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Surface-induced charge disturbances and piezoelectricity in insulating crystals

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The charge disturbance induced by a surface in a three-dimensional insulating crystal is studied in the self-consistent-field approximation, when the surface is parallel to one of the lowest-index crystal planes. The disturbance is shown to decay exponentially into the interior of the crystal with a decay rate which depends only on the band structure of the infinite crystal and the position of the Fermi level relative to any surface states that may be formed. We then show that the macroscopic piezoelectric response of a semiconducting crystal does not depend on the way in which the crystal is terminated, thus resolving a previous controversy.

I. INTRODUCTION

It is commonly believed that piezoelectricity is a bulk effect and that the vanishing coefficients of the piezoelectric tensor can be inferred from the symmetry of the unit cell of the crystal.[1] In particular, one expects that, if the unit cell is symmetric under spatial inversion, then all components of the piezoelectric tensor are zero. Indeed, it is clear that this is the case for a molecular solid, where the dipole moment of the solid is just the sum of the dipole moments of the individual molecules, and the molecular moments in turn are determined by the local electric fields and local strain fields at the molecules.

For the case of an ionic solid, the situation is slightly less obvious. Even though a crystal structure has inversion symmetry (e.g., the NaCl structure), a finite crystal may be terminated in an asymmetric manner [e.g., a (111) plane of Na^+ ions on one side and a plane of Cl^- on the other side], so that the finite crystal can have a macroscopic dipole moment, proportional to the volume of the sample. Indeed, if one chooses as the center of the unit cell a point midway between a Na^+ and a Cl^- ion, the unit cell will have a finite dipole moment; this dipole moment would vary with pressure applied to the sample, and one might then be tempted to conclude that NaCl is a piezoelectric. In fact, if the large electric field due to the surface ions were not cancelled by external charges, the field would produce a relative displacement of the positive and negative ions in the bulk of the crystal, and the magnitude of this additional polarization would change in a nontrivial fashion as the pressure is varied.

Of course, NaCl is not a piezoelectric. The piezoelectric coefficient must be measured, in principle, under conditions of vanishing macroscopic electric field. For example one may place the sample between the plates of a shorted capacitor, which is a geometry that leads to vanishing average electric field in the crystal.[2] The piezoelectric coefficient then is determined by measuring the *current flow* through the shorting wire, as one varies the stress on the sample. For an ionic crystal with an inversion-symmetric unit cell, such as NaCl, one can readily demonstrate that for a given stress variation, the current in the shorting wire will vanish in the limit of a thick sample, inversely as the thickness of the sample, and hence there is no bulk piezoelectric effect, regardless of how the crystal is terminated. The essence of the argument here is that the displacements of the ions are entirely determined by their *local* environments once the macroscopic electric field is cancelled, and thus the termination of the surface has no effect on the sample interior in the shorted capacitor geometry.

It is less clear, however, that one can make these locality arguments in the case of a semiconducting crystal. Here, the natural starting point for a quantum-mechanical description involves electrons in Bloch states, which are spread throughout the crystal. There is then no obvious way to talk about the displacement of a particular electron, and one may especially question whether the sample boundaries will have a negligible effect on the interior. In fact, it has been proposed[3–6] that the surface effects cannot be ignored in this case, and that there should be a nonvanishing bulk piezoelectric coefficient for a crystal with asymmetric termination, even when there is an inversion center in the unit cell of the infinite crystal.

In the present paper we argue that the effects of the semiconductor surface fall off exponentially as one enters the interior of the crystal, and that one can define a local piezoelectric response in the semiconductor just as in the case of the ionic crystal or a molecular solid with local dipole moments. It is well known that under appropriate conditions surface perturbations on the charge density $\rho(\vec{r})$ of an insulating crystal fall off exponentially as a function of distance from the surface. However, the polarization $\vec{P}(\vec{r})$ is related to the integral of $\rho(\vec{r})$, so it does not immediately follow that there is no constant correction to $\vec{P}(\vec{r})$. In the simplest case of a nonpiezoelectric crystal, we can establish that there is no correction by making use of the demonstrations of surface charge quantization by Appelbaum and Hamann[7] and Claro.[8] To establish that there is vanishing effect of the surface on the piezoelectric response of a bulk sample in the more general case, we show that the current response function is independent of sample termination, far from the surface layers. The condition for this to be true is that the Fermi level lie within an energy gap in the interior of the crystal, between a completely full valence band and a completely empty conduction band.

It follows from our arguments that there is a unique piezoelectric coefficient, which can be calculated in principle for an infinite sample or for a finite sample with any convenient boundary conditions, and that the piezoelectric coefficient does vanish when the unit cell has inversion symmetry. These results are in agreement with the conclusions of Martin,[9] and our work may be considered to provide a quantum-mechanical justification for Martin's arguments.

The analyses in this paper are carried out in the self-consistent potential approximation, i.e., the self-consistent potential $V(\vec{r})$ is determined by Poisson's equation

$$\nabla^2 V(\vec{r}) = -4\pi e^2[\rho(\vec{r}) - \rho_{\rm ion}(\vec{r})] , \tag{1.1}$$

where $\rho_{\rm ion}(\vec{r})$ is the number density of the ionic charge and $\rho(\vec{r})$ is the density of electrons obtained by solving the one-particle Schrödinger equation in the potential $V(\vec{r})$. (A local exchange and correlation potential could also be included with little additional effort.) We assume that the time-varying applied stress causes a known variation in the ionic charge $\rho_{\rm ion}$, and we examine the resulting electron flow in the adiabatic ($\omega \to 0$) limit.

In this paper we consider a sample which is between two parallel capacitor plates, and we assume that the sample surfaces are parallel to one of the elementary planes of the crystal, so that the sample remains *periodic* in the direction *parallel* to the plates. Effects of the sample termination are found to fall off exponentially, in this case, with a decay rate which depends on the details of the surface only through the position of the Fermi level relative to any surface states which are formed. In the case of a surface parallel to a crystal plane of high Miller index, or of a reconstructed surface with a large unit cell, there will still be exponential decay of surface effects, but the decay length can be much longer, proportional to the size of the surface unit cell, and controlled by the electrostatic potential of the periodic variations in surface charge density.

In the case of a disordered sample surface, there will only be power-law falloff of the surface effects, controlled by the random electrostatic dipole fields of the surface charges. Even in this case, the surface effects fall off quickly enough so that the measured piezoelectric constant of a large sample should reduce to the bulk value, independent of the details of the surface. However, we shall not discuss the disordered surface here.

In the following section we shall discuss in greater detail the model considered in this paper. In Sec. III we examine in detail the self-consistent potential and charge density in the neighborhood of a surface, and see how they approach exponentially the values for the ideal bulk crystal. The quantization of surface charge is discussed in Sec. IV for the simplest case of a nonpiezoelectric crystal. In Sec. V these results are used to establish the vanishing of the piezoelectric coefficient in the simple case. The more general case is also treated in this section. Here we show that the current response function is independent of the details of the surface potential and that this implies that the surface has a vanishing effect on the piezoelectric response of a bulk sample. Appendix A contains a review of the analytic properties of Bloch functions used in the paper. In Appendix B we present details of our analysis of the wave functions and charge density in the vicinity of a surface.

Although portions of Secs. III and IV are recapitulations of derivations that have previously appeared in the literature, other portions, such as our discussions of the linear-response function $\chi(\vec{r},\vec{r}\,')$ and our analysis of the self-consistency problem are presented here for the first time, to the best of our knowledge. Previous discussions of the falloff of the charge-density perturbation $\Delta\rho_1(\vec{r})$ arising from a localized surface potential are extended, in Appendix B, to three-dimensional crystals.

II. MODEL CONSIDERED

In the following sections we consider a semiconducting crystal, in a quantum-mechanical treatment, and show that the effect of the surface on the charge density and self-consistent potential decays exponentially into the interior of the crystal. There is, in fact, a minimum decay rate independent of the details of the surface potential, if the Fermi energy is located near the middle of the bulk gap. Using these results and the quantization of surface charge, or, more generally, the properties of the current response function, we show that the piezoelectric polarization is independent of the nature of the surfaces, neglecting terms of order $1/L$, where L is the thickness of the sample.

We consider a semiconducting crystal between shorted capacitor plates that are oriented perpendicular to the z direction. If the ions in the crystal are displaced due to an applied ac pressure on the capacitor plates there will be a change in the electron-ion potential, and we would like to know what the response to this change in potential is; or, specifically, what current is induced in the shorting wire.

Within the self-consistent potential approximation, we may answer these questions by an iterative procedure. We may first guess the positions of the ions and an approximate form of electronic charge density $\rho(\vec{r})$. We then compute $V(\vec{r})$ from Poisson's equation, (1.1). We next solve Schrödinger's equation in this $V(\vec{r})$ to get a new estimate of $\rho(\vec{r})$, use the new $\rho(\vec{r})$ to compute a new $V(\vec{r})$, and iterate until self-consistency is achieved for $V(\vec{r})$ and $\rho(\vec{r})$. In general, however, we may find at this point that the forces on the ions are not zero. Then we must displace the ions slightly, so that the forces vanish, and then begin the procedure again. Ultimately, after several iterations, one must find self-consistency for the positions of the ions, the electron charge density $\rho(\vec{r})$, and the potential $V(\vec{r})$.

In the present paper we shall discuss the problem of self-consistency between $V(\vec{r})$ and $\rho(\vec{r})$. Self-consistency of the ionic positions can be discussed with a minor generalization of our arguments, but will not be explicitly treated. Rather, we shall assume that, except near the surface, the interionic distances are the same as for an infinite crystal, and that the *bare* ionic potentials are also the same as in the infinite crystal. The effect of varying stress will be incorporated in the model by a variation of some parameter of the bare ion potentials, which conserves the bulk symmetry. Any effects of the surface will then result from the perturbation of the electron charge density $\rho(\vec{r})$ and the self-consistent potential $V(\vec{r})$.

Figure 1 shows an example of the bare electron-ion potential for a crystal with two types of ions and an inversion-symmetric unit cell in the bulk. A simple example of a change in this potential which preserves the bulk symmetry is one in which the relative depths of the A and B wells change but their positions remain the same. In this case one would expect charge to be transferred between the A and B wells. If the crystal is terminated in a symmetric way, such that it has an inversion center, then, by symmetry, applying pressure cannot induce a dipole moment in the crystal and no current will flow in the shorting wire. However, if the crystal is terminated in an asymmetric way, as in Fig. 1, it is not so obvious that a dipole moment cannot be induced.

III. THE SELF-CONSISTENT POTENTIAL

A. Potential arising from specified surface charges

Consider a finite crystal in the region $-s \le z \le L-s$, terminated in an asymmetric manner. Let us first assume that the change in potential, arising from each surface, is entirely due to charges within a finite surface layer of thickness s. Then, from *Laplace's equation,* the difference in the total potential of this finite crystal and the corresponding infinite crystal in the region $0 < z < L-2s$ is

$$\Delta V(\vec{r}) = Az + \sum_{\vec{G}_{\parallel}(\neq \vec{0})} e^{i\vec{G}_{\parallel}\cdot\vec{r}_{\parallel}}\left(B_{\vec{G}_{\parallel}} e^{-(z+s)G_{\parallel}} + C_{\vec{G}_{\parallel}} e^{(z-L+s)G_{\parallel}}\right), \tag{3.1}$$

where $\vec{G}_{\parallel}$ is a reciprocal-lattice vector parallel to the surfaces and the coefficients $B_{\vec{G}_{\parallel}}$ and $C_{\vec{G}_{\parallel}}$ are determined by the surface charges. If we remove the macroscopic electric field by shorting the electrodes, then A must be zero (Ref. 2) and $\Delta V(\vec{r})$ decays exponentially inside the solid (at a rate corresponding to the smallest reciprocal-lattice vector $|\vec{G}_{\parallel}|$).

