagger_{\alpha,-\boldsymbol{\kappa}})(C_{\alpha,\boldsymbol{\kappa}}-C^\dagger_{\alpha,-\boldsymbol{\kappa}})T_\alpha^{(-)}] \quad (47)$$

where a proper theory of quantizations requires that

$$T_\alpha^{(+)}=T_\alpha^{(-)}\equiv T=1 \quad (48)$$

so that

$$H=\sum_{\boldsymbol{\kappa},\alpha}\hbar\omega_\alpha(\kappa)\left[C^\dagger_{\alpha,\boldsymbol{\kappa}}C_{\alpha,\boldsymbol{\kappa}}+\frac{1}{2}\right]. \quad (49)$$

The surface polariton Hamiltonian is written in standard boson form.

We derive these expressions using

$$\mathcal{D}_{\boldsymbol{\kappa},l,\mu}=i\frac{\omega_i}{\omega^2}Q_{SP}\sqrt{\frac{\hbar\omega}{2}}(C_{SP,\boldsymbol{\kappa}}-C^\dagger_{SP,-\boldsymbol{\kappa}})\psi_{\boldsymbol{\kappa},l,\mu}, \quad (50)$$

$$\psi_{\boldsymbol{\kappa},l,\mu}=\sum_{l'\neq l}[T_{\mu\nu}(l-l')-S_{\mu\nu}(l-l')]\phi_{\boldsymbol{\kappa},l',\nu}, \quad (51)$$

$$\frac{P_{\boldsymbol{\kappa},l,\mu}}{\sqrt{M}}=-iQ_{SP}\sqrt{\frac{\hbar\omega}{2}}(C_{SP,\boldsymbol{\kappa}}-C^\dagger_{SP,-\boldsymbol{\kappa}})U_{\boldsymbol{\kappa},l,\mu}, \quad (52)$$

$$U_{\boldsymbol{\kappa},l,\mu}=\phi_{\boldsymbol{\kappa},l,\mu}+\frac{\omega_i^2}{\omega^2}\psi_{\boldsymbol{\kappa},l,\mu}. \quad (53)$$

In terms of these variables, the desired functions are

$$T_\alpha^{(+)}=\frac{\omega_0^2}{\omega_\alpha^2}\sum_{l,\mu}\phi_{\boldsymbol{\kappa},l,\mu}\phi_{-\boldsymbol{\kappa},l,\mu}-\frac{\omega_i^2}{\omega_\alpha^2}\sum_{ll'\mu\nu}\phi_{\boldsymbol{\kappa},l,\mu}S_{\mu\nu}(l-l')\phi_{-\boldsymbol{\kappa},l',\nu}+\omega_i^2\omega_\alpha^2\sum_{ll'\mu\nu}\phi_{\boldsymbol{\kappa},l,\mu}N_{\mu\nu}(l-l')\phi_{-\boldsymbol{\kappa},l',\nu}$$

$$T_\alpha^{(-)}=\sum_{l\mu}\phi_{\boldsymbol{\kappa},l,\mu}\phi_{-\boldsymbol{\kappa},l,\mu}+\omega_i^2\sum_{ll'\mu\nu}\phi_{\boldsymbol{\kappa},l,\mu}H_{\mu\nu}(l-l')\phi_{-\boldsymbol{\kappa},l',\nu}. \quad (54)$$

The first term in $T^{(-)}$ is $\Sigma\phi^2=1$. A similar result is found for $T^{(+)}$. In the definition of $H_{\mu\nu}$ write

$$\frac{\omega_k^2}{(\omega_k^2-\omega^2)^2}=\frac{1}{\omega_k^2-\omega^2}+\frac{\omega^2}{(\omega_k^2-\omega^2)^2}. \quad (55)$$

The first term gives

$$G_{\mu\nu}=\frac{1}{\omega^2}[T_{\mu\nu}-S_{\mu\nu}] \quad (56)$$

and the second term gives $\omega^2N_{\mu\nu}$

$$H_{\mu\nu}=G_{\mu\nu}+\omega^2N_{\mu\nu}, \quad (57)$$

$$\omega^2N_{\mu\nu}=H_{\mu\nu}-\frac{1}{\omega^2}[T_{\mu\nu}-S_{\mu\nu}]. \quad (58)$$

