Bulk charge neutrality in semiconductors*

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Extending a method applied by Heine in one dimension, we prove for an intrinsic semiconductor slab N unit cells thick with a twofold rotation axis normal to the surface and reflection symmetry through the central plane that the valence bands are electrically neutral to order N^{-1}. From this we are able to show that the surface-state energy bands lying entirely within the absolute energy gaps of semiconductors are exactly half occupied.

I. INTRODUCTION

Appelbaum and Hamann[1] have recently calculated the approximately self-consistent charge density at the (111) surface of silicon. They found four[2] bands of surface states when they allowed the surface plane of atoms to relax inward. The uppermost surface band lies entirely within the absolute energy gap; i.e., at any point $\vec{k}$ within the two-dimensional Brillouin zone the surface state lies within the gap for all $\vec{k}$. They determined that for surface-charge neutrality this band must contain (including a factor of 2 for spin) 0.7016 or 0.6350 electrons per surface atom depending on the amount of surface relaxation they took. This upper band is almost certainly of the nearly-free-electron[3,4] type. That is, this band and its degenerate partner from the opposite surface have their origin in a pair of bands, one pushed down from the conduction band and the other up from the valence band. Thus one has to account for exactly one electron per surface atom which comes from the band pushed up from the valence band. Now the simplest possibility is that the surface band is exactly half filled, containing one electron per surface atom. On the other hand, because seven valence-band states per surface atom have become surface states (three lower pairs of surface bands and half of the upper pair of surface bands), one might expect some bulk–valence-band-charge deficit to occur. Then band bending would occur and the bottom of the bulk conduction band would drop until sufficient charge flowed from the surface to restore bulk-charge neutrality. There would, of course, remain the band-bending region several thousand angstroms thick over which there was no charge neutrality. The matching of wave functions calculated inward from the surface to bulk wave functions would have to be made beyond this region, making it computationally impossible to obtain surface-charge densities. We shall prove, however, that independent of the number of surface states pushed out of a bulk band, charge neutrality is maintained within the band, providing one discusses a slab whose central plane is a reflection plane with a two fold normal rotation axis. Thus our proof is valid for (110) but not (100) or (111) silicon. If in spite of this one assumes the result holds for any face, then it is not possible for the 0.3 electron deficit in the surface band obtained by Appelbaum and Hamann to be due to charge flow into the bulk conduction band, for, if this were to occur, the band bending would be in the direction to raise the bulk conduction band even higher above the surface band. Thus we suspect that their calculation is in error, probably because they chose the surface matching plane to lie between the second and third planes of atoms. If the bulk is electrically neutral, so must be the surface; however, the plane dividing the two regions must undoubtedly be taken somewhat deeper. This is apparently what Appelbaum and Hamann now believe. They are currently repeating their calculation with the matching plane taken two atoms deeper into the crystal and expect to find the requirement of integral occupancy of the surface state much better satisfied.[5]

In Sec. II we derive a formula for the bulk-charge density which contains two terms; one involves phase shifts and the other is just the number of states pushed out of the band. In Sec. III we show that these two terms always cancel and bulk-charge neutrality is always maintained.

II. CHARGE-DENSITY FORMULAS

Consider a slab of infinite extent in two dimensions consisting of slab-adapted unit cells of volume $\vec{a}\times\vec{b}\cdot\vec{c}$, where $\vec{c}$ lies in the normal direction and $\vec{a}$ and $\vec{b}$ are perpendicular to $\vec{c}$ but not necessarily to each other. Take matching planes at $z=0$ and $z=Nc$ which are sufficiently far from the surface that the potential is that of the bulk and any evanescent contribution to the wave functions is negligible. We shall assume the existance of a twofold z rotation axis and a reflection plane at $z=\frac{1}{2}Nc$. We now derive the charge-density formula by generalizing the work done by Heine[6] in one dimension. Because he considered a closed ring with an insertion which destroyed the periodicity, he was unable to extend his results to three dimen-

sions. However, because we consider a surface which does not destroy the periodicity in the $\vec{a}$ and $\vec{b}$ directions, the generalization becomes straightforward.