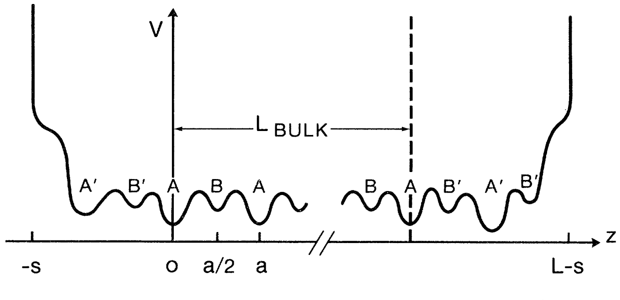

FIG. 1. An example of the electron-ion potential $V(\vec{r}_{\parallel},z)$ for fixed $\vec{r}_{\parallel}$, in the simple case where the bulk crystal is nonpiezoelectric, is shown. The potential is periodic in the region $0 \le z \le L_{\text{BULK}}$.

In the self-consistent-field approximation the change in the charge density, due to the surfaces, is not perfectly localized within a finite surface layer. The potential arising from a general surface charge density $e\Delta\rho(\vec{r})$ is obtained from Poisson's equation and the condition that the macroscopic electric field vanish. In Fourier space, the resulting surface potential ΔV must satisfy

$$\Delta V(\vec{G}_{\parallel},q_z) = 4\pi e^2 \frac{\Delta\rho(\vec{G}_{\parallel},q_z)}{G_{\parallel}^2 + q_z^2} , \tag{3.2a}$$

$$\lim_{q_z \to 0} [q_z \Delta V(0,q_z)] = 0 , \tag{3.2b}$$

where we have assumed that $\Delta\rho(\vec{r})$ is periodic in $\vec{r}_{\parallel}$. If $\Delta\rho$ decays exponentially into the bulk with exponent γ, then from (3.2) it follows that ΔV will decay exponentially with exponent β, where

$$\beta = \min_{\{\vec{G}_{\parallel}\}} (\gamma, |\vec{G}_{\parallel}|) . \tag{3.3}$$

In general, for a semiconductor we expect that the exponential decay length γ^{-1} for the surface perturbation will be larger than the lattice constant of the crystal. If the surface is parallel to one of the lowest-order crystal planes, so that $\min|\vec{G}_{\parallel}|$ is equal to one of the lowest few reciprocal-lattice vectors of the bulk, then $\beta=\gamma < \min|\vec{G}_{\parallel}|$; the charge density perturbation and the potential perturbation both decay exponentially into the bulk with a decay rate γ which is smaller than the minimum reciprocal-lattice vector $G_{\parallel}$.

B. Charge density resulting from a specified surface potential

To calculate the charge density resulting from a specified surface potential $\Delta V(\vec{r})$, we need to solve Schrödinger's equation in the presence of this potential. This is a difficult problem because of the infinite extent of the surface potential (i.e., the exponential tail). However, this problem can be solved by dividing the surface potential ΔV into a sum of two parts: one of arbitrary strength but nonzero only in a finite region, which we denote ΔV_1, and a second part ΔV_2, which is small everywhere and decays exponentially for z far from the surface. The charge density resulting from ΔV_1 can be found exactly by solving Schrödinger's equation and that resulting from ΔV_2 can be found approximately by using linear-response theory. This is a good approximation because ΔV_2 is weak but, in fact, the following analysis can be extended beyond linear-response theory, if desired.

We first consider the short-ranged potential $\Delta V_1(\vec{r})$. In Appendix B we show that, for $\Delta V_1(\vec{r})$ localized near the surface of a semi-infinite crystal, the perturbation in the charge density arising from the surface decays exponentially into the bulk. In particular, we consider a potential of the form

$$V_1(\vec{r}) = \begin{cases} V_0(\vec{r}), & z \geq 0 \\ V_0(\vec{r}) + \Delta V_1(\vec{r}), & -s < z < 0 \\ \infty, & z < -s, \end{cases} \tag{3.4}$$

where V_0 is the potential of the infinite crystal and where the surface potential $\Delta V_1(\vec{r})$ is periodic in $\vec{r}_{||}$. It is shown that the electron density $\rho_1(\vec{r}) = \rho_0(\vec{r}) + \Delta\rho_1(\vec{r})$ satisfies

$$\lim_{z \to \infty} \Delta\rho_1(\vec{r}_{||}, z) \propto e^{-\alpha_1 z} , \tag{3.5}$$

where ρ_0 is the electron density of the infinite crystal and $1/\alpha_1$ is a microscopic length which depends only on the nature of the band gap in the bulk and the position of the Fermi level, relative to any surface states in the gap.

In the proof of (3.5) it is assumed that ΔV_1 remains bounded inside the surface region $-s < z < 0$. The fact that we have placed an infinite potential barrier at a point $z = -s$ (which we may take to be outside the crystal) should not affect the results.

The analysis in Appendix B can be briefly summarized as follows. The electron charge density is the total charge density of all filled bands and all filled surface states (if any):

$$\rho_1(\vec{r}) = \sum_n{}' \sum_{\vec{k}_{||}} \left[\int dk_z \, |\psi_{\vec{k}n}(\vec{r})|^2 + \sum_{\kappa_z} |\psi_{\vec{k}_{||}\kappa_z n}(\vec{r})|^2 \right] \tag{3.6a}$$

$$\equiv \rho_B(\vec{r}) + \rho_s(\vec{r}) \; . \tag{3.6b}$$

The continuum wave functions $\psi_{\vec{k}n}$ and the surface states $\psi_{\vec{k}_{||}\kappa_z n}$ are defined in Appendix B, and ρ_B and ρ_S denote the band and surface-state contributions, respectively, to the density of electrons. The asymptotic behavior of $\Delta\rho_1(\vec{r})$ is determined by the singularities of $P_{\vec{k}n}(\vec{r},\vec{r})$ in the complex k_z plane, where $P_{\vec{k}n}(\vec{r},\vec{r}\,') \equiv \psi_{\vec{k}n}(\vec{r})\psi_{\vec{k}_{||},-k_z,n}(\vec{r}\,')$. Now $P_{\vec{k}n}$ has *poles* at the complex values $k_z = \kappa_z(\vec{k}_{||})$, where κ_z is the complex k_z component of the wave vector $(\vec{k}_{||}, \kappa_z)$ of a decaying Bloch wave which contributes to a surface state of the semi-infinite crystal. In addition $P_{\vec{k}n}$ has, in general, *branch points* at certain complex wave vectors $k_z = \tilde{k}_z(\vec{k}_{||})$, where there is a merger between bands n and $n \pm 1$. The branch points are characteristics of the bulk band structure, while the surface states depend on the nature of the potential in the surface region.

If there are no surface states between the conduction and valence bands, then the closest singularities to the real axis arise from the branch points between the valence and conduction bands, and the decay constant in (3.5) may be written as

$$\alpha_1 = \alpha_0 \equiv 2 \min_{\{\vec{k}_{||}\}} |\mathrm{Im}\tilde{k}_z(\vec{k}_{||})| \; . \tag{3.7}$$

Note that α_0 depends on the bulk band structure and not on the surface.

If surface states are present, the decay rate α_1 may still equal the bulk coefficient α_0, under certain conditions. In the simplest cases, we find that $\alpha_1 = \alpha_0$, provided that any surface state with energy below a value $E_1(\vec{k}_{||})$ is filled and provided that any surface state with energy greater than a value $E_2(\vec{k}_{||})$ is empty, where $E_1(\vec{k}_{||})$ and $E_2(\vec{k}_{||})$ lie in the gap between the valence and conduction bands. In this case the contributions of the pole singularities to the integral of (3.6a) are just cancelled by the sum over surface states. This result has previously been established in one dimension by Rehr and Kohn.[10]

Under more general conditions there will not be a cancellation between the poles of the integral and the sum in (3.6a). Then the decay rate α_1 which governs the falloff of $\Delta\rho_1$ will be determined by the decay rate of the surface-state wave functions near the Fermi energy, and in general we will have $\alpha_1 < \alpha_0$. The decay rate α_1 can tend to zero, however, only under very peculiar conditions—if the Fermi energy approaches the edge of the bulk valence or conduction band, and there happens to be a marginally bound surface state at the band edge. Otherwise, α_1^{-1} will be a microscopic length comparable to α_0^{-1}.

The intrinsic decay rate α_0 is closely related to the energy gap between the conduction and valence band. We expect that α_0 will tend to zero if the parameters of the crystal are modified in such a way that the direct band gap tends to zero.

C. The self-consistency problem

Having established that a potential ΔV_1 strictly limited to a finite surface region produces a charge density $\Delta\rho_1$ which decays exponentially into the crystal, we now turn to the effects of the exponentially decaying potential ΔV_2, and we prepare to consider the self-consistency problem.

Let us write the total self-consistent potential as

$$V(\vec{r}) = V_1(\vec{r}) + \Delta V_2(\vec{r}) \; , \tag{3.8}$$

where $V_1(\vec{r})$ is a potential of the form (3.4), including the repulsive wall at $z = -s$, the potential V_0 of the infinite crystal for $z > 0$, and the perturbed potential $V_0 + \Delta V_1$, for $-s < z < 0$. We write the electron number density $\rho(\vec{r})$ and the ionic charge density $\rho_{\text{ion}}(\vec{r})$, for $z \geq -s$, as

$$\rho(\vec{r}) = \rho_0(\vec{r}) + \Delta\rho_1(\vec{r}) + \Delta\rho_2(\vec{r}) \; , \tag{3.9}$$

$$\rho_{\text{ion}}(\vec{r}) = \rho^0_{\text{ion}}(\vec{r}) + \Delta\rho_{\text{ion}}(\vec{r}) \; , \tag{3.10}$$

where $\rho_0(\vec{r})$ and $\rho^0_{\text{ion}}(\vec{r})$ are the charge densities of the infinite crystal, $\Delta\rho_{\text{ion}}$ is assumed to be confined to the surface region $-s < z < 0$, and $\rho_0 + \Delta\rho_1$ is the electron charge density resulting from the potential $V_1(\vec{r})$, discussed above. The charge density $\Delta\rho_2$ and the potential ΔV_2

represent the balance necessary for self-consistency. Also there is a certain degree of arbitrariness in the definition of ΔV_1; we assume that it has been chosen carefully enough so that the remainder ΔV_2 is small. Then $\Delta\rho_2$ is related to ΔV_2 by

$$\Delta\rho_2(\vec{r})=e\int \chi(\vec{r},\vec{r}\,')\Delta V_2(\vec{r}\,')d\vec{r}\,' , \qquad (3.11)$$

where $\chi(\vec{r},\vec{r}\,')$ is the polarizability of the semi-infinite crystal in the presence of the short-ranged surface potential ΔV_1:

$$\chi(\vec{r},\vec{r}\,')={\sum_{n,n'}}'\sum_{\vec{k}_{\|},\vec{k}\,'_{\|}}\left[\int\int dk_z dk_z' \frac{P_{\vec{k}n}(\vec{r},\vec{r}\,')P_{\vec{k}\,'n'}(\vec{r}\,',\vec{r})}{E_{\vec{k}n}-E_{\vec{k}\,'n'}}+\int dk_z\sum_{\kappa_z'}\frac{P_{\vec{k}n}(\vec{r},\vec{r}\,')P_{\vec{k}\,'_{\|}\kappa_z'n'}(\vec{r}\,',\vec{r})}{E_{\vec{k}n}-E_{\vec{k}\,'_{\|}\kappa_z'n'}}\right.$$
$$\left.+\sum_{\kappa_z}\int dk_z'\frac{P_{\vec{k}_{\|}\kappa_z n}(\vec{r},\vec{r}\,')P_{\vec{k}\,'n'}(\vec{r}\,',\vec{r})}{E_{\vec{k}_{\|}\kappa_z n}-E_{\vec{k}\,'n'}}+\sum_{\kappa_z,\kappa_z'}\frac{P_{\vec{k}_{\|}\kappa_z n}(\vec{r},\vec{r}\,')P_{\vec{k}\,'_{\|}\kappa_z'n'}(\vec{r}\,',\vec{r})}{E_{\vec{k}_{\|}\kappa_z n}-E_{\vec{k}\,'_{\|}\kappa_z'n'}}\right]+(\vec{r}\leftrightarrow\vec{r}\,') , \qquad (3.12)$$

for $z,z'\geq -s$, and $\chi(\vec{r},\vec{r}\,')=0$ otherwise. The band indices n and n' run over all filled and all empty bands, respectively.

In order to close our equations, we invoke Poisson's equation (1.1), in the region $-s<z<\infty$. Since we assume that $V_0(\vec{r})$ is the self-consistent potential with the charge density $e(\rho_0-\rho_{\rm ion}^0)$ as source, we may write (1.1) as

$$\nabla^2(\Delta V_1+\Delta V_2)=-4\pi e^2(\Delta\rho_1+\Delta\rho_2-\Delta\rho_{\rm ion}) . \qquad (3.13)$$

Also, since we have assumed that there is no macroscopic electric field in the interior of the sample, we employ the boundary condition that $\Delta V_2(\vec{r})\to 0$ for $z\to\infty$.

Because our system is assumed periodic in the direction parallel to the x-y plane, we may take a partial Fourier transform in the plane and write the solution to Eq. (3.13) as

$$\Delta V_1(\vec{G}_{\|},z)+\Delta V_2(\vec{G}_{\|},z)=e^2\int_{-s}^{\infty}dz'u_{\vec{G}_{\|}}(z-z')[\Delta\rho_1(\vec{G}_{\|},z')+\Delta\rho_2(\vec{G}_{\|},z')-\Delta\rho_{\rm ion}(\vec{G}_{\|},z')] , \qquad (3.14)$$

where $\{\vec{G}_{\|}\}$ are the reciprocal-lattice vectors in the plane, and $u_{\vec{G}_{\|}}(z-z')$ is the Green's function for Poisson's equation. For $G_{\|}\neq 0$ we have

$$u_{\vec{G}_{\|}}(z-z')=\frac{2\pi}{|\vec{G}_{\|}|}\exp(-|\vec{G}_{\|}|\,|z-z'|) , \qquad (3.15)$$

while for $G_{\|}=0$ we have

$$u_0(z-z')=\begin{cases}4\pi(z-z') & \text{for } z<z'\\ 0 & \text{for } z>z' .\end{cases} \qquad (3.16)$$

We may also rewrite Eq. (3.11) in the form

$$\Delta\rho_2(\vec{G}_{\|},z)=e\sum_{\vec{G}\,'_{\|}}\int_{-s}^{\infty}dz'\chi_{\vec{G}_{\|}\vec{G}\,'_{\|}}(z,z')\Delta V_2(\vec{G}\,'_{\|},z') , \qquad (3.17)$$

where the kernel is the partial Fourier transform of $\chi(\vec{r},\vec{r}\,')$.

The expression (3.12) for $\chi(\vec{r},\vec{r}\,')$ can be studied by the same techniques used for the one-electron correlation function $G(\vec{r},\vec{r}\,')$ in Appendix B. One finds that χ has similar asymptotic behavior to G. Specifically, if we write

$$\chi=\chi^0+\Delta\chi , \qquad (3.18)$$

where χ^0 is the response function of the infinite crystal, then we have

$$\chi^0_{\vec{G}_{\|}\vec{G}\,'_{\|}}(z,z')\sim e^{-\alpha_0|z-z'|} \quad \text{as } |z-z'|\to\infty \qquad (3.19a)$$

$$\Delta\chi_{\vec{G}_{\|}\vec{G}\,'_{\|}}(z,z')\sim e^{-\alpha_1\max(z,z')} \quad \text{as } z+z'\to\infty \qquad (3.19b)$$

where the decay rates α_0 and α_1 are the same as in Sec. III B and in Appendix B.

Now we can write a formal solution to Eqs. (3.14) and (3.17) in the form

$$\Delta V_2(\vec{G}_{\|},z)=\sum_{\vec{G}\,'_{\|}}\int dz'R_{\vec{G}_{\|}\vec{G}\,'_{\|}}(z,z') \times[S_{\vec{G}\,'_{\|}}(z')+S'_{\vec{G}\,'_{\|}}(z')] , \qquad (3.20)$$

where

$$S_{\vec{G}_{\|}}(z)\equiv-\Delta V_1(\vec{G}_{\|},z) +e^2\int dz'u_{\vec{G}_{\|}}(\vec{z}-\vec{z}\,') \times[\Delta\rho_1(\vec{G}_{\|},z')-\Delta\rho_{\rm ion}(\vec{G}_{\|},z')] , \qquad (3.21)$$

$$S'_{\vec{G}_{\|}}(z)\equiv\sum_{\vec{G}\,'_{\|}}\int\int dz'dz''u_{\vec{G}_{\|}}(z-z')\Delta\chi_{\vec{G}_{\|}\vec{G}\,'_{\|}}(z',z'') \times\Delta V_2(\vec{G}\,'_{\|},z'') , \qquad (3.22)$$

and where R is the inverse dielectric function of the *infinite* crystal, which may be defined, with the use of a matrix notation, by

$$(\underline{1}-e^2\underline{u}\underline{\chi}^0)\underline{R}=\underline{1} . \qquad (3.23)$$

Now invoking (3.19), we see that, for large z, $S_{\vec{G}_{\|}}(z) \leq \text{const} \times e^{-\alpha_1 z}$ and $S'_{\vec{G}_{\|}}(z) \leq \text{const} \times e^{-\alpha_1 z}$. Furthermore, we shall see that

$$R_{\vec{G}_{\|}\vec{G}'_{\|}}(z,z') \sim e^{-\alpha|z-z'|} \quad \text{as } |z-z'| \rightarrow \infty \tag{3.24}$$

where α is less than α_0, but

$$\alpha \rightarrow \alpha_0 \tag{3.25}$$

if the coupling constant e^2 is small. It is clear then that

$$\Delta V_2(\vec{r}) \lesssim \text{const} \times e^{-\gamma z} , \tag{3.26}$$

where γ is the minimum of α and α_1. We may note that α^{-1} is a microscopic decay length characteristic of the self-consistent dielectric response of the infinite crystal, and that tending to zero would signal the onset of a dielectric instability in the bulk crystal. If there are no contributions from slowly decaying surface states near the Fermi energy, as discussed above and in Appendix B, then $\alpha_1 = \alpha_0 > \alpha$, and hence ΔV_2 decays with the bulk decay rate α.

In order to derive (3.25), it is convenient to take the Fourier transform of R and χ^0 in the z direction as well as in the x-y plane. Then (3.23) may be written as

$$\sum_{\vec{Q}'} \left[\delta_{\vec{Q},\vec{Q}'} - \frac{4\pi e^2}{|\vec{Q}+\vec{q}\,|^2} \chi^0(\vec{q}+\vec{Q},\vec{q}+\vec{Q}\,') \right] R(\vec{q}+\vec{Q},\vec{q}+\vec{Q}\,') = \delta_{\vec{Q},\vec{Q}'} , \tag{3.27}$$

where $\{\vec{Q}\}$ are the reciprocal-lattice vectors of the bulk crystal, and $\vec{q}$ is a wave vector parallel to the z axis. We wish to continue R analytically in q_z and look for the singularity closest to the real axis.

The response function χ^0 diverges at $q = \pm i\alpha_0$. This can be demonstrated from the expression for χ^0:

$$\chi^0(\vec{q}+\vec{Q},\vec{q}+\vec{Q}\,') = \sum_{n,n'}{}' \int d\vec{r} \int d\vec{r}\,' \int d\vec{k} \left[\frac{P_{\vec{k}n}(\vec{r},\vec{r}\,') P_{\vec{k}+\vec{q},n'}(\vec{r},\vec{r}\,')}{E_{\vec{k}n} - E_{\vec{k}+\vec{q},n'}} e^{i(\vec{q}+\vec{Q})\cdot\vec{r}} e^{-i(\vec{q}+\vec{Q}\,')\cdot\vec{r}\,'} + (\vec{r} \leftrightarrow \vec{r}\,') \right] , \tag{3.28}$$

and from the form of $P_{\vec{k}n}$, Eq. (A2), and $E_{\vec{k}n}$, Eq. (A5), near the branch points $\tilde{k}_z(\vec{k}_{\|})$. If we ignore the dependence of $\text{Im}\tilde{k}_z$ on the wave vector $\vec{k}_{\|}$, then χ^0 has a simple pole at $q = \pm i\alpha_0$, and we may approximate χ^0 by the expression

$$\chi^0(\vec{q}+\vec{Q},\vec{q}+\vec{Q}\,') \approx \frac{A_{\vec{Q}} A^*_{\vec{Q}} \, |\vec{q}+\vec{Q}\,| \, |\vec{q}+\vec{Q}\,'|}{(q-i\alpha_0)(q+i\alpha_0)} + B_{\vec{Q}\vec{Q}'} , \tag{3.29}$$

where $A_{\vec{Q}}$ is a constant and $B_{\vec{Q}\vec{Q}'}$ is analytic in q in the region of interest. If we ignore all the terms in (3.26) except $\vec{Q} = \vec{Q}\,' = 0$, then we find a pole in R at $q = \pm i\alpha$ with $\alpha = \alpha_0 - 2\pi e^2 \alpha_0^{-1} |A_0|^2$.

When we take into account the variation of $\text{Im}\tilde{k}$ with the wave vector $\vec{k}_{\|}$, then the divergence of χ^0 is reduced to a logarithmic divergence, close to $q = \pm i\alpha_0$. Then for sufficiently small e^2, R has a simple pole at $q = \pm i\alpha$, with

$$\alpha_0 - \alpha \sim \text{const} \times \exp(-\text{const}/e^2) . \tag{3.30}$$

IV. SURFACE CHARGE QUANTIZATION

In this section we will restrict ourselves to the case where the bulk crystal has inversion symmetry and a twofold rotation axis normal to the surface. Then there exists a set of symmetry planes for the bulk crystal, which are parallel to the cut surface. We assume that the twofold rotational symmetry is preserved in the semi-infinite crystal. We take $z=0$ to be a symmetry plane of the bulk crystal, and assume that the potential for $z>0$ is the same as for the infinite crystal. It is then possible to introduce a concept of excess surface charge, and show that this excess is quantized in half-integer values. This result will be used in Sec. V to give a very simple argument for a vanishing bulk piezoelectric response in this system.