Put the last equation into the definition (54) of $T^{(+)}$. The terms with $S_{\mu\nu}$ cancel

$$T_\alpha^{(+)}=\frac{\omega_0^2}{\omega_\alpha^2}\sum_{l,\mu}\phi_{\boldsymbol{\kappa},l,\mu}\phi_{-\boldsymbol{\kappa},l,\mu}-\frac{\omega_i^2}{\omega_\alpha^2}\sum_{ll'\mu\nu}\phi_{\boldsymbol{\kappa},l,\mu}T_{\mu\nu}(l-l')\phi_{-\boldsymbol{\kappa},l',\nu}+\omega_i^2\sum_{ll'\mu\nu}\phi_{\boldsymbol{\kappa},l,\mu}H_{\mu\nu}(l-l')\phi_{-\boldsymbol{\kappa},l',\nu}. \quad (59)$$

The first two terms are just the eigenvalue Eq. (24) for the surface polariton and give unity. Thus we have shown Eq. (48) is valid, where

$$T=Q_{SP}^2[1+\delta T], \quad (60)$$

$$Q_{SP}^2\delta T=\omega_i^2\sum_{ll'\mu\nu}\phi_{\boldsymbol{\kappa},l,\mu}H_{\mu\nu}(l-l')\phi_{-\boldsymbol{\kappa},l',\nu}. \quad (61)$$

Since ultimately $T=1$ the definition of Q_{SP} is

$$Q_{SP}=\frac{1}{\sqrt{1+\delta T}}. \quad (62)$$

Evaluating the integral in Eq. (44) gives

$$H_{\mu\nu}(l-l')=\frac{a}{4p^3c^2}e^{-pa|l-l'|}[A_{\mu\nu}+pa|l-l'|B_{\mu\nu}], \quad (63)$$

$$A_{\mu\nu} = (\kappa^2 + p^2)\delta_{\mu\nu} - p^2\delta_{\mu\nu z} - \kappa_\mu\kappa_\nu, \tag{64}$$

$$B_{\mu\nu} = (\kappa^2 - p^2)\delta_{\mu\nu} + \eta_\mu^- \eta_\nu^-, \quad \text{if } l > l', \tag{65}$$

$$= (\kappa^2 - p^2)\delta_{\mu\nu} + \eta_\mu^+ \eta_\nu^+, \quad \text{if } l < l'. \tag{66}$$

In doing the above summations in Eq. (61)

$$Q_{SP}^2 \delta T = - Q_{SP}^2 N_\kappa^2 \sum_{ll'} e^{-\gamma a(l+l') - pa|l-l'|} \sum_{\mu\nu} \eta_\mu^- (A_{\mu\nu} + pa|l-l'|B_{\mu\nu})\eta_\nu^+. \tag{67}$$

The summations are

$$\sum_{\mu\nu} \eta_\mu^- A_{\mu\nu} \eta_\nu^+ = -2p^2\kappa^2, \tag{68}$$

$$\sum_{\mu\nu} \eta_\mu^- B_{\mu\nu} \eta_\nu^+ = 0, \tag{69}$$

$$\sum_{ll'} e^{-\gamma a(l+l') - pa|l-l'|} = \frac{1}{a^2\gamma(\gamma + p)} = \frac{p}{a^2\gamma(p^2 + \kappa^2)}, \tag{70}$$

where we used $p\gamma = \kappa^2$ to simplify the last expression. Collecting all these terms gives

$$\delta T = \frac{\omega_i^2 \kappa^2}{c^2(p^2 + \kappa^2)^2} = \frac{\omega_L^2 - \omega^2}{c^2(p^2 + \kappa^2)}. \tag{71}$$

We use Eq. (62) to define a new normalization coefficient

$$Q_{\kappa,l,\mu} = \tilde{N}_{SP}\sqrt{\frac{\hbar}{2M\omega}}(C_{SP,\kappa} + C_{SP,-\kappa}^\dagger)\eta_\mu^- e^{-\gamma al}, \tag{72}$$

$$\tilde{N}_{SP} = \frac{N_{SP}}{\sqrt{1 + \delta T}} = c\sqrt{\frac{2\gamma a}{W}}, \tag{73}$$

$$W = c^2(p^2 + \kappa^2)(1 + \delta T) = c^2(p^2 + \kappa^2) + \omega_L^2 - \omega^2, \tag{74}$$

$$= [(2c^2\kappa^2 + \omega_L^2)^2 - 8c^2\kappa^2\omega_S^2]^{1/2}. \tag{75}$$

Note that the quantity W is identical to the square-root part of the surface polariton dispersion in Eq. (21). The quantization of the surface polariton is now determined.

