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# Phase rule for the semiconductor-vacuum interface*

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An expression for the integrated surface charge of a semiconductor-vacuum interface is derived in terms of phase shifts in the one-electron approximation. For a semi-infinite one-dimensional Kronig-Penney model the charge is quantized and obeys a simple phase rule involving the surface charge and the number of surface states split from the band.

## I. INTRODUCTION

The electronic-charge density in the surface region of a semiconductor is known to depart significantly from its bulk values. Because of its relevance to most surface effects and the surface geometry itself, an important theoretical effort has been made in the past few years to develop models and computational techniques for determining electron energies and density contours near the surface.[1] Also, the effect in the bulk of surface-charge deformation has been studied. Heine first showed that to order $N^{-2}$ a defect in a one-dimensional ring of $N$ atoms does not affect the mean-charge density of a full band far away from the defect.[2] Kleinman later extended this result to the case of a semiconductor slab with a twofold rotation axis normal to the surface and reflection symmetry through the central plane.[3]

In this work we explore the effect of the semiconductor-vacuum interface on the integrated surface charge. In Sec. II we derive an expression for the integrated charge in terms only of phase shifts. In Sec. III the one-dimensional Kronig-Penney model is used to study the phase shifts. This model, being unrealistic in many respects, has been very useful in the past for understanding surface effects.[4,5] We use it here because of its feature of being exactly solvable in the presence of a surface. We show explicitly how the quantization of surface charge as reported by Appelbaum and Hamann[5] arises in this model and others of its kind. Finally, in Sec. IV we give a phase rule in terms of the net surface charge and the number of surface states split from the band. The rule is proved exact for the one-dimensional case and suggested as valid in three dimensions.

## II. SURFACE CHARGE INTEGRAL

We proceed first to derive an expression for the integrated charge near the surface. Langreth[6] and Appelbaum and Blount[7] studied this quantity in connection with the sum rule for the metal-vacuum interface. The methods used by Heine[2] and Kleinman[3] in the evaluation of the average bulk charge for a finite semiconductor follow similar lines, and we shall adapt in this section some of their formula to our choice of coordinates and phases.

Consider a semi-infinite crystal whose primitive translation vectors are $\vec{a}$, $\vec{b}$, $\vec{c}$. $\vec{a}$ and $\vec{b}$ define a plane parallel to the surface and are normal to $\vec{c}$ but not necessarily to each other. We use a coordinate system with its origin in a lattice site of the outermost plane and the $z$ axis pointing into the crystal, along $\vec{c}$.[8] The region occupied by the lattice is then the entire half-space $z \geqslant 0$. If $\phi_{\vec{k}}$ is an eigenstate of the system it obeys Schrödinger's equation (we use atomic units)

$$[-\tfrac{1}{2}\nabla^2 + V(\vec{r})]\phi_{\vec{k}} = E(\vec{k})\phi_{\vec{k}}\,, \tag{1}$$

where $E(\vec{k})$ is the energy and $V(\vec{r})$ the potential. $V(\vec{r})$ is periodic along an $x$-$y$ plane, oscillates along the positive $z$ direction and tends to a constant as $z \rightarrow -\infty$. We shall also assume that sufficiently deep into the crystal the potential is perfectly periodic and invariant under inversion and reflection on an $x$-$y$ atomic plane. $\phi_{\vec{k}}$ is bounded to the crystal and obeys the boundary condition $\phi_{\vec{k}}(z=-\infty)=0$. Let $z_0$ be a depth into the crystal beyond which distortions in the periodic potential can be neglected. For $z > z_0$,

$$\phi_{\vec{k}} = 2^{-1/2}(\psi_{\vec{k}} e^{i\delta} + \text{c.c.})\,, \tag{2}$$

where $\delta$ is the phase shift[9] and c.c. stands for complex conjugate. $\psi_{\vec{k}}$ is an eigenstate of the infinite crystal and in our symmetry may be written in the form[3]