One can define the surface charge of our semi-infinite semiconductor to be the number of excess electrons to the left of a symmetry plane of the crystal:

$$\delta N(m/2) = \int_{-\infty}^{ma/2} dz \int d\vec{r}_{\|} \rho(\vec{r}_{\|}) - n_{\|} n_0 m/2 , \tag{4.1}$$

where a is the length of a unit cell (containing one A and one B site, for example, as in Fig. 1), $m>0$ is an integer, n_0 is the number of filled bands, and $z = ma/2$ is a symmetry plane. We have assumed that the crystal has a large but finite area, containing a number $n_{\|}$ of unit cells parallel to the surface, and we shall assume periodic boundary conditions at the lateral edges of the sample. The band contribution to this surface charge is given by

$$\delta N_B(m/2) = \int_{-\infty}^{ma/2} dz \int d\vec{r}_{\|} \sum_n{}' \sum_{\vec{k}_{\|}} \int dk_z \, |\psi_{\vec{k}n}(\vec{r})|^2 - n_{\|} n_0 m/2 . \tag{4.2}$$

We can consider the contribution from a single $\vec{k}_{\|}$ only:

$$\delta N_B(\vec{k}_{\|}, m/2) = \int_{-\infty}^{ma/2} dz \int d\vec{r}_{\|} \sum_n{}' \int dk_z \, |\psi_{\vec{k}_{\|}k_z n}(\vec{r})|^2 - n_0 m/2 , \tag{4.3}$$

and we can define $\delta N(\vec{k}_{\|}, m/2)$ similarly.

For a surface potential which is zero in the bulk (i.e., the ΔV_1 part of the self-consistent potential only), the value $\delta N(\vec{k}_\parallel, m/2)$ has been shown to be quantized for each value of $\vec{k}_\parallel$, to order $1/m$, in integer or half-integer values in both one dimension[8] and three dimensions.[11] If we further assume that the band structure is simple, such that for fixed $\vec{k}_\parallel$ and energy $E_{\vec{k}_\parallel}$ there are only two solutions corresponding to the infinite crystal, then the quantization in each $\vec{k}_\parallel$ is evident from Eq. (7) of Ref. 8:

$$\delta N_B(\vec{k}_\parallel, m/2) = \left((1/\pi)[\delta(\vec{k}_\parallel, \pi/a) - \delta(\vec{k}_\parallel, 0)] + \tfrac{1}{4}\{\epsilon_1 \cos[2\delta(\vec{k}_\parallel, 0)] + \epsilon_2 \cos[2\delta(\vec{k}_\parallel, \pi/a)]\} + O(1/m)\right) n_0 \,, \tag{4.4}$$

where $\epsilon_{1,2} = \pm 1$ and $\delta(\vec{k}_\parallel, k_z)$ is the phase shift due to the surface potential. Since for $k_z = 0$ or $k_z = \pi/a$, $\delta = j\pi/a$, where j is an integer,[8,11] it follows from the above equation that the band surface charge is quantized in integer or half-integer values to order $1/m$. This accuracy was obtained by considering the analytic properties of the wave functions on the real k_z axis only. By extending the analysis to the complex plane, it can be shown[12] that the error is *actually* of order $e^{-\gamma ma/2}$, where γ is the smallest decay rate of the surface states associated with the filled bands (or $\gamma = \alpha_0$ if there are no surface states). Of course γ can be very small in the case where a surface state is just barely pulled out of the valence band. However, if the Fermi level is in the middle of the energy gap between the conduction and valence bands, any such surface state will be filled. When the Fermi level lies near the middle of the gap, the total charge density from states of the wave vector $\vec{k}_\parallel$, including the surface state and filled valence states, will exponentially approach the bulk values with a decay rate $\alpha_1(\vec{k}_\parallel)$, so that

$$\delta N(\vec{k}_\parallel, m/2) = l/2 + O(e^{-\alpha_1(\vec{k}_\parallel) ma/2}) \,, \tag{4.5}$$

where l is an integer and $1/\alpha_1(\vec{k}_\parallel)$ is a microscopic length, independent of the surface potential (other than its dependence on the position of the Fermi level relative to the surface states, if any).

In this analysis of surface charge quantization we have ignored the long-ranged part of the self-consistent surface potential [$\Delta V_2(\vec{r})$ from Sec. III], which decays like e^{-az} as $z \to \infty$. The net effect of introducing $\Delta V_2(\vec{r})$ into our analysis is to change the error from $O(e^{-\alpha_1 ma/2})$ to $O(e^{-ama/2})$ in (4.5).

We remark also that if there are no surface states that cross the Fermi level (i.e., no partially filled surface band) then the value of l is the same for all values for $\vec{k}_\parallel$, so that the total surface charge obeys

$$\delta N(m/2) = n_\parallel [l/2 + O(e^{-ama/2})] \,. \tag{4.6}$$

Equation (4.5) gives only the asymptotic form of the surface charge. Our analysis does not give the amplitude of the asymptotic correction or the depth into the crystal required to reach this asymptotic form. Such information can be obtained from the numerical work of Appelbaum and Hamann[7] on a one-dimensional Kronig-Penney model (one atom per unit cell). The striking cancellation in the charge disturbance that occurs between the contributions from the band and the surface states is clearly in their paper. The total surface charge is shown to be accurately quantized as near as five lattice spacings from the surface (for neutral crystals).

V. PIEZOELECTRIC RESPONSE

We turn now to the piezoelectric response of a large slab of material. We will first discuss the piezoelectric response of a finite (or semi-infinite) crystal for the simple case where the previous analysis of surface charge quantization is valid. That is, we first consider a crystal with an inversion-symmetric unit cell in the bulk and a set of symmetry planes parallel to the surface, and where the bulk band structure meets the restriction of not more than two states for any given energy and given $\vec{k}_\parallel$, as discussed in the preceding section. We present a simple argument for the vanishing of the bulk piezoelectric response in that case, independent of the detailed surface potential. (Note that a *one*-dimensional crystal with inversion symmetry will always fall into this simple case.) The piezoelectric response in the more general case is discussed in Sec. V B.

A. The simple case

Suppose an adiabatic ac perturbation is applied to the crystal in such a way that the local inversion symmetry of the bare ion potential is preserved in the interior of the crystal but the change in the surface potential is arbitrary other than to preserve the periodicity in the x-y plane. Then, from the analysis of Sec. III, the difference in the ac self-consistent potential from that of the infinite crystal is localized to the surface region.

If the potential $V(\vec{r})$ is changed by a small amount, for example as a result of strain in a piezoelectric experiment, then one might naturally expect $\delta N(\vec{k}_\parallel, m/2)$ to change by a small amount. However, the quantization of surface charge implies that surface charge discrepancy, $\delta N(\vec{k}_\parallel) \equiv \lim_{m\to\infty} \delta N(\vec{k}_\parallel, m/2) = l/2$, can only change by a discrete amount. In fact, the surface charge discrepancy $\delta N(\vec{k}_\parallel)$ will not change at all, unless there is a *change in occupancy* of a surface state, in which case we will have a change of ± 1 in $\delta N(\vec{k}_\parallel)$.

At low temperature, an electron can be scattered from one state to another only if both states are very close to the Fermi level. If there are *no* surface states at the Fermi level, then no scattering is possible, so there will be no changes in $\delta N(\vec{k}_\parallel)$. If there *are* surface states at the Fermi level, electrons can be transferred from a surface state at one value of $\vec{k}_\parallel$ to a surface state at another value of $\vec{k}_{||}$. It is clear, however, that such scattering processes will not change the total surface charge at the given crystal surface. (There can be no scattering process which transfers an electron from a state at one crystal surface to a state at the opposite crystal surface, because there is negligible overlap between the wave functions of those states.)

We see, therefore, that the number of electrons to the left of a symmetry plane at $z=ma/2$ remains unchanged during the variation of stress, except for corrections which fall off exponentially as one enters the crystal. It follows, then, that the total current through the symmetry plane is zero, except for corrections of order $e^{-\alpha z}$:

$$\int d\vec{r}_{||} J_z(\vec{r}_{||},z)\,|_{z=ma/2} = O(e^{-\alpha z}) \ . \tag{5.1}$$

The polarization of the sample is defined by

$$P_z = \int d\vec{r}_{||} \int_{-\infty}^{\infty} dz\, z[\rho(\vec{r}) - \rho_0(\vec{r})] \ , \tag{5.2}$$

where $\rho_0(\vec{r})$ is now the charge density in the absence of stress. Taking into account charge conservation, $\partial\rho/\partial t = -\vec{\nabla}\cdot\vec{J}$, we have

$$\frac{dP_z}{dt} = \int d\vec{r}_{||} \int_{-\infty}^{\infty} dz\, J_z(\vec{r}) \ . \tag{5.3}$$

Also, we have

$$\int d\vec{r}_{||} \int_{(m-1)a/2}^{(m+1)a/2} dz [J_z(\vec{r}_{||},z) - J_z(\vec{r}_{||},ma/2)] = \frac{d}{dt} \int d\vec{r}_{||} \int_{(m-1)a/2}^{(m+1)a/2} dz (z-ma/2)\rho(\vec{r}_{||},z) \ . \tag{5.4}$$

Now, except for surface effects which vanish as $e^{-\alpha ma/2}$, the integral on the right-hand side of (5.4) vanishes by symmetry. Then the only contribution to dP_z/dt comes from the surface layers and is independent of the thickness of the sample. The average polarization density of the sample is therefore inversely proportional to the thickness L. In a piezoelectric experiment, the current in the shorting wires of the capacitor plates, per unit area in the x-y plane, is proportional to the average polarization density of the sample, and therefore the contribution due to asymmetric termination of the sample will vanish as $1/L$, for large L.

B. The general case

We now consider more general semi-infinite crystals and show that the piezoelectric response is the same as that of the bulk crystal, neglecting terms of order $1/L$, provided that the Fermi level lies in a nonvanishing energy gap in the bulk.

We shall use linear-response theory in this section. Specifically, we assume for convenience that the applied strain is sufficiently minute that the resulting ion displacements are small compared to the interatomic spacing, and the resulting change in electron-ion potential is small. However, it is clear physically that the piezoelectric response is actually linear as long as the strain is small. (If it is desired to calculate directly the response to a finite strain, one should transform to a coordinate system moving with the ions, at the expense of some complication in our equations.)