C. Quantization of bulk transverse modes

(1) The bulk transverse mode $t_\mu \sin(k_z al + \phi)$ has

$$\dot{\mathcal{D}}_{\mathbf{k},l,\mu} = -\sqrt{M}\frac{\omega_i}{\varepsilon(\omega) - 1}Q_{\mathbf{k},l,\mu}, \tag{76}$$

$$\frac{\dot{P}_{\mathbf{k},l,\mu}}{M} = -\omega_T^2 Q_{\mathbf{k},l,\mu}. \tag{77}$$

We quantize it using

$$Q_{\mathbf{k},l,\mu} = Q_{BT1}\sqrt{\frac{\hbar}{2M\omega(k)}}(C_{\mathbf{k},BT1} + C_{-\mathbf{k},BT1}^\dagger)\phi_{\mathbf{k},l,\mu}^{(BT1)}, \tag{78}$$

$$\phi_{\mathbf{k},l,\mu}^{(BT1)} = N_{\mathbf{k},1} t_\mu \sin(k_z al + \phi), \tag{79}$$

$$N_{\mathbf{k},1} = \sqrt{\frac{2}{\kappa^2(N + \delta_1)}}, \quad \delta_1 = \frac{\sin(k_z a - 2\phi)}{\sin(k_z a)}. \tag{80}$$

Using this form, the expression for δT_1 in Eq. (61) is

$$\delta T_1 = \frac{\omega_i^2 k^2}{c^2(p^2 + k_z^2)^2}, \tag{81}$$

$$\tilde{N}_{\mathbf{k},1} = \sqrt{\frac{2}{\kappa^2(N_z + \delta_1)(1 + \delta T_1)}}. \tag{82}$$

(2) The other bulk transverse mode has

$$Q_{\mathbf{k},l,\mu} = Q_{BT2}\sqrt{\frac{\hbar}{2M\omega(k)}}(C_{\mathbf{k},BT2} + C_{-\mathbf{k},BT2}^\dagger)\phi_{\mathbf{k},l,\mu}^{(BT2)}, \tag{83}$$

$$\phi_{\mathbf{k},l,\mu}^{(BT2)} = N_{\mathbf{k},2}[k_z i\kappa_\mu \sin(k_z al + \alpha), -\kappa^2\cos(k_z al + \alpha)], \tag{84}$$

$$\dot{\mathcal{D}}_{\mathbf{k},l,\mu} = -\sqrt{M}\omega_i\left[\frac{Q_{\mathbf{k},l,\mu}}{\varepsilon(\omega) - 1} + \frac{Q_{BT2}\kappa}{2}\cos(\alpha)q_\mu^- e^{-\kappa al}\right], \tag{85}$$

$$\frac{\dot{P}_{\mathbf{k},l,\mu}}{M} = -\omega_T^2 Q_{\mathbf{k},l,\mu} - \omega_i^2\frac{Q_{BT2}\kappa}{2}\cos(\alpha)q_\mu^- e^{-\kappa al}. \tag{86}$$

Use a form similar to Eq. (78) and find

$$\tilde{N}_{\mathbf{k},2} = \frac{1}{k\kappa}\sqrt{\frac{2}{(N_z + \delta_2)(1 + \delta T_2)}}, \tag{87}$$

$$\delta T_2 = \frac{\omega_i^2(\kappa^4 + k_z^4)}{c^2 k^2(p^2 + k_z^2)^2}. \tag{88}$$

IV. POTENTIAL FIELDS OUTSIDE OF THE SURFACE

The modes of the crystal may generate electrostatic potentials outside of the crystal surface ($z < 0$).