$$\begin{aligned} \psi_{\vec{k}} &= 2^{1/2} \sum_{\vec{G}} C_{\vec{G}}(\vec{k})[\cos(\bar{k}+\bar{G})\cdot\vec{r}]e^{i(G_z+k_z)z}\,, \\ \psi_{\vec{k}} &= 2^{1/2} \sum_{\vec{G}} C_{\vec{G}}(\vec{k})[\sin(\bar{k}+\bar{G})\cdot\vec{r}]e^{i(G_z+k_z)z}\,, \end{aligned} \tag{3}$$

with $C_{\vec{G}}$ real. $\vec{G}$ is a reciprocal lattice vector and a bar indicates a vector in the $x$-$y$ plane. We fix normalization by imposing

$$\sum_{\vec{G}} C_{\vec{G}}^2 = \Omega^{-1}\,, \tag{4}$$

where $\Omega = \vec{a} \times \vec{b} \cdot \vec{c}$ is the unit-cell volume. Note that Eq. (4) follows if the constituent Bloch states of Eq. (3) are normalized to one in the unit cell. Transforming Eq. (1) and using Eqs. (2)–(4) one gets for the surface charge of state $\vec{k}$ to the left of the plane at $z = nc$ (see Appendix A)

$$\int_{z \leq nc} \phi^2 d\vec{r} = n_\perp \left( n + \frac{1}{c} \frac{\partial \delta}{\partial k_z} + \alpha(\vec{k}) \right), \tag{5}$$

where

$$\alpha(\vec{k}) = \frac{\epsilon(\vec{k})}{4i} \frac{e^{i(2\delta - k_z c)}}{\sin k_z c} e^{2ink_z c} + \text{c.c.},$$
$$\epsilon(\vec{k}) = \int_\Omega \psi^2 d\vec{r}. \tag{5a}$$

Here $n_\perp$ is the number of cells in the $x$-$y$ plane. In order to get the total charge in the band under consideration we must sum over $\vec{k}$ in the Brillouin zone. This is trivial for the first two terms of Eq. (5). The third term represents the Friedel oscillations in the density and its contribution to the band charge decreases rapidly with $n$ except near the origin and the zone boundary. We account for these contributions to order $n^{-1}$ using the formula proved in Appendix B, and get for the integral over $k_z$

$$\frac{c}{\pi} \int_0^{\pi/c} \alpha(\vec{k}) dk_z = \tfrac{1}{4} \left[ \epsilon(\bar{k}, 0) \cos 2\delta(0) + \epsilon\left(\bar{k}, \frac{\pi}{c}\right) \cos 2\delta\left(\frac{\pi}{c}\right) \right] + O\left(\frac{1}{n}\right).$$

The quantity $\epsilon$ can take the values ±1 depending upon the parity of the wave function. Calling $\epsilon(\bar{k}, 0) = \epsilon_1$ and $\epsilon(\bar{k}, \pi/c) = \epsilon_2$ one may in fact write

$$\psi_{\bar{k}0}(\bar{r}, -z) = \epsilon_1 \psi_{\bar{k}0}(\bar{r}, z), \tag{6a}$$

$$\psi_{\bar{k}\pi/c}(\bar{r}, -z) = \epsilon_2 \psi_{\bar{k}\pi/c}(\bar{r}, z), \tag{6b}$$

which follow from the symmetry of our potential, and where $\epsilon_{1,2} = \pm 1$. Summation over $\bar{k}$ is then immediate and we finally have from Eq. (5),

$$\int_{z \leq nc} \rho_b(\vec{r}) d\vec{r} = n_\perp \left\{ n + \frac{1}{\pi} \left[ \delta\left(\frac{\pi}{c}\right) - \delta(0) \right] + \tfrac{1}{4} \left[ \epsilon_1 \cos 2\delta(0) + \epsilon_2 \cos 2\delta\left(\frac{\pi}{c}\right) \right] + O\left(\frac{1}{n}\right) \right\}, \tag{7}$$

where $\rho_b$ is the charge density of the filled band and the quantities in square brackets are to be taken in general as averages over $\bar{k}$ at the corresponding values of $k_z$. This expression gives to order $n^{-1}$ the total band-surface charge per spin in the volume up to the $n+1$ atomic plane and enclosing $n_\perp$ surface cells, simply in terms of the phase shifts at $k_z = 0$ and $\pi/c$. Subtracting from this integral the corresponding expression taken up to the $n$th plane and dividing through by $n_\perp$ we find that to order $n^{-2}$ a cell on the $n$th plane can accommodate in the band up to one electron per spin. Taking into account the charge of the ion in the cell, this implies charge neutrality deep into the solid, a result previously found by Kleinman.[3] Equation (7) does not give much information as to the rate at which the disturbance to the density created by the surface heals. The reader is referred to the work of Rehr and Kohn[10] and to Ref. 5 for more insight into this point.