The z component of the current in the sample is related to the complete self-consistent ac potential $V(\vec{r},\omega)$ by

$$J_z(\vec{r},\omega) = \int d\vec{r}\,' K(\vec{r},\vec{r}\,';\omega) V(\vec{r}\,',\omega) \ , \tag{5.5}$$

where K is the z component of the current response function of the semi-infinite crystal in the presence of the short-ranged potential ΔV_1. The ac potential can be written as

$$V(\vec{r},\omega) = V_0(\vec{r},\omega) + \Delta V(\vec{r},\omega) \ , \tag{5.6}$$

where $V_0(\vec{r},\omega)$ is the self-consistent ac potential of the infinite crystal. It follows from our analysis in Sec. III that

$$\lim_{z\to\infty} \Delta V(\vec{Q}_{||},z,\omega) \propto e^{-\alpha z} \ , \tag{5.7}$$

if the frequency ω is sufficiently small. It will also be useful to take the Fourier transform of (5.5) in the x-y plane:

$$J_z(\vec{Q}_{||},z,\omega) = \sum_{\vec{Q}\,'_{||}} \int dz' K(\vec{Q}_{||},\vec{Q}\,'_{||},z,z';\omega) V(\vec{Q}\,'_{||},z',\omega) \ . \tag{5.8}$$

In the adiabatic limit ($\omega\to 0$) the current response function is given, for $z,z' > -s$, by

$$\begin{aligned} K(\vec{r},\vec{r}\,';\omega) = {} & \frac{ie^2\omega}{m} \sum_{n,n'} \left[\frac{\partial}{\partial z_1} - \frac{\partial}{\partial z_2} \right] \\ & \times \sum_{\vec{k}_{||},\vec{k}\,'_{||}} \left[\int dk_z \int dk_z' \frac{P_{\vec{k}n}(\vec{r}\,',\vec{r}_1) P_{\vec{k}\,'n'}(\vec{r}_2,\vec{r}\,')}{(E_{\vec{k}n} - E_{\vec{k}\,'n'})^2} + \int dk_z \sum_{\kappa_z'} \frac{P_{\vec{k}n}(\vec{r}\,',\vec{r}_1) P_{\vec{k}\,'_{||}\kappa_z' n'}(\vec{r}_2,\vec{r}\,')}{(E_{\vec{k}n} - E_{\vec{k}\,'n'})^2} \right. \\ & + \sum_{\kappa_z} \int dk_z' \frac{P_{\vec{k}_{||}\kappa_z n}(\vec{r}\,',\vec{r}_1) P_{\vec{k}\,'n'}(\vec{r}_2,\vec{r}\,')}{(E_{\vec{k}n} - E_{\vec{k}\,'n'})^2} \\ & \left. \left. + \sum_{\kappa_z} \sum_{\kappa_z'} \frac{P_{\vec{k}_{||}\kappa_z n}(\vec{r}\,',\vec{r}_1) P_{\vec{k}\,'_{||}\kappa_z' n'}(\vec{r}_2,\vec{r}\,')}{(E_{\vec{k}n} - E_{\vec{k}\,'n'})^2} \right] \right|_{\vec{r}_1=\vec{r}_2=\vec{r}} + (\vec{r} \leftrightarrow \vec{r}\,') \ . \end{aligned} \tag{5.9}$$

The asymptotic behavior of K is determined by the singularities of the integrands, in the complex k_z and k_z' planes, which lie closest to the real k_z and k_z' axes. By comparing (5.7) to the expression for χ, (3.12), one sees that the analytic structure of the integrands is very similar in these two expressions. There are singularities at the branch points of $P_{\vec{k}n}$ and $E_{\vec{k}n}$ and poles at complex values of $k_z=\kappa_z$ which correspond to surface states. As in Sec. III and Appendix B, these poles will be cancelled by the sums over surface states, if the corresponding surface states are filled. From our previous analysis it follows that K_z has the following asymptotic properties, for $\omega\to 0$:

$$\lim_{(z+z')\to\infty} |K(\vec{Q}_{||},\vec{Q}'_{||},z,z';\omega)-K_0(\vec{Q}_{||},\vec{Q}'_{||},z,z';\omega)| \propto e^{-\alpha_1 \max(z,z')} , \qquad (5.10a)$$

$$\lim_{|z-z'|\to\infty} K_0(\vec{Q}_{||},\vec{Q}'_{||},z,z';\omega)\propto e^{-\alpha_0|z-z'|} , \qquad (5.10b)$$

where K_0 is the current response of the infinite crystal [and is given by the first term in (5.9)], and α_1 and α_0 are as defined in Sec. III and Appendix B.

It follows from (5.7), (5.8), and (5.10) that the current satisfies

$$\lim_{z\to\infty} |J_z(\vec{Q}_{||},z,\omega)-J_z^0(\vec{Q}_{||},z,\omega)| \propto e^{-\alpha z} \qquad (5.11)$$

in the adiabatic limit, where J_z^0 is the current in the infinite sample:

$$J_z^0(\vec{Q}_{||},z,\omega)=\sum_{\vec{Q}'_{||}} \int dz' K_0(\vec{Q}_{||},\vec{Q}'_{||},z,z';\omega) \times V_0(\vec{Q}'_{||},z',\omega) . \qquad (5.12)$$

The fact that the current approaches that of the bulk crystal exponentially away from the surface immediately implies that the polarization

$$P_z(\omega)=\frac{-i}{\omega}\int d\vec{r}_{||}\int_{-\infty}^{\infty} dz\, J_z(\vec{r},\omega) \qquad (5.13)$$

differs from that of the bulk only in the contribution from the surface layers. Thus the current in the shorting wire will be independent of the manner in which the sample is terminated, neglecting contributions of order $1/L$, for large L.

In a general crystal, one does not have surface charge quantization because there are, in general, no symmetry planes through which zero current flows. However, if we consider the special case discussed in the preceding section, then surface charge quantization follows from the linear-response analysis of this section. To see this, we make use of the bulk symmetry, which implies

$$V(\vec{Q}_{||},-z+na/2,\omega)=V(\vec{Q}_{||},z+na/2,\omega) , \qquad (5.14a)$$

$$K_0(\vec{Q}_{||},\vec{Q}'_{||},-z+ma/2,-z'+na/2;\omega) = -K_0(\vec{Q}_{||},\vec{Q}'_{||},z+ma/2,z'+na/2;\omega) . \qquad (5.14b)$$

Using these symmetry relations in (5.12), it follows that $J_z^0(\vec{Q}_{||},z=ma/2,\omega)=0$. Then from (5.11),

$$\int d\vec{r}_{||} J_z(\vec{r}_{||},z=ma/2,\omega)=O(e^{-\alpha ma/2}) \qquad (5.15)$$

in the adiabatic limit, which is Eq. (5.1).

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APPENDIX A: ANALYTIC PROPERTIES OF BLOCH FUNCTIONS

In this appendix we briefly summarize some analytic properties of the Bloch functions $\phi_{\vec{k}n}$ for the infinite crystal, which will be used in Appendix B. The analyticity of Bloch waves in one dimension has been studied thoroughly by Kohn.[13] A general analysis of the analytic properties of three-dimensional Bloch waves has been performed by des Cloizeaux.[14] We will need the properties of $\phi_{\vec{k}n}$ for complex k_z and real k_x and k_y only. These can be found in Blount,[15] Heine,[16] and Krieger.[17]

The Bloch functions are solutions to the three-dimensional Schrödinger equation

$$[-\nabla^2+V_0(\vec{r})]\phi_{\vec{k}n}=E_{\vec{k}n}\phi_{\vec{k}n} , \qquad (A1)$$

where V_0 is a periodic potential and $\phi_{\vec{k}n}$ transforms as $e^{i\vec{k}\cdot\vec{r}}$ under the translations by a lattice vector of V_0. This last condition may be expressed by writing

$$\phi_{\vec{k}n}(\vec{r})=e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}n}(\vec{r}) , \qquad (A2)$$

where $u_{\vec{k}n}$ is a periodic function. Bloch wave solutions can be found, in general, for complex as well as real values of $\vec{k}$, though the corresponding eigenvalues $E_{\vec{k}n}$ will generally be complex, and of course the $\phi_{\vec{k}n}$ are exponentially growing in some directions, if $\vec{k}$ is not real.

A section of a three-dimensional band structure is shown in Fig. 2. The dashed curves correspond to complex values of k_z for which the energy is real and are called real-energy curves. Real-energy curves either run off to $\mathrm{Im}k_z=\pm\infty$ and $E=-\infty$, similar to the ones originating at B and B' in Fig. 2, or connect one band to another, similar to the ones joining A to A' and C to C'. Considered as a function of complex k_z, $E_{\vec{k}n}$ is a branch of a multivalued function $E_{\vec{k}}$. In general, the projection onto the complex k_z plane of each real-energy loop, connecting one band to another, encloses at least one pair of complex conjugate branch points of $E_{\vec{k}}$. If the real-energy loop lies in a symmetry plane of the Brillouin zone (such as $\mathrm{Re}k_z=\pm\pi/a$ in Fig. 2) then the branch points

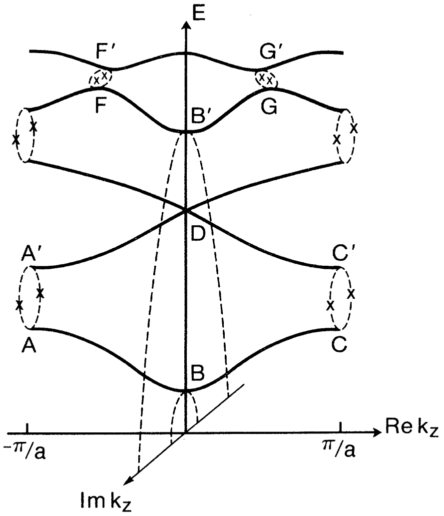

FIG. 2. A section of a three-dimensional band structure, with fixed $\vec{k}_{\parallel}$, is shown. The dashed lines denote curves along which k_z is complex and $E_{\vec{k}}$ is real. The positions of the branch points of $E_{\vec{k}}$, which occur in complex-conjugate pairs, are indicated by crosses.

will lie on the loop. In this case the two branch points correspond to the same *real* energy $E_{\vec{k}}$. (In general, the branch points correspond to complex-conjugate values of the energy also.) Near the branch point $\vec{k}_0$, $E_{\vec{k}}$ has the following form:

$$E_{\vec{k}} = a_0 + a_1 (k_z - k_{0z})^{1/2} + \cdots \, . \tag{A3}$$

To derive the analytic structure of $\phi_{\vec{k}n}$, the choice of phase and normalization must be specified. We choose the phase, for real $\vec{k}$, such that $u^*_{\vec{k}n} = u_{-\vec{k}n}$, and the normalization condition to be

$$\int_{\text{unit cell}} u_{\vec{k}n}(\vec{r})\, u_{-\vec{k}n}(\vec{r})\, d\vec{r} = 1 \, . \tag{A4}$$

Equation (A4) will then remain valid when we analytically continue $\phi_{\vec{k}n}$ to complex k_z. (The fact that we have not uniquely specified the phase of $\phi_{\vec{k}n}$ does not matter since we will actually only need to analytically continue the product $\phi_{\vec{k}n}\phi_{-\vec{k}n}$ and not $\phi_{\vec{k}n}$ itself.)