A. Scalar potential

$$\phi(\mathbf{r}) = \sum_j e_j \vec{Q}_j \cdot \vec{\nabla}_j \frac{1}{|\mathbf{R}_j - \mathbf{r}|}, \tag{89}$$

$$= \sum_{\boldsymbol{\kappa}} \frac{2\pi e}{A_0\kappa\sqrt{N_\perp}} e^{i\vec{\kappa}\cdot\vec{\rho} + \kappa z}\mathcal{L}, \tag{90}$$

$$\mathcal{L} = -\sum_{l,\mu} Q_{\kappa,l,\mu} q_\mu^+ e^{-\kappa al}. \tag{91}$$

This expression is useful once we determine $Q_{\boldsymbol{\kappa},l,\mu}$.

1. Surface polaritons

For the surface polariton, the result is

$$\phi(\mathbf{r}) = -\frac{\omega_i c}{\sqrt{A}} \sum_{\boldsymbol{\kappa}} \sqrt{\frac{\pi \hbar p}{\omega(\kappa) W(\kappa)}} (C_{SP,\boldsymbol{\kappa}} + C^{\dagger}_{SP,-\boldsymbol{\kappa}}) e^{i\vec{\kappa}\cdot\vec{\rho}+\kappa z}, \tag{92}$$

where $z<0$. Note that this exact result does not resemble the matrix element $M(\kappa)$ in Eq. (5).

2. Bulk transverse phonon

In this case the summation over $\mathcal{L}$ gives

$$\mathcal{L} = -\sum_{l,\mu} \phi^{(BT2)}_{\mathbf{k},l,\mu} q^{+}_{\mu} e^{-\kappa a l}, \tag{93}$$

$$= \tilde{N}_{\mathbf{k},2} \kappa^2 \frac{\cos(\alpha)}{a} = -\tilde{N}_{\mathbf{k},2} \frac{\omega^2 k_z \kappa^2}{a\sqrt{p^2 c^4 k^4 + k_z^2 \omega^4}}. \tag{94}$$

In this case the matrix element $M(\mathbf{k})$ in Eq. (3) is

$$M(\mathbf{k}) = \frac{q\omega_i \cos(\alpha)}{k\sqrt{\Omega}} \sqrt{\frac{\hbar\pi}{\omega(1+\delta T_2)}} \tag{95}$$

and the image potential $(z<0)$

$$V_{BT2}(z) = -q^2 \pi \omega_i^2 \int \frac{d^3k}{(2\pi)^3} \frac{e^{2\kappa z}}{k^2(1+\delta T_2)} \frac{k_z^2 \omega^2}{k_z^2 \omega^4 + p^2 c^4 k^4}. \tag{96}$$

At first it appears this integral diverges as $k \to 0$, However, the product $k^2 \delta T_2$ goes to a constant in this limit, so the integrand does not converge. Since the image potential at large $|z|$ is determined by the integrand for small values of wave vector, the factor δT_2 provides a major contribution to the long-range image potential. It is rather easy to evaluate the above integral in the limit that $|z| \to \infty$ and to show that it goes to a constant divided by $|z|$. The above integral, which is the contribution from the transverse acoustic bulk phonons, is an important contribution to the image potential at long range.

In the limit that $k \to 0$ then $\omega(k)^2 \to c^2k^2/R$ where $R = \omega_L^2/\omega_T^2 = \varepsilon(0) > 1$. At large $|z|$ the image potential from the bulk transverse phonons is

$$\lim_{|z|\to\infty} V_{BT2}(z) = -\frac{q^2\omega_i^2}{2\pi} \int_0^{\infty} dk \int_0^{\theta_0} d\theta \sin(\theta) e^{-2k|z|\sin(\theta)} \times \frac{\cos^2(\theta)}{c^2k^2 + \omega_i^2 f(\cos\theta)} \frac{R}{\cos^2(\theta) - R + R^2 \sin^2(\theta)}, \tag{97}$$

$$\sin(\theta_0) = \frac{1}{\sqrt{R}}, \quad f(\nu) = (1 - 2\nu^2 + 2\nu^4)\left(\frac{R}{R-1}\right)^2. \tag{98}$$