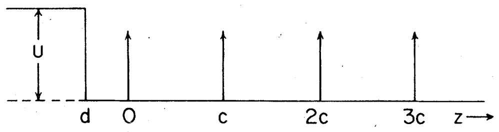

FIG. 1. Semi-infinite Kronig-Penney model. The potential step $U$ simulates the surface barrier.

### III. ANALYSIS OF PHASE SHIFTS

In a neutral semiconductor, the neutrality of a bulk cell, as predicted by Eq. (7), implies that the total surface charge, including that of the ions, must vanish. It is tempting then to extract directly from Eq. (7) a condition for surface-charge neutrality. We shall first, however, analyze the phase shifts using the one-dimensional Kronig-Penney (KP) model,[4] which allows an exact treatment. We shall find that two different cases may occur.

Consider the model potential in one dimension shown in Fig. 1. It is represented by

$$V(z) = \sum_{n=0}^{\infty} V_0 \delta(z - nc) + UH(d - z), \tag{8}$$

where $H$ is Heaviside's unit function. Its associated band structure is entirely determined by the delta-function strength $V_0$ and the lattice constant $c$. Since an isolated attractive delta function is capable of only one bound state, there is only one band possible for negative energies. Above this band there is a sequence of bands of positive energies. Repulsive delta functions have no bound states and can only form bands of positive energy.

Our purpose is to study the phase shifts at the bottom and top of the band as we vary the surface parameters $U$ and $d$. Phase shifts are obtained by equating at $z = d$ the logarithmic derivative of the one-dimensional analog of Eq. (2) to a function decaying exponentially to the left. This yields

$$e^{2i\delta} = -(\Gamma^* / \Gamma), \tag{9}$$

with

$$\Gamma = \left[\frac{\partial\psi}{\partial z} - L\psi\right]_{z=d},$$

$$L = [2(U-E)]^{1/2}.$$

It is convenient to study positive and negative energies separately. The one-dimensional version of Eq. (7) is

$$\int_{-\infty}^{nc} \rho_b(z)\,dz = n + \frac{1}{\pi}\left[\delta\left(\frac{\pi}{c}\right) - \delta(0)\right] + \tfrac{1}{4}\left[\epsilon_1 \cos 2\delta(0) + \epsilon_2 \cos 2\delta\left(\frac{\pi}{c}\right)\right] + O\left(\frac{1}{n}\right), \tag{10}$$

as can be shown following similar steps as for Eq. (7). $\epsilon_1$ and $\epsilon_2$ are defined by the one-dimensional analog of Eqs. (6a) and (6b).

### A. Case $E<0$

For this case we take for $z \leq 0$

$$\psi = iA(k)e^{-ikc/2}\left(\sin\frac{(i\eta - k)c}{2}\, e^{\eta(z+c/2)} + \sin\frac{(i\eta + k)c}{2}\, e^{-\eta(z+c/2)}\right), \tag{11}$$

with $A$ real. $\eta = (-2E)^{1/2}$ is given in terms of $k$ by

$$\cos kc = \cosh\eta c + (V_0/\eta)\sinh\eta c. \tag{11$'$}$$

One can readily verify that this last relation has no solution for $\eta$ unless $V_0 < 0$, a necessary condition for the existence of a negative energy band as stated earlier. From Eq. (11), and apart from a real factor, one gets

$$\Gamma = \left[(V_0 + L)\cosh\eta d - \left(\frac{V_0 L}{\eta} + \eta\right)\sinh\eta d\right]\sinh\eta c + i\,(L\sinh\eta d - \eta\cosh\eta d)\sin kc, \tag{12}$$

which together with Eqs. (9) and (11′) gives the phase shift for any value of $k$. We have summarized the results of interest to us in Table I. Using these results we get

$$\tfrac{1}{4}[\epsilon_1\cos 2\delta(0) + \epsilon_2 \cos 2\delta(\pi/c)] = -\tfrac{1}{2} \tag{13a}$$

and

$$(1/\pi)[\delta(\pi/c) - \delta(0)] = l_<, \tag{13b}$$

with $l_<$ an integer. Substitution in (10) then yields a half-integer surface charge for this case.