Considered as a function of complex k_z, $\phi_{\vec{k}n}$ is a branch of a multivalued function $\phi_{\vec{k}}$, which has branch points coinciding with those of $E_{\vec{k}}$. At the branch point $\vec{k}_0$, the form of $\phi_{\vec{k}}$ is

$$\phi_{\vec{k}} = (k_z - k_{0z})^{-1/4} [b_0 + b_1 (k_z - k_{0z})^{1/2} + \cdots] \, . \tag{A5}$$

The projection operator, defined as

$$P_{\vec{k}n}(\vec{r},\vec{r}\,') \equiv \phi_{\vec{k}n}(\vec{r})\, \phi_{-\vec{k}n}(\vec{r}\,') \, , \tag{A6}$$

when analytically continued to the branch point $\vec{k}_0$, has the form

$$P_{\vec{k}n} = (k_z - k_{0z})^{-1/2} [d_0 + d_1 (k_z - k_{0z})^{1/2} + \cdots] \, . \tag{A7}$$

The projection operator of the $n+1$ band, $P_{\vec{k},n+1}$, has the same form as (A7) but with the opposite sign in front of all square roots. Therefore the sum $P_{\vec{k}n} + P_{\vec{k},n+1}$ is analytic at $\vec{k} = \vec{k}_0$.

The only other singularities of $\phi_{\vec{k}}$ occur at points where two or more bands cross. At these points $\phi_{\vec{k}}$ can have a branch point at real values of k_z. However, the sum $\sum'_n P_{\vec{k}n}$, where n is summed over all bands which cross at the point $\vec{k} = \vec{k}_1$, is analytic at $\vec{k}_1$.[14]

APPENDIX B: SOME PROPERTIES OF THE SEMI-INFINITE CRYSTAL

In this appendix we show that, for a semi-infinite semiconductor at zero temperature, the effects of the surface on the charge density decay exponentially away from the surface. These results are used in Sec. III B, where we consider the charge density resulting from a specified surface potential. We assume that the potential $V_1(\vec{r})$ is piecewise continuous and of the form

$$V_1(\vec{r}) = \begin{cases} V_0(\vec{r}), & z \geq 0 \\ V_0(\vec{r}) + \Delta V_1(\vec{r}), & -s < z < 0 \\ \infty, & z < -s, \end{cases} \tag{B1}$$

where V_0 is perfectly periodic and ΔV_1 breaks the z symmetry only.

We define a one-electron correlation function

$$G(\vec{r},\vec{r}\,') = \sum_n{}' \left[\sum_{\vec{k}_{\parallel}} \int dk_z\, \psi_{\vec{k}n}(\vec{r})\, \psi^*_{\vec{k}n}(r') + \sum_{\vec{k}_s} \psi_{\vec{k}_s n}(\vec{r})\, \psi^*_{\vec{k}_s n}(\vec{r}\,') \right] , \tag{B2}$$

where $\psi_{\vec{k}n}$ satisfies the Schrödinger equation $(-\nabla^2 + V)\psi_{\vec{k}n} = E_{\vec{k}n}\psi_{\vec{k}n}$, $\sum'_n$ extends over all occupied bands, and $\sum_{\vec{k}_s}$ is over all occupied surface states between the n and $n+1$ bands. We shall assume a large system with periodic boundary conditions in the x-y plane. The surface states are then normalized to unity in this region, while the extended states have δ-function normalization in k_z. Our aim is to show that the correlation function satisfies

$$\lim_{z+z' \to \infty} [e^{\alpha_1 (z+z')/2} \,|\, G(\vec{r},\vec{r}\,') - G_0(\vec{r},\vec{r}\,') \,|\,] = 0 \, , \tag{B3}$$

$$\lim_{|z-z'| \to \infty} [e^{\alpha_1 |z-z'|/2} G(\vec{r},\vec{r}\,')] = 0 \, . \tag{B4}$$

$G_0(\vec{r},\vec{r})$ is the one-electron correlation function of the infinite crystal and $1/\alpha_1$ is a microscopic length.

The electron charge density is $\rho(\vec{r}) = G(\vec{r},\vec{r})$, and hence it will follow from (B3) that the charge density exponentially approaches that of the infinite lattice $\rho_0(\vec{r})$ as one moves into the interior of the crystal:

$$\lim_{z\to\infty} [e^{\alpha_1 z} \,|\, \rho(\vec{r})-\rho_0(\vec{r}) \,|\,]=0 \,. \tag{B5}$$

1. Jost solutions

We begin by discussing the properties of the Jost solutions, $f_{\vec{k}n}(\vec{r})$, for the semi-infinite crystal. The Jost solutions are defined to be the solutions to the Schrödinger equation

$$[-\nabla^2+V_1(\vec{r})]f_{\vec{k}n}=E_{\vec{k}n}f_{\vec{k}n} \tag{B6}$$

in the region $-s<z<\infty$, which satisfy the condition

$$f_{\vec{k}n}(\vec{r})=\phi_{\vec{k}n}(\vec{r}) \text{ for } z\geq 0 \,, \tag{B7}$$

where $\phi_{\vec{k}n}$ are the Bloch functions for the infinite crystal with potential $V_0(\vec{r})$ and where $V_1(\vec{r})$ is given by (3.4). The Jost solutions are *not* valid wave functions for the semi-infinite crystal because they do not satisfy the boundary condition that the wave function must vanish at $z=-s$; however, the Jost solutions will be used to construct these wave functions. The Jost solutions may be defined for complex values of k_z, and we shall see that they are analytic in the same domain as the $\phi_{\vec{k}n}$. This has been shown in one dimension by Rehr and Kohn[10] and their analysis is easily generalized to the three-dimensional case.

It is convenient to take a partial Fourier transform, writing

$$f_{\vec{k}n}(\vec{r})=\sum_{\vec{G}_{||}} e^{i(\vec{k}_{||}+\vec{G}_{||})\cdot\vec{r}_{||}} f_{\vec{k}n}(\vec{G}_{||},z) \,, \tag{B8}$$

and similarly for ϕ_{kn}, where the sum is over the reciprocal-lattice vectors $\vec{G}_{||}$ for the periodicity parallel to the surface.

Then the partial Fourier transforms satisfy

$$\left[-\frac{d^2}{dz^2}+|\vec{k}_{||}+\vec{G}_{||}|^2-E_{\vec{k}n}\right]f_{\vec{k}n}(\vec{G}_{||},z)+\sum_{\vec{G}'_{||}} V_1(\vec{G}_{||}-\vec{G}'_{||},z)f_{\vec{k}n}(\vec{G}'_{||},z)=0 \tag{B9}$$

for $z>-s$, with

$$f_{\vec{k}n}(\vec{G}_{||},z)=\phi_{\vec{k}n}(\vec{G}_{||},z) \text{ for } z\geq 0 \,. \tag{B10}$$

We write the potential $V_1(\vec{r})$ as

$$V_1(\vec{r})=\begin{cases} V_0(\vec{r}), & z>0 \\ E_0+\Delta\tilde{V}(\vec{r}), & -s<z<0 \end{cases} \tag{B11}$$

where E_0 can be chosen to be any convenient constant. Then the Jost solutions $f_{\vec{k}n}$ satisfy the following integral equation:

$$f_{\vec{k}n}(\vec{G}_{||},z)=\tilde{\phi}_{\vec{k}n}(\vec{G}_{||},z)-\int_z^0 dz'\mathcal{G}_{\vec{k}n}(\vec{G}_{||};z,z')\sum_{\vec{G}'_{||}}\Delta\tilde{V}(\vec{G}_{||}-\vec{G}'_{||},z')f_{\vec{k}n}(\vec{G}'_{||},z') \,. \tag{B12}$$

Where $\mathcal{G}$ is a Green's function and

$$\tilde{\phi}_{\vec{k}n}(\vec{G}_{||},z)=\begin{cases} \phi_{\vec{k}n}(\vec{G}_{||},z), & z>0 \\ \alpha_+e^{Qz}+\alpha_-e^{-Qz}, & -s<z<0 \end{cases} \tag{B13}$$

where $Q\equiv(E_0+|\vec{k}_{||}+\vec{G}_{||}|^2-E_{\vec{k}n})^{1/2}$ and $\alpha_\pm=\frac{1}{2}[\phi_{\vec{k}n}(\vec{G}_{||},0)\pm(\partial/\partial z)\phi_{\vec{k}n}(\vec{G}_{||},0)/Q]$. The Green's function has the simple form

$$\mathcal{G}_{\vec{k}n}(\vec{G}_{||};z,z')=\begin{cases} \sinh[Q(z-z')]/2Q, & z<z' \\ 0, & \text{otherwise} \end{cases} \tag{B14}$$

where we have $-s\leq z,z'<0$.

The integral equation (B12) can be iterated to obtain

$$\begin{aligned} f_{\vec{k}n}(\vec{G}_{||},z)=\tilde{\phi}_{\vec{k}n}(\vec{G}_{||},z)+\sum_{m=1}^{\infty}(-1)^m\int_z^0 dz_1\cdots\int_{z_{m-1}}^0 dz_m \sum_{\vec{G}^{(1)}_{||}}\cdots\sum_{\vec{G}^{(m)}_{||}}\mathcal{G}_{\vec{k}n}(\vec{G}_{||};z,z_1) \\ \times\mathcal{G}_{\vec{k}n}(\vec{G}^{(1)}_{||};z_1,z_2)\cdots\mathcal{G}_{\vec{k}n}(\vec{G}^{(m-1)}_{||};z_{m-1},z_m)\Delta\tilde{V}(\vec{G}_{||}-\vec{G}^{(1)}_{||},z_1) \\ \times\Delta\tilde{V}(\vec{G}^{(1)}_{||}-\vec{G}^{(2)}_{||},z_2)\cdots\Delta\tilde{V}(\vec{G}^{(m-1)}_{||}-\vec{G}^{(m)}_{||},z_m)\tilde{\phi}_{\vec{k}n}(\vec{G}^{(m)}_{||},z_m) \,. \end{aligned} \tag{B15}$$

If $\Delta\tilde{V}(\vec{G}_{\parallel},z)$ is bounded in the region $-s<z<0$ and $\Delta\tilde{V}(\vec{r}_{\parallel},z)$ is sufficiently smooth in $\vec{r}_{\parallel}$, then each term in (B15) can be bounded. For example, if $\Delta\tilde{V}(\vec{G}_{\parallel},z)=0$ for $|\vec{G}_{\parallel}|>G_M$ then each term can be bounded by $A(\Delta\tilde{V}_M Be^{2G_M s})^m/m!$, where

$$\Delta\tilde{V}_M \equiv \max_{\vec{G}_{\parallel},-s<z<0} |\Delta\tilde{V}(\vec{G}_{\parallel},z)| \; ,$$

$$|\phi_{\vec{k}n}(\vec{G}_M,z)| \le Ae^{G_M z} \; ,$$

and

$$|\mathscr{G}_{\vec{k}n}(\vec{G}_M;z,z')| \le Be^{G_M(z'-z)}$$

in the region $-s<z<z'<0$ [these bounds follow from (B13) and (B14)], and the sum in (B15) converges uniformly. It follows that the Jost solutions $f_{\vec{k}n}$ are analytic in the same domain of the complex k_z plane as $\phi_{\vec{k}n}$ and $\mathscr{G}_{\vec{k}n}$. The $\phi_{\vec{k}n}$ are analytic in k_z except at the branch points of $\phi_{\vec{k}n}$. [This can be seen immediately from (B13) if E_0 is chosen such that $E_{\vec{k}n}<E_0+|\vec{k}_{\parallel}+\vec{G}_{\parallel}|^2$, but in fact $\phi_{\vec{k}n}$ is analytic at $Q=0$ as well.] Also, from (B14), $\mathscr{G}_{\vec{k}n}$ is analytic. Therefore the solutions $f_{\vec{k}n}$ are analytic everywhere except at the branch points of $\phi_{\vec{k}n}$.