The first denominator is from $c^2k^2(1+\delta T_2)$ and the second is from $\cos^2(\alpha)$. Set $k^2=0$ in the denominator and the integral over dk becomes trivial. One is left with an angular integral

$$\lim_{|z|\to\infty} V_{BT2}(z) = -\frac{q^2}{4\pi|z|} \int_0^{\theta_0} d\theta \frac{\cos^2(\theta)}{f(\cos\theta)} \frac{R}{\cos^2(\theta) - R + R^2\sin^2(\theta)}. \tag{99}$$

The value of the integral depends upon R, which is $\varepsilon(0)$. The above integral is slightly less than 50%. About half of the image potential at long range is supplied by the bulk-transverse optical phonons. The rest is provided by the radiation modes.[22] They exist partly in the vacuum outside of the solid surface and have a dispersion relation $\omega^2 = c^2k^2$. None of the long-range image potential is provided by the surface polaritons, which has been the traditional theory. Ekardt[22] provided a theory of the image potential from bulk and radiation modes. However, he took a continuum model of the solid, which ignored local-field effects and our theory is different than his.

B. Vector potentials

A current of particles outside of the surface can also interact with the substrate through the vector potential. The electric field contains the time derivative of the vector potential, which in our notation is proportional to $\Pi_{\mathbf{k}\lambda}$. Our solution gives for this quantity

$$\Pi_{\mathbf{k}\lambda} = -\frac{\omega_i \omega^2}{c^2k^2 - \omega^2(\kappa)} \sqrt{\frac{aM}{L}} \hat{\xi}(\mathbf{k}\lambda) \left(\sum_l \vec{Q}_{\boldsymbol{\kappa},l} e^{ik_z z} \right) \tag{100}$$

In order to discuss the electric field from a surface wave with wave vector $\vec{\kappa}$, we construct a function such as[5]

$$\dot{\mathcal{D}}_{\boldsymbol{\kappa},\mu}(z) = \sqrt{\frac{a}{L}} \sum_{k_z,\lambda} \xi_\mu(\mathbf{k}\lambda) \Pi_{\mathbf{k}\lambda} e^{-ik_z z}. \tag{101}$$

This function is $\dot{\mathcal{D}}_{\boldsymbol{\kappa},l,\mu}$ when $z=la$. However, now our interest is outside the surface where $z<0$. Insert Eq. (100) into Eq. (101) and evaluate the summation over k_z

$$\dot{\mathcal{D}}_{\boldsymbol{\kappa},\mu}(z) = -\omega_i \omega^2 \sqrt{M} \sum_{l,\nu} G_{\mu\nu}(z - al) Q_{\boldsymbol{\kappa},l,\nu}, \tag{102}$$

$$= -\omega_i \sqrt{M} \sum_{l,\nu} [T_{\mu\nu}(al - z) - S_{\mu\nu}(al - z)] Q_{\boldsymbol{\kappa},l,\nu}. \tag{103}$$

The electric field has the vector potential term, and a scalar potential term. Both terms contain the factor of $S_{\mu\nu}$ and cancel. One is left with only the retarded interaction

$$E_{\boldsymbol{\kappa},\mu}(z) = \omega_i \sqrt{\frac{4\pi M}{\Omega_0}} e^{pz} \sum_{l,\nu} T_{\mu\nu}(al) Q_{\boldsymbol{\kappa},l,\nu}. \tag{104}$$

This interaction agrees with the classical answer. It is zero for the surface polariton at the longitudinal frequency.