TABLE I. Parity of our wave functions and phase shifts at the band edges. Note that the latter are given modulo $\pi$.

| Band | $\epsilon_1$ | $\epsilon_2$ | $kc$ | $\delta (\text{mod } \pi)$ |
|---|---|---|---|---|
| $E<0$ | $+1$ | $+1$ | 0 | $\pi/2$ |
| | | | $\pi$ | $\pi/2$ |
| $E>0$ | | | | |
| $s$ odd | $+1$ | $-1$ | 0 | $\pi/2$ |
| | | | $\pi$ | 0 |
| $s$ even | $-1$ | $+1$ | 0 | 0 |
| | | | $\pi$ | $\pi/2$ |

### B. Case $E>0$

Now we take for $z<0$

$$\psi = B(k)e^{-ikc/2}\left[\sin\frac{(\kappa + k)c}{2}\, e^{i\kappa(z+c/2)} + \sin\frac{(\kappa - k)c}{2}\, e^{-i\kappa(z+c/2)}\right], \tag{14}$$

with $B$ real and $\kappa = (2E)^{1/2}$ related to $k$ through

$$\cos kc = \cos\kappa c + (V_0/\kappa)\sin\kappa c. \tag{14$'$}$$

wave function (14) yields

$$\Gamma = \left[(V_0 + L)\cos\kappa d - \left(\frac{V_0 L}{\kappa} - \kappa\right)\sin\kappa d\right]\sin\kappa c + i\,(L\sin\kappa d - \kappa\cos\kappa d)\sin kc, \tag{15}$$

and the corresponding limit values of the phase shift have been entered in Table I. Note that we have labeled bands starting from $s=1$ for the lowest, $s=2$ for the next up, and so forth. From these results we obtain Eq. (13a) once again and Eq. (13b) gets replaced by

$$\frac{1}{\pi}\left[\delta\left(\frac{\pi}{c}\right) - \delta(0)\right] = l_> + \tfrac{1}{2}, \tag{16}$$

with $l_>$ an integer. Substituting in Eq. (10) we find for this case that the surface charge per spin is an integer.

The integers $l_<$ and $l_>$ defined in Eqs. (13b) and (16) can be simply related to the occurrence of surface states. One can see this by taking a closer look at the behavior of the phase shifts as a function of $k$. Figure 2 is a plot of the phase shift for the negative energies band in the case $V_0 c = -3.0$ and $d = -0.25c$. As the height of the potential barrier is increased from $Uc^2 = 6.0$ to 10.0, $l_<$ changes from 1 to 0 and the band loses one state. $l_< = 1$ can occur only if $\delta$ crosses the zero axis and the condition for this is $\text{Re}\Gamma = 0$. With the aid of this condition, inspection of Eq. (12) shows that as one increases $U$ the value of $kc$, for which the phase shift vanishes moves to the right and eventually reaches $\pi$, after which no solution is found and $l_<$ jumps from 1 to 0. One can show further that $\text{Re}\Gamma = 0$ for $kc = \pi$ corresponds exactly to the condition for existence of a surface state right at the edge of the gap.[11] The emergence of this surface state from the band into the gap therefore explains the loss of a state by the band. Calling $\sigma$ the num-

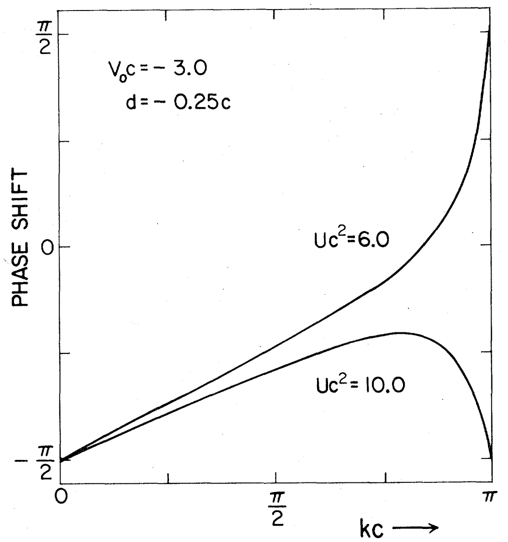

FIG. 2. Phase shift as a function of $kc$ for a band of negative energies.

ber of surface states split from the band, then $\sigma=0$ characterizes the case $Uc^2=6.0$ and $\sigma=1$ the case $Uc^2=10.0$.