In the following, we shall assume for convenience that the potential $V(\vec{r})$ in our system has a twofold rotational symmetry about the z axis. Then the Jost solutions $f_{\vec{k}n}$ may be combined to give

$$f^{(e)}_{\vec{k}n}(\vec{r})=\sqrt{2}\sum_{\vec{G}_{\parallel}} f_{\vec{k}n}(\vec{G}_{\parallel},z)\cos[(\vec{k}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{r}] \; , \tag{B16a}$$

$$f^{(o)}_{\vec{k}n}(\vec{r})=\sqrt{2}\sum_{\vec{G}_{\parallel}} f_{\vec{k}n}(\vec{G}_{\parallel},z)\sin[(\vec{k}_{\parallel}+\vec{G}_{\parallel})\cdot\vec{r}] \; , \tag{B16b}$$

where

$$f^{(i)*}_{\vec{k}n}(\vec{r})=f^{(i)}_{\vec{k}_{\parallel},-k_z,n}(\vec{r}), \quad i=e,o \; .$$

2. Wave functions of the semi-infinite crystal

The wave functions of the semi-infinite crystal are solutions of the Schrödinger equation which satisfy the boundary condition of vanishing at $z=-s$. These wave functions may be chosen to be linear combinations of either the even or odd solutions $f^{(i)}_{\vec{k}n}$ which are labeled by the same $\vec{k}_{\parallel}$ and correspond to the same energy. An *extended* wave function is constructed by fixing $\vec{k}_{\parallel}$ and choosing $E=E_{\vec{k}n}$ where k_z is real. For $z\ge -s$, the extended wave functions may be written as

$$\psi^{(i)}_{\vec{k}n}(\vec{r})=c^{(i)}_{\vec{k}n}f^{(i)}_{\vec{k}n}(\vec{r})+c^{(i)}_{\vec{k}_{\parallel},-k_z,n}f^{(i)}_{\vec{k}_{\parallel},-k_z,n}(\vec{r}) + \sum_j c^{(i)}_{\vec{k}_{\parallel}\kappa_{z_j}n_j}f^{(i)}_{\vec{k}_{\parallel}\kappa_{z_j}n_j}(\vec{r}) \tag{B17}$$

$$\equiv c^{(i)}_1 f^{(i)}_1 + c^{(i)}_2 f^{(i)}_2 + \sum_{j=3}^{\infty} c^{(i)}_j f^{(i)}_j \; . \tag{B18}$$

For now, we are assuming that there are only two solutions $f^{(i)}_{\vec{k}n}$ with the given $\vec{k}_{\parallel}$ and $E_{\vec{k}n}$ and with k_z real. The functions f_j for $j\ge 3$ are evanescent solutions to (B6) which satisfy $E_{\vec{k}_{\parallel}k_{z_j}n_j}=E_{\vec{k}n}$ and $\mathrm{Im}\kappa_{z_j}>0$.

The coefficients $c^{(i)}$ appearing in (B18) are determined by the normalization condition and the boundary condition $\psi^{(i)}_{\vec{k}n}(\vec{r}_{\parallel},-s)=0$, or equivalently,

$$\psi^{(i)}_{\vec{k}n}(\vec{G}_{\parallel},-s)=0 \quad \text{for all } \vec{G}_{\parallel} \; . \tag{B19}$$

If we approximate the Schrödinger equation by a finite-difference equation in space, then there will be a maximum value of $G_{\parallel}$ and a finite number of evanescent waves (one less than the number of $\vec{G}_{\parallel}$ in this case).

Let us define the matrix $A^{(i)}$ by

$$A^{(i)}_{lm}\equiv f^{(i)}_m(\vec{G}^{(l)}_{\parallel},-s) \; , \tag{B20}$$

where $f^{(i)}_m$ is defined in (B17) and (B18) and l numbers the reciprocal-lattice vectors $\vec{G}_{\parallel}$. Then the solution to (B19) is

$$c^{(i)}_m=\mathrm{const}(-1)^m \det B^{(i)}_m \; , \tag{B21}$$

where the matrix $B^{(i)}_m$ is formed by deleting the mth column of $A^{(i)}$. We shall choose the constant in (B21) such that

$$(c^{(i)}_1 c^{(i)}_2)^{1/2}=1 \; . \tag{B22}$$

The wave functions $\psi^{(i)}_{\vec{k}n}$ are then δ-function normalized in k_z.

We now construct the surface states. If we fix $\vec{k}_{\parallel}$ and look at an energy E in a region where no $f^{(i)}_{\vec{k}n}$ with real k_z exists, we still find solutions to the Schrödinger equation of the form of (B17) and (B18) but unbounded in general since either $f^{(i)}_1$ or $f^{(i)}_2$ will grow exponentially as $z\to\infty$, depending on the sign of $\mathrm{Im}k_z$. If we restrict ourselves to $\mathrm{Im}k_z>0$, the necessary condition for a surface state to exist is $c^{(i)}_2=0$ since $f^{(i)}_z=f^{(i)}_{\vec{k}_{\parallel},-k_z,n}$ grows exponentially with z. Thus surface states have the form

$$\psi^{(i)}_{\vec{k}n}(\vec{r})=N^{(i)}_{\vec{k}n}\left[c^{(i)}_1 f^{(i)}_1(\vec{r})+\sum_{j=3}^{\infty}c^{(i)}_j f^{(i)}_j(\vec{r})\right] \tag{B23}$$

for $z\ge -s$, where k_z is now complex. The normalization constant is (see below)

$$N^{(i)}_{\vec{k}n}=\left[\frac{-2\pi i}{c^{(i)}_1 \partial c^{(i)}_2/\partial k_z}\right]^{1/2} \; . \tag{B24}$$

3. Normalization of surface states

This section is a generalization to three dimensions of Appendix B of Ref. 10, where the normalization of one-dimensional surface states was obtained. The normalization constant is given by

$$N^{(i)}_{\vec{k}n}=\left[\int_{z\ge -s} d\vec{r}\,\chi^2_{\vec{k}n}(\vec{r})\right]^{-1/2} \; , \tag{B25}$$

where

$$\chi_{\vec{k}n}(\vec{r}) \equiv c_1^{(i)} f_1^{(i)} + \sum_{j=3}^{\infty} c_j^{(i)} f_j^{(i)} \, .$$

Multiplying the Schrödinger equation for $\chi_{\vec{k}n}$ by $\partial\chi_{\vec{k}n}/\partial k_z$ and subtracting the Schrödinger equation for $\partial\chi_{\vec{k}n}/\partial k_z$ multiplied by $\chi_{\vec{k}n}$, we obtain the identity

$$\int_{z\geq -s} d\vec{r}\, \chi_{\vec{k}n}^2(\vec{r}) = -\left[\frac{\partial E_{\vec{k}n}}{\partial k_z}\right]^{-1} \times \int d\vec{r}_{\|} \frac{\partial \chi_{\vec{k}n}}{\partial k_z} \frac{\partial \chi_{\vec{k}n}}{\partial z}\bigg|_{z=-s} \, . \tag{B26}$$

Using the fact that $\sum_{j=1}^{\infty} c_j^{(i)} f_j^{(i)}(\vec{r}_{\|}, -s) = 0$ for all k_z and $\chi_{\vec{k}n}(\vec{r}_{\|}, -s)$ and $c_2^{(i)} = c_{\vec{k}_{\|}, -k_z, n}^{(i)}$ are 0, we find

$$\int_{z\geq -z_0} d\vec{r}\, \chi_{\vec{k}n}^2(\vec{r}) = \left[\frac{\partial E_{\vec{k}n}}{\partial k_z}\right]^{-1} \frac{\partial \alpha_2^{(i)}}{\partial k_z} \times \int d\vec{r}_{\|} W(f_2^{(i)}, \chi_{\vec{k}n}) \, . \tag{B27}$$

The Wronskian $W(f_2^{(i)}, \chi_{\vec{k}n})$ can be evaluated by repeating the above procedure for $\chi_{\vec{k}n}$ and $\partial f_2^{(i)}/\partial k_z$, but integrating over $0 \leq z \leq a$ only. The result is

$$\int d\vec{r}_{\|} W(f_2^{(i)}, \chi_{\vec{k}n}) = -\left[\frac{\partial E_{\vec{k}n}}{\partial k_z}\right] \frac{c_1^{(i)}}{2\pi i} \, . \tag{B28}$$

Substituting (B27) and (B28) into (B18) gives the desired result, Eq. (B24).

4. Asymptotic properties of $G(\vec{r}, \vec{r}\,')$

From (B2), (B18), and (B22), the one-electron correlation function is

$$G(\vec{r}, \vec{r}\,') = \sum_{i=e,o} \sum_{n}{}' \left[\sum_{\vec{k}_{\|}} \int_{k_z>0} dk_z \left[\frac{c_1^{(i)}}{c_2^{(i)}} f_1^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,') + \frac{c_2^{(i)}}{c_1^{(i)}} f_2^{(i)}(\vec{r}) f_2^{(i)}(\vec{r}\,') + f_1^{(i)}(\vec{r}) f_2^{(i)}(\vec{r}\,') + f_2^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,') \right] - \sum_{\vec{k}_{\|}} \sum_{k_z}{}' \frac{2\pi i c_1^{(i)}}{\partial c_2^{(i)}/\partial k_z} f_1^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,') \right] + (\cdots) \, , \tag{B29}$$

for $z, z' > -s$, and 0 otherwise. In the last summation, k_z takes on complex values corresponding to filled surface states [see (B23)]. All terms involving evanescent waves are denoted by $(\cdots)$. We can combine terms to eliminate the restriction $k_z > 0$ on the integral over the Brillouin zone:

$$G(\vec{r}, \vec{r}\,') = \sum_{i} \sum_{\vec{k}_{\|}} \left[\int dk_z \sum_{n}{}' \left[\frac{c_1^{(i)}}{c_2^{(i)}} f_1^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,') + f_1^{(i)}(\vec{r}) f_2^{(i)}(\vec{r}\,') \right] - 2\pi i \sum_{n}{}' \sum_{k_z}{}' \frac{c_1^{(i)} f_1^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,')}{\partial c_2^{(i)}/\partial k_z} \right] + (\cdots) \, . \tag{B30}$$

It follows from the analysis of Appendixes A and B 1 that the integrand of (B30),

$$\frac{c_{\vec{k}n}^{(i)} f_{\vec{k}n}^{(i)}(\vec{r}) f_{\vec{k}n}^{(i)}(\vec{r}\,')}{c_{\vec{k}_{\|}, -k_z, n}^{(i)}} + f_{\vec{k}n}^{(i)}(\vec{r}) f_{\vec{k}_{\|}, -k_z, n}^{(i)}$$

is analytic in k_z except at the points where $c_{\vec{k}_{\|}, -k_z, n}^{(i)}$ vanishes and at the branch points of $f_{\vec{k}n}^{(i)}$ (which coincide with those of $f_{k_{\|}, -k_z, n}^{(i)}$ by symmetry). However, if we sum this integrand over all filled bands, the singularities at all branch points cancel, except those which lie between the valence and conduction bands. This can be seen from (A5)–(A7). The fact that the coefficients $c^{(i)}$ are determinants of infinite matrices $B^{(i)}$ involving the $f_{\vec{k}n}^{(i)}$ does not introduce any additional singularities because the determinants are uniformly convergent in k_z. This can be seen by expanding $B_{ij}^{(i)}$, for large i or j, in the nearly-free-electron approximation. One finds that $B_{ij}^{(i)}$ approaches δ_{ij} sufficiently fast for uniform convergence.