For the surface polariton, the electric field outside of the surface is

$$\sum_{l,\mu} T_{\mu\nu}(al) \eta^{-}_{\mu} e^{-\gamma a l} = -\frac{p}{p+\gamma} \Lambda^{+}_{\mu} = -\frac{p^2}{p^2+\kappa^2} \Lambda^{+}_{\mu}, \tag{105}$$

$$\Lambda_\mu^{\pm} = \left(i\kappa_\mu, \pm \frac{\kappa^2}{p}\right) \tag{106}$$

which gives an electric field

$$E_{\boldsymbol{\kappa},\mu} = -\frac{4\pi e}{\Omega_0}\frac{p^2}{p^2+\kappa^2}\Lambda_\mu^+ e^{pz}\tilde{N}_\kappa\sqrt{\frac{\hbar}{2\omega(\kappa)M}}(C_{SP,\boldsymbol{\kappa}} + C_{SP,-\boldsymbol{\kappa}}^\dagger). \tag{107}$$

We also need the electric field at a lattice within a layer. It is given by the script symbol

$$E_\mu(\mathbf{r}) = \frac{1}{\sqrt{N_{xy}}}\sum_{\boldsymbol{\kappa}} e^{i\vec{\kappa}\cdot\vec{\rho}}\mathcal{E}_{\boldsymbol{\kappa},l,\mu}, \tag{108}$$

$$\mathcal{E}_{\boldsymbol{\kappa},l,\mu} = \frac{4\pi e}{\Omega_0}\sum_{l',\nu} T_{\mu\nu}(l-l')Q_{\boldsymbol{\kappa},l',\nu}. \tag{109}$$

In the classical theory, the z component of the electric field is discontinuous at the surface since $\varepsilon E_z^{(in)} = E_z^{(out)}$. In our theory the discontinuity is due to the term in $T_{\mu\nu}(l-l')$ which has $l=l'$. For the surface layer and all interior layers, this term is included. Outside the surface it is not included. This causes a discontinuity in the normal component of the electric field.

The interaction between a charged particle and the surface polariton is also through the p-dot-A interaction

$$V = -\frac{e}{mc}\int d^3r[\psi^\dagger(\mathbf{r})\mathbf{p}\psi(\mathbf{r})]\cdot\mathbf{A}(\mathbf{r}), \tag{110}$$

$$\frac{e}{c}A_\mu(\mathbf{r}) = M\omega_i^2\sum_{\boldsymbol{\kappa}} e^{i\vec{\kappa}\cdot\vec{\rho}}\sum_{l\nu} G_{\mu\nu}(z-al)\dot{Q}_{\boldsymbol{\kappa},l,\nu}, \tag{111}$$

$$M\dot{Q}_{\boldsymbol{\kappa},l,\mu} = -i\tilde{N}_\kappa\eta_\mu^- e^{-\gamma al}(C_{SP,\boldsymbol{\kappa}} + C_{SP,-\boldsymbol{\kappa}}^\dagger)\sqrt{\frac{\hbar\omega(\kappa)M}{2}}. \tag{112}$$

The resulting interaction contains

$$\sum_{l\nu} G_{\mu\nu}(z-al)\,\eta_\mu^- e^{-\gamma al} = \frac{1}{\omega^2(\kappa)}\left[\frac{p}{2\kappa}q_\mu^+ e^{\kappa z} - \frac{p^2}{p^2+\kappa^2}\Lambda_\mu^+ e^{pz}\right]. \tag{113}$$

A charge outside of the surface of a polar crystal interacts with the surface polaritons through two interactions: (1) the scalar potential and (2) the p-dot-A interaction.

V. CLASSICAL THEORY OF SURFACE POLARITONS

Here we provide the standard theory[1] of surface polaritons and then quantize the classical Hamiltonian. We solve Maxwell's equations at a surface

$$\vec{\nabla}\times\mathbf{B}(\mathbf{r},t) = \frac{1}{c}\frac{\partial}{\partial t}\varepsilon\mathbf{E}(\mathbf{r},t), \tag{114}$$

$$\vec{\nabla}\times\mathbf{E}(\mathbf{r},t) = -\frac{1}{c}\frac{\partial}{\partial t}\mathbf{B}(\mathbf{r},t). \tag{115}$$

Assume the surface is the plane $z=0$, where $z<0$ is vacuum, and $z>0$ is a solid with a dielectric constant $\varepsilon(\omega)$. The above six equations group into two sets of three. One set describe transverse magnetic modes (TM) while the other set describes transverse electric modes. Only TM modes describe surface plasmons.