The analysis of case $E>0$ yields more interesting results. For $V_0c=0.5$, Fig. 3 shows a plot of phase shifts for band $s=1$ and a few values of $d$, again with $Uc^2=6.0$ and 10.0. For $d=-0.7c$ (and also higher values) the situation is similar to that already discussed. Now, however, $l_>=1$ occurs if $\mathrm{Im}\Gamma=0$ has a solution in the range $0<kc<\pi$, that is, $\delta$ must cross the horizontal axis at $\pi/2$. The same identification with the emergence of a surface state as for $E<0$ can be made[12] and again $l_>=0$ means that one such state has been split from the band, so $\sigma=1$. A new situation arises due to the periodic nature of Eq. (15). If one decreases $d$, the equation $\mathrm{Im}\Gamma=0$ may have more than one solution, and $l_>$ may become greater than one. This is shown in Fig. 3 for the case $d=-1.7c$, where $l_>$ becomes equal to two. To illustrate this behavior we have plotted in Fig. 4 both sides of the equations

$$\tan\kappa d=\kappa/L\,, \tag{17a}$$

and

$$\tan\kappa d=\kappa[(L+V_0)/(LV_0-\kappa^2)]\,, \tag{17b}$$

which arise from setting $\mathrm{Im}\Gamma=0$ and $\mathrm{Re}\Gamma=0$, respectively. Full triangles and circles label the plots of the right-hand sides of Eqs. (17a) and (17b), respectively, and the unmarked curves represent the tangent. Inspection of Fig. 4 shows that in between two solutions of Eq. (17a) (shown as empty triangles) there is always a solution of Eq. (17b) (empty circles), and vice versa. Since these solutions correspond to crossing of the axes $\pi/2$ (mod $\pi$) and 0 (mod $\pi$), respectively, this explains that for $d=-1.7c$, $\delta$ is a monotonous in-

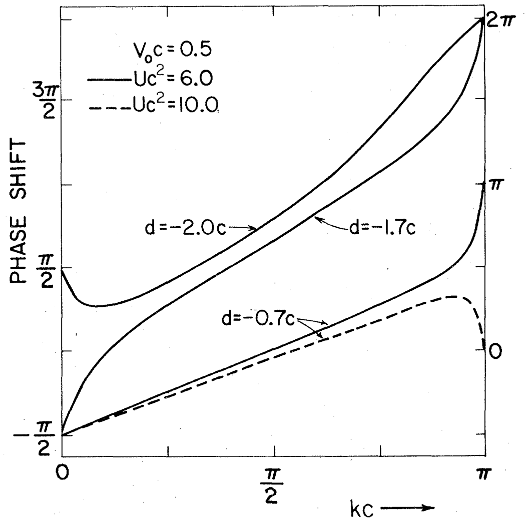

FIG. 3. Phase shift as a function of $kc$ for the first positive-energy band with $V_0c=0.5$.