Thus the integrand of the k_z integral in (B30) is analytic at all branch points of $f_{\vec{k}n}^{(i)}$, as we sum over n, except at the branch point, $\tilde{k}_z(\vec{k}_{\|})$, which lies in the energy gap between the valence and conduction bands. (In the case of simple bands, which we are considering, any other branch point in the gap is related to $\tilde{k}_z(\vec{k}_{\|})$ by complex conjugation or a reciprocal-lattice vector.) We can now deform the contour of integration as shown in Fig. 3. The contour C is chosen to lie (at constant $\mathrm{Im} k_z$) just below the branch point $\tilde{k}_z(\vec{k}_{\|})$. The vertical portions of the contour cancel because of the periodicity in k_z of the integrand. There will be a contribution to the integral from the poles of $1/c_2^{(i)}$, which lie between the real-k_z axis and the contour C. In the case of simple bands these are poles corresponding to surface states with energies less than $\tilde{E}_{\vec{k}_{\|}} \equiv E_{\vec{k}_{\|}, \tilde{k}_z(\vec{k}_{\|})}$. However, if these states are filled, then the contribution to the integral from these poles is exactly cancelled by the sum over surface states in (B30). Therefore the correlation function may be written as

$$G(\vec{r}, \vec{r}\,') = \sum_{i} \sum_{\vec{k}_{\|}} \int_C dk_z \sum_{n}{}' \left[\frac{c_1^{(i)}}{c_2^{(i)}} f_1^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,') + f_1^{(i)}(\vec{r}) f_2^{(i)}(\vec{r}\,') \right] - 2\pi i \sum_{n}{}' \sum_{k_z}{}' \frac{c_1^{(i)} f_1^{(i)}(\vec{r}) f_1^{(i)}(\vec{r}\,')}{\partial c_2^{(i)}/\partial k_z} + (\cdots) \, . \tag{B31}$$

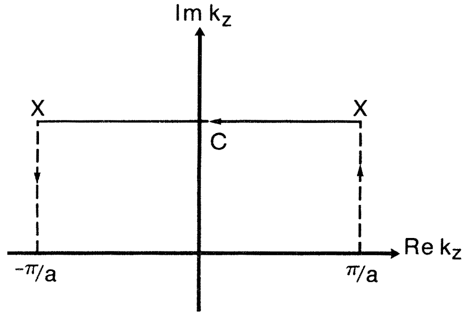

FIG. 3. Integration contour C is shown for the simple case where the only branch points in the energy gap occur at $\mathrm{Re}k_z = \pm\pi/a$. This would be the case, for example, if the Fermi level lay between the lowest two bands in Fig. 2. The contour is chosen to lie just below the branch points, which are indicated by crosses. The contributions to the integral from the two vertical dashed contours cancel by symmetry.

Here the sum over k_z is only over (complex) wave vectors with $\mathrm{Im}k_z > 0$ and which either lie *below* the contour C and correspond to *empty* surface states or lie *above* the contour C and correspond to *filled* surface states. From the Bloch condition, $\phi_{\vec{k}n}(\vec{r}_{||}, z+a) = e^{ik_z a}\phi_{\vec{k}n}(\vec{r}_{||}, z)$, we have, on the contour C, the following bound on $f^{(i)}$, for large z:

$$| f^{(i)}_{\binom{1}{2}} | < \mathrm{const}\, e^{\pm\alpha_0(\vec{k}_{||})/2} , \tag{B32}$$

where $\alpha_0(\vec{k}_{||}) \equiv 2 | \mathrm{Im}\, \tilde{k}_z(\vec{k}_{||}) |$. If we define $\gamma(\vec{k}_{||})$ to be the smallest decay rate of the surface states appearing in the sum in (B31), then we obtain the following properties of the one-electron correlation function:

$$\lim_{z+z' \to \infty} [e^{\alpha_1 \epsilon (z+z')/2} | G(\vec{r}, \vec{r}\,') - G_0(\vec{r}, \vec{r}\,') |] = 0 , \quad \text{for } z, z' > 0 , \tag{B33}$$

$$\lim_{|z-z'| \to \infty} [e^{\alpha_1 \epsilon |z-z'|/2} G(\vec{r}, \vec{r}\,')] = 0 , \tag{B34}$$

for $0 < \epsilon < 1$, where the decay rate is defined as

$$\alpha_1(\vec{k}_{||}) \equiv \min(\alpha_0(\vec{k}_{||}), \gamma(\vec{k}_{||})) , \tag{B35}$$

$$\alpha_1 \equiv \min_{\vec{k}_{||} \in \mathrm{BZ}} \alpha_1(\vec{k}_{||}) , \tag{B36}$$

where BZ refers to the Brillouin zone. The first property (B35) follows from the equivalence of the infinite-crystal correlation function,

$$G_0(\vec{r}, \vec{r}\,') = \sum_{i,n}{}' \sum_{\vec{k}_{||}} \int dk_z \phi_{\vec{k}n}(\vec{r}) \phi_{\vec{k}_{||}, -k_z, n}(\vec{r}\,') \tag{B37}$$

and the second term in (B31), for $z, z' > 0$, and from the bound on $| f^{(i)}_{\binom{1}{2}} |$, (B32). The evanescent terms are bounded by $(\mathrm{const}) e^{-\beta z}$, where $\beta > \alpha_1$, since the evanescent waves originate from bands which are higher in energy than the conduction band.

If the Fermi level is such that all surface states (if any) with energy less than $\tilde{E}_{\vec{k}_{||}}$ are occupied and all with energy greater that $\tilde{E}_{\vec{k}_{||}}$ are unoccupied, then $\alpha_1 = \alpha_0 \equiv \min_{\vec{k}_{||} \in \mathrm{BZ}} \alpha_0(\vec{k}_{||})$.

In deriving the asymptotic properties of $G(\vec{r}, \vec{r}\,')$, we assumed that the potential $V(\vec{r})$ had a twofold rotation axis and that there were no more than two degenerate extended Bloch functions labeled by the same $\vec{k}_{||}$. These assumptions simplify the analysis [by constraining the number of relevant coefficients in (B17) and (B18) to only two, namely, c_1 and c_2] but they are not necessary conditions; the results are true in general. The generalizations in our analysis needed to consider crystals which lack a twofold rotation axis and those needed to consider more complicated band structures are identical, so we will only discuss the latter.

Consider the case where four Bloch functions (with the same $\vec{k}_{||}$) are degenerate in energy, for example, the case where the Fermi level lies between the two highest bands in Fig. 2. In this case there will be two degenerate extended wave functions of the semi-infinite crystal. These are found by arbitrarily fixing one of the coefficients in the expansion analagous to (B17) and (B18). There will be two inequivalent branch points (not related by complex conjugation or a reciprocal-lattice vector) in the gap, and two different real-energy curves.[16] As in the simple case, our contour of integration in the evaluation of $G(\vec{r}, \vec{r}\,')$ will be chosen to lie just below the branch point which is closest to the real k_z axis. An example is shown in Fig. 4, where we have not assumed any symmetry between k_z and $-k_z$. The real-energy curves are also shown in Fig. 4. For each surface state in the gap there will be a corresponding point on each of the real-energy curves at which the integrand will have a pole. (In Fig. 4 we have shown

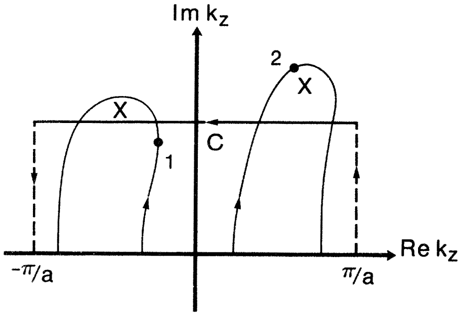

FIG. 4. An example of the integration contour C is shown for a more general band structure. The contour C is chosen to lie just below the lowest branch point. The branch points are indicated by crosses. This is similar to the situation one would have if the Fermi level lay between the highest two bands in Fig. 2, except we have assumed here an asymmetry between k_z and $-k_z$, which one would have in the most general case. The projection of the real-energy curves are shown and the arrows indicate the direction of increasing energy. The points labeled 1 and 2 correspond to the (same) energy of a surface state in the gap. The integral in Eq. (B30) will have a contribution from the pole at point 1. This contribution will be cancelled by a term in the sum over surface states, however, if the state in question is filled.

the case where there is a single surface state in the gap.) Again, as in the simple case, the contribution from the poles below the contour C (and on the low-energy side of the branch point) will be cancelled if the corresponding surface state is filled. The states above the contour C (or those below C but on the high-energy side of the branch point) will not contribute to $G(\vec{r},\vec{r}\,')$ if they are empty. There is also a contribution from the evanescent waves appearing in (B17), which may not be negligible now as these waves may originate from the conduction band and hence decay slowly in the gap. However, one still finds the same asymptotic properties of G as in the simple case (B33) and (B34); the effects of the surface decay with a finite decay rate α_1. One can define two energies $E_1(\vec{k}_{||}) < E_2(\vec{k}_{||})$ such that if all surface states with energy less than $E_1(\vec{k}_{||})$ are filled and all with energy greater than $E_2(\vec{k}_{||})$ are empty, then $\alpha_1(\vec{k}_{||}) = \alpha_0(\vec{k}_{||})$, where α_0 is determined by the branch point which lies closest to the real axis, and depends only on the bulk band structure. (It may now depend on the properties of the evanescent waves.) In general, $\alpha_1 < \alpha_0$; but the important point is that α_1 will be nonzero provided that the Fermi level lies in a nonvanishing energy gap in the bulk, and will approach zero only if the Fermi level approaches the edge of either the bulk valence or conduction band and there happens to be a marginally bound surface state at the band edge.

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[*] Present address.

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[2] Strictly speaking, although the average electric field between the two shorted capacitor plates is zero, the field inside the *sample* may be nonzero by a small amount, of order $4\pi(\delta+\sigma d)/L$, where L is the thickness of the sample, d is the distance between the capacitor plate and the sample (assumed to be small), and σ and δ are the surface charge density and surface dipole density, which are different on the two ends of the sample. We shall assume that L is sufficiently large so that the polarization produced by this electric field can be neglected, and thus we use a vanishing macroscopic electric field in our discussions.

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[12] The error in Eq. (3.13) arises from the approximation of the integral

$$\int_{-\pi/a}^{\pi/a} dk_z e^{2i\delta(\vec{k})} e^{2i(m-1)k_z a} / \sin(k_z a) \, .$$

From Appendix B, this error is of order $e^{-\gamma m a}$. If one adds the contribution from the filled surface states to this one finds, from an analysis as in Appendix B, that the error in (3.13) is of order $e^{-\alpha_1(\vec{k}_{||})m}$.

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