A. TM modes

In the plane of the surface, all fields have the phase factor of $\exp[i(\vec{\kappa}\cdot\vec{\rho}\pm\omega t)]$, so that derivatives with respect to t give $\mp i\omega/c$, derivatives with respect to x give $i\kappa_x$, and derivatives with respect to y give $i\kappa_y$. Introduce an unknown amplitude $B(\kappa)$. The transverse magnetic field is

$$\mathbf{B}(\mathbf{r},t) = i\sum_{\boldsymbol{\kappa}} B(\kappa)e^{i\vec{\kappa}\cdot\vec{\rho}}(\hat{x}\kappa_y - \hat{y}\kappa_x)(a_{\boldsymbol{\kappa}}e^{-i\omega t} + a_{-\boldsymbol{\kappa}}^\dagger e^{i\omega t})\phi_B(\vec{\kappa},z), \tag{116}$$

$$\phi_B(\vec{\kappa},z) = \begin{cases} e^{-\gamma z} & z>0 \\ e^{pz} & z<0 \end{cases}, \tag{117}$$

$$\gamma^2 = \kappa^2 - \frac{\omega^2}{c^2}\varepsilon(\omega), \quad p^2 = \kappa^2 - \frac{\omega^2}{c^2}, \tag{118}$$

where $(a_\kappa, a_\kappa^\dagger)$ are the raising and lowering operators for surface polaritons. The prefactor of i in $\mathbf{B}(\mathbf{r},t)$ makes the magnetic field Hermitian. The electric field, and vector potential, associated with this magnetic field, are

$$\mathbf{E}(\mathbf{r},t) = i\sum_{\boldsymbol{\kappa}} B(\kappa)e^{i\vec{\kappa}\cdot\vec{\rho}}\frac{cp}{\omega}(a_{\boldsymbol{\kappa}}e^{-i\omega t} - a_{-\boldsymbol{\kappa}}^\dagger e^{i\omega t})\vec{\phi}_A(\vec{\kappa},z), \tag{119}$$

$$\mathbf{A}(\mathbf{r},t) = \sum_{\boldsymbol{\kappa}} B(\kappa)e^{i\vec{\kappa}\cdot\vec{\rho}}\frac{c^2p}{\omega^2}(a_{\boldsymbol{\kappa}}e^{-i\omega t} + a_{-\boldsymbol{\kappa}}^\dagger e^{i\omega t})\vec{\phi}_A(\vec{\kappa},z), \tag{120}$$

$$\phi_{A,\mu}(\vec{\kappa},z) = \begin{cases} \eta_\mu^- e^{-\gamma z} & z>0 \\ \Lambda_\mu^+ e^{pz} & z<0 \end{cases}, \tag{121}$$

$$\eta_\mu^- = (i\kappa_\mu, -p), \quad \Lambda_\mu^+ = (i\kappa_\mu, \gamma). \tag{122}$$

All fields are Hermitian. The components of the electric and magnetic field that are parallel to the surface are conserved at $z=0$. The normal component of the electric field has a component equation $-p\varepsilon=\gamma$, which is one way to express the dispersion relation for surface polaritons.

B. Quantization

The next step is to calculate the energy density in these fields. Evaluate the space integrals

$$\mathcal{E}_B = \int \frac{d^3r}{8\pi} B(\mathbf{r},t)^2 = \frac{A}{16\pi} \sum_{\boldsymbol{\kappa}} B(\kappa)^2 (a+a^\dagger)(a+a^\dagger)\left(\frac{1}{\gamma}+\frac{1}{p}\right)\kappa^2, \quad (123)$$

$$\mathcal{E}_E = \int \frac{d^3r}{8\pi} \varepsilon E(\mathbf{r},t)^2 = -\frac{A}{16\pi} \sum_{\boldsymbol{\kappa}} B(\kappa)^2 (a-a^\dagger)(a-a^\dagger)\frac{p^2c^2}{\omega^2} \times \left[\frac{\varepsilon(p^2+\kappa^2)}{\gamma} + \frac{\kappa^2+\gamma^2}{p}\right]. \quad (124)$$

The terms in $\mathcal{E}_B$ can be simplified to

$$\kappa^2\left(\frac{1}{\gamma}+\frac{1}{p}\right) = \frac{\kappa^2}{p\gamma}(p+\gamma) = p+\gamma = \frac{1}{p}(p^2+\kappa^2). \quad (125)$$