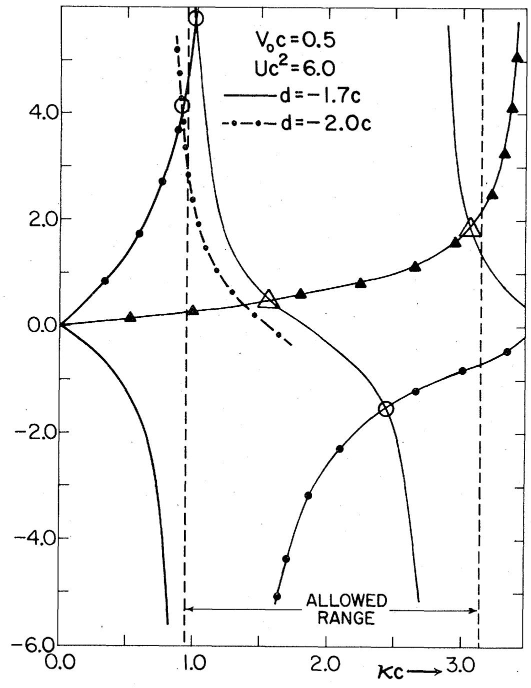

FIG. 4. Plot of the right-hand sides of Eq. (17a) (full triangles) and Eq. (17b) (full circles). The full and broken lines represent the $\tan\kappa d$ for two different values of $d$. Empty triangles and circles are the solutions to these equations, respectively. Vertical lines delimit the allowed values of $\kappa c$.

creasing function of $k$. When a solution moves outside the range of allowed values of $\kappa$ (delimited by vertical broken lines on our figure) the phase shift may show a maximum or a minimum as with the broken curve in Fig. 3 and the top curve, respectively. We have included in Fig. 4 a segment of the tangent for $d=-2.0c$ (broken curve) to show that for the latter case a solution of Eq. (17b) has just moved across the boundary to the left of allowed values of $\kappa$. This actually corresponds to the emergence into the lower gap of a surface state that has split from the bottom of the band, and while $l_>$ has decreased by one, $\sigma$ has jumped one unit upwards. One can easily see that $l_>$ is the number of solutions of Eq. (17a) in the allowed range of $\kappa$ minus the number of solutions of Eq. (17b) to the left of this range so that for $d=-1.7c$, $l_>=2$ ($\sigma=0$), and for $d=-2.0c$, $l_>=1$ ($\sigma=1$).

Although we have been discussing the $s=1$ band, our results remain qualitatively the same for higher index bands that are bounded to the solid. The same is true for other parameter values than those chosen in our discussion both for $E \lessgtr 0$. It can be shown further that for $-0.5c<d<0.0$, $l_>=0$ or 1 only, and that these are the only values that $l_<$ can assume for any negative value of $d$.

It is apparent from Eq. (10) that the quantization of surface charge into integer or half-integer values arises from the fact that the phase shift at the origin and zone boundary is a multiple of $\pi/2$. Any model with a center of inversion and giving rise to an equation such as Eq. (9) will, for example, exhibit this feature. Table I can in fact be obtained using just these assumptions as can be readily verified from Eq. (9) and the coincidence of the wave function and its complex conjugate at $k=0$, $\pi/c$.[13] The same holds true in three dimensions, since Eq. (7) is identical in structure to Eq. (10).

## IV. DISCUSSION AND PHASE RULE

The quantization of surface charge for full bands into integer or half-integer values as described in Sec. III for the semi-infinite KP model was found earlier by Appelbaum and Hamann in their numerical study of the model.[5] They interpreted it as arising from the atomic nature of the states associated with the case $E<0$, and the molecular nature of those associated with $E>0$. Figure 5 shows these two situations. Imagine now that the lattice is finite and the two ends terminate as in Fig. 5(a) for a band of $E<0$. If we were to think of the $\delta$ functions carrying two units of charge each, the surface would be neutral on account of the band only, provided that $l_<=1$ and all pair of spin states are occupied. If a state has been split from the band into the gap, then for charge neutrality the surface state must be doubly occupied. For $E>0$, charge neutrality is attained if $l_>=0$, the band is full, and the surface state singly occupied.

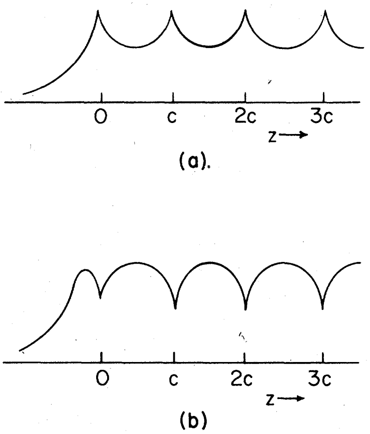

FIG. 5. Shape of the electron density in the band for the (a) $E<0$ case and (b) $E>0$ case.

We have shown, however, that $l_>$ can also be a positive integer and there still be a surface state in the upper or lower gap. This would mean that there are more states in the band than those required for charge neutrality and a neutral system would have an unfilled band, and therefore a non-neutral bulk cell. The band would bend to permit some charge to flow to the bulk and achieve, in the end, local bulk-charge neutrality. A self-consistent procedure would presumably then do away with the extra states in the band, since otherwise the band would have metallic properties. This need not be the case if the system is charged with extra electrons. This extra charge would be localized at the surface and with energy below the gap.

Gathering these results and taking into account spin degeneracy, we can state the following phase rule for the surface charge in a band

$$\frac{2}{\pi}\left[\delta\left(\frac{\pi}{c}\right)-\delta(0)\right]+\tfrac{1}{2}\left[\epsilon_1\cos 2\delta(0)+\epsilon_2\cos 2\delta\left(\frac{\pi}{c}\right)\right] = 1-2\sigma\ (E<0)=2l\ (E>0). \qquad (18)$$

For $E<0$, the number of surface states per spin $\sigma$ can be either 0 or 1. For $E>0$, $l$ is a non-negative integer and $2l-1$ is the surface charge per surface atom in the band. If $l=0$, a surface state must be present, whereas for $l>0$ there may or may not be a surface state in the gap.

We have no general proof that the above phase rule holds in three dimensions as it stands. As pointed out by Appelbaum and Hamann,[5] one can expect a band to be of atomic type if the set of planes parallel to the surface and separated by the normal projection of the primitive basis vectors cut the center of the charge distribution, and of molecular type if the charge is concentrated between these planes. These correspond to the cases $E<0$ and $E>0$, respectively. One can then conjecture the validity of Eq. (18) on the basis of charge neutrality setting $l=0$ and for crystals with the appropriate symmetry so that Eq. (7) is obeyed. Bands of atomic nature do not allow extra electrons to be accommodated within the band or its associated surface states. Bands of molecular nature could have a foreign electron fill the available surface state at a surface atom, a picture used in models of chemisorption.[1] The filled state could in this case become a resonant state of the band without affecting bulk neutrality. The case $l\neq 0$, corresponding to having more than one extra electron per surface atom, would imply large local electric fields near the surface, thus calling for a different treatment than the simple one-electron theory used here.

## ACKNOWLEDGMENTS

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## APPENDIX A

Following Ref. 3 one easily gets from Eq. (1), on account of the symmetry of the wave function and the boundary condition at $z=-\infty$,

$$2\frac{\partial E}{\partial k_z}\int_{z<nc}\phi^2\,d\vec{r}=\int_{z=nc}\Delta(\phi,\phi)\,dS\,, \tag{A1}$$

where

$$\Delta(\mu,\nu)=\frac{\partial\mu}{\partial k_z}\,\frac{\partial\nu}{\partial z}-\nu\frac{\partial^2\mu}{\partial z\,\partial k_z}\,.$$

One further has from Eq. (3) and the reality of $C_{\vec{G}}$,

$$\Delta(\phi,\phi)=i\left(\psi\frac{\partial\psi^*}{\partial z}-\psi^*\frac{\partial\psi}{\partial z}\right)\left(nc+\frac{\partial\delta}{\partial k_z}\right)+\tfrac{1}{2}[\Delta(\psi,\psi)e^{2i\delta}+\text{c.c.}]\,. \tag{A2}$$

The factor in the first term in the right-hand side is proportional to the current flowing in the $z$ direction, and its surface integral yields[14]

$$\int_{z=nc}i\left(\psi\frac{\partial\psi^*}{\partial z}-\psi^*\frac{\partial\psi}{\partial z}\right)dS=2A\frac{\partial E}{\partial k_z}\sum_{\vec{G}}C_{\vec{G}}^2=2\frac{n_\perp}{c}\,\frac{\partial E}{\partial k_z}\,, \tag{A3}$$

where we have used Eq. (4) and $A=n_\perp|\vec{a}\times\vec{b}|$ is the area in the $x$-$y$ plane. The second term in Eq. (A2) is simplified if we note that $\psi$ is a solution of Eq. (1) for $z>z_0$. Again, from Eq. (1)

$$2\frac{\partial E}{\partial k_z}\psi^2=\frac{\partial\psi}{\partial k_z}\nabla^2\psi-\psi\nabla^2\frac{\partial\psi}{\partial k_z}\,.$$