In the expression for $\mathcal{E}_E$, the κ^2 terms cancel using $\varepsilon = -\gamma/p$, and the other two terms are simplified using $\gamma = \kappa^2/p$

$$\left[\frac{\varepsilon(p^2+\kappa^2)}{\gamma} + \frac{\kappa^2+\gamma^2}{p}\right] = \frac{\gamma^2-p^2}{p}, \quad (126)$$

$$= \frac{\kappa^4-p^4}{p^3} = \frac{(\kappa^2-p^2)(\kappa^2+p^2)}{p^3} = \frac{\omega^2}{c^2}\frac{\kappa^2+p^2}{p^3}. \quad (127)$$

Both factors in the two energy densities are the same. So we can set

$$\frac{A}{16\pi} B(\kappa)^2 \frac{\kappa^2+p^2}{p} = \frac{1}{4}\hbar\omega(\kappa), \quad (128)$$

$$B(\kappa) = \sqrt{\frac{4\pi\hbar\omega(\kappa)p}{A(\kappa^2+p^2)}}. \quad (129)$$

This form for $B(\kappa)$ has the advantage that it is valid for very dielectric function $\varepsilon(\omega)$. The total energy in the system is

$$\mathcal{E}_B + \mathcal{E}_E = \sum_{\boldsymbol{\kappa}} \hbar\omega(\kappa)\left[a^\dagger_{\boldsymbol{\kappa}} a_{\boldsymbol{\kappa}} + \frac{1}{2}\right]. \quad (130)$$

The final result for the electric field outside the surface is

$$E_{\boldsymbol{\kappa},\mu}(z) = icp\sqrt{\frac{4\pi\hbar p}{A_0\omega(p^2+\kappa^2)}}(a_{\boldsymbol{\kappa}} - a^\dagger_{-\boldsymbol{\kappa}})e^{i\vec{\kappa}\cdot\vec{\rho}+zp}\Lambda^-_\mu. \quad (131)$$

This classical result should be compared with the quantum result in Eq. (107) which we try to write in a similar way using $C_{SP,\kappa} = ia_\kappa$

$$E_{\boldsymbol{\kappa},\mu}(z) = i\frac{\omega_i cp\kappa}{p^2+\kappa^2}\sqrt{\frac{4\pi\hbar p}{A_0 W\omega}}(a_{\boldsymbol{\kappa}} - a^\dagger_{-\boldsymbol{\kappa}})e^{i\vec{\kappa}\cdot\vec{\rho}+zp}\Lambda^-_\mu. \quad (132)$$

The two results, from classical and quantum physics, are obviously different. They differ for all wave vectors.

VI. DISCUSSION

We have solved the quantum mechanical problem of coupling between photon fields and phonon fields, near the surface of a polar dielectric. We show how to quantize each of the modes. We also repeated the standard classical quantization and showed that it is different. We also derived the eigenfunctions for the bulk optical phonons for the layered geometry. We also showed how to quantize these modes.

We also discussed in detail the interaction of a charged particle, outside of the surface, with the surface and bulk polaritons. There are two interaction terms. One is the scalar potential and the other is by a vector potential. Both expressions are new. They replace Eq. (2) by the proper quantum expressions.

The classical derivation of the Fuchs-Kliewer mode gives only a vector potential. That theory has no scalar potential and cannot actually have an expression such as Eq. (2). The form of Eq. (2) is from a scalar potential. Our theory shows that surface polaritons generate both a scalar potential and a vector potential, which both act on a charged particle outside of a surface.

We also used our version of the scalar potential to calculate the image potential. For the surface polariton it decayed exponentially away from the surface, because of the cut-off κ_i. The Fuchs-Kliewer mode does not explain the classical image potential far from the surface. The actual source of the image potential is a volume transverse phonon-polaritons and also the radiation modes. We presented the image potential from the transverse phonon-polariton and showed that it gave less than half of the classical value at long distance. The rest is from radiation modes. Ekardt[22] came to similar conclusions. However, our derivations differ since he took the solid to be continuous media and omitted local field corrections. As a result, our matrix elements are different.

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