We take a volume integral in the range $nc\leqslant z\leqslant nc+c$ and use Green's theorem and the symmetry of $\psi$ to get

$$2\frac{\partial E}{\partial k_z}\int_{nc\leq z\leq nc+c}\psi^2\,d\vec{r}=\int\Delta(\psi,\psi)\,dA\Big|_{z=nc}^{z=nc+c}$$

$$=(e^{2ik_zc}-1)\int_{z=nc}\Delta(\psi,\psi)\,dA\,.$$

Replacing Eq. (A2) in Eq. (A1), using Eq. (A3) and the above result Eq. (5) follows after some rearrangement and the aid of Eq. (3).

## APPENDIX B

Consider the integral

$$I=\mathrm{Im}\int_0^{\pi/c}\frac{f(k)}{\sin kc}e^{2inkc}\,dk$$

$$=\mathrm{Im}\int_{-\infty}^{\infty}g(k)e^{2inkc}\,dk\,, \tag{B1}$$

where $f(k)$ is regular and

$$g(k)=\frac{f(k)}{\sin kc}H(k)H\left(\frac{\pi}{c}-k\right),$$

with $H(k)$ Heaviside's unit function. $g(k)$ has singularities at $k=0$ and $\pi/c$. Near these points,

$$g(k)=\frac{f(0)}{kc}H(k)+f'(0)H(k)+O(k)\,,\quad k\to 0$$

$$g(k)=\frac{f(\pi/c)}{\pi-kc}H\left(\frac{\pi}{c}-k\right)-f'\left(\frac{\pi}{c}\right)H\left(\frac{\pi}{c}-k\right)+O\left(\frac{\pi}{c}-k\right),\quad kc\to\pi\,.$$

We have isolated the singularities in both cases with a remainder whose first derivative is absolutely integrable in an interval containing the corresponding singularity. We can then apply a well-known theorem of Fourier analysis which to order $n^{-1}$ allows to express Eq. (B1) in terms of the Fourier transforms of the singular term.[15] This leads to the result

$$I=\frac{\pi}{c}\left\{\frac{1}{2}\left[f(0)-f\left(\frac{\pi}{c}\right)\right]+O\left(\frac{1}{n}\right)\right\}. \tag{B2}$$

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[1] For a review, see, Joel A. Appelbaum and D. R. Hamann, Rev. Mod. Phys. 48, 479 (1976).

[2] Volker Heine, Phys. Rev. 145, 593 (1966).

[3] Leonard Kleinman, Phys. Rev. B 11, 858 (1975).

[4] See, for example, S. G. Davison and J. D. Levine, Solid State Phys. 25, 1 (1970).

[5] J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 10, 4973 (1974).

[6] D. C. Langreth, Phys. Rev. B 5, 2842 (1972).

[7] J. A. Appelbaum and E. I. Blount, Phys. Rev. B 8, 483 (1973).

[8] Our results of this section are actually independent of the location of the origin.

[9] Our definition for the phase shift follows that of Refs. 2 and 3.

[10] J. J. Rehr and W. Kohn, Phys. Rev. B 10, 448 (1974).

[11] A treatment of surface states may be found in Ref. 5. Our wave functions differ from theirs by the factors $i\exp(ikc/2)$ for $E<0$ and $\exp(ikc/2)$ for $E>0$, which we chose to make the coefficients of the expansion of the Bloch states real.

[12] To prove this one must notice that for $ka=\pi$ and $s=1$, $\psi=(2/c)^{1/2}\sin(\pi z/c)$.

[13] For completeness one may add to Table I the line $\epsilon_1=-1$; $\epsilon_2=-1$; $kc=0$, $(\pi)$; $\delta(\mathrm{mod}\ \pi)=0$, $(0)$.

[14] Reference 3, Eqs. (12)–(14). Note that our Hamiltonian differs from Kleinman's by the factor $\frac{1}{2}$ in front of the Laplacian.

[15] See, for example, M. J. Lighthill, *Introduction to Fourier Analysis and Generalized Functions* (Cambridge U.P., London, 1964), theorem 19 and Table I.