The Bloch functions are

$$\chi_{\bar{k}k_z} = \sum_{\bar{G}G_z} C_{\bar{G}G_z} e^{i(\bar{k}+\bar{G})\cdot\vec{r}} e^{i(k_z+G_z)z}, \tag{1}$$

where $\bar{G}$ and G_z are slab-adapted reciprocal-lattice vectors and the bars indicate two-dimensional vectors. The Bloch states degenerate by the twofold rotation may be combined to give[7]

$$\Psi_{\bar{k}k_z} = 2^{1/2} \sum_{\bar{G}G_z} C_{\bar{G}G_z} \cos(\bar{k}+\bar{G})\cdot\vec{r}\, e^{i(k_z+G_z)z} \tag{2}$$

where $C_{\bar{G}G_z}$ is real and the corresponding function with $\sin(\bar{k}+\bar{G})\cdot\vec{r}$. The slab eigenfunctions in the region $0 \le z \le Nc$ may then be written $\phi_{\bar{k}k_z} = \mathrm{Re}\, e^{i\delta}\Psi_{\bar{k}k_z}$ i.e.,

$$\phi_{\bar{k}k_z} = 2^{1/2} \sum_{\bar{G}G_z} C_{\bar{G}G_z} \cos(\bar{k}+\bar{G})\cdot\vec{r}\cos[(k_z+G_z)z+\delta]. \tag{3}$$

Using the reflection plane at $z = \frac{1}{2}Nc$ one sees that

$$k_{ze} = (n\pi - \delta_n)/\tfrac{1}{2}Nc \qquad \text{for even } \phi, \tag{4a}$$

$$k_{zo} = [(n+\tfrac{1}{2})\pi - \delta_n]/\tfrac{1}{2}Nc \quad \text{for odd } \phi. \tag{4b}$$

where n is an integer. If two states with the same $\bar{k}$ are degenerate, the most general eigenfunction will be of the form $\Phi_1 = \alpha\phi_{\bar{k}k_{z1}} + (1-\alpha^2)^{1/2}\phi_{\bar{k}k_{z2}}$, where each ϕ has a different phase shift δ. However, $\Phi_2 = (1-\alpha^2)^{1/2}\phi_{\bar{k}k_{z1}} - \alpha\phi_{\bar{k}k_{z2}}$ is also an eigenfunction with the same energy. One can always combine these degenerate eigenfunctions to obtain eigenfunctions with a single k_z. One might suppose that the degenerate partner of Φ_1 is formed by allowing both phase shifts to change by $\pm\frac{1}{2}\pi$. From (4) we see that this would shift the k_z's, thus destroying the degeneracy. Hence (3) has complete generality.

Now $\phi_{\bar{k}k_z}$ obeys the Schrödinger equation

$$[-\nabla^2 + V(\vec{r})]\phi(\vec{r}) = E\phi(\vec{r}). \tag{5}$$

Before applying the boundary condition at $z = Nc$ and thus quantizing k_z we may differentiate (3) to obtain

$$[-\nabla^2 + V(\vec{r})]\frac{\partial\phi}{\partial k_z} = \frac{\partial E}{\partial k_z}\phi + E\frac{\partial\phi}{\partial k_z}. \tag{6}$$

Multiplying (5) by $\partial\phi/\partial k_z$ and (6) by ϕ and subtracting, we have

$$\phi^2\frac{\partial E}{\partial k_z} = \frac{\partial\phi}{\partial k_z}\nabla^2\phi - \phi\nabla^2\frac{\partial\phi}{\partial k_z}. \tag{7}$$

Integrating this over the half-space $-\infty < z \le \frac{1}{2}Nc$, using Green's theorem and the two-dimensional Bloch periodicity together with the vanishing of ϕ at $z = -\infty$, one obtains

$$\frac{\partial E}{\partial k_z}\int_{z\le Nc/2}\phi^2 d^3r = \int_{z=Nc/2}\left(\frac{\partial\phi}{\partial k_z}\frac{\partial\phi}{\partial z} - \phi\frac{\partial^2\phi}{\partial k_z\,\partial z}\right)dS. \tag{8}$$

Differentiating (3) one obtains

$$\frac{\partial\phi}{\partial z} = -2^{1/2}\sum_{\bar{G}G_z} C_{\bar{G}G_z}(k_z+G_z)\cos(\bar{k}+\bar{G})\cdot\vec{r}\sin[(k_z+G_z)z+\delta], \tag{9}$$

$$\frac{\partial\phi}{\partial k_z} = 2^{1/2}\sum_{\bar{G}G_z}\cos(\bar{k}+\bar{G})\cdot\vec{r}\left[\frac{\partial C_{\bar{G}G_z}}{\partial k_z}\cos[(k_z+G_z)z+\delta] - C_{\bar{G}G_z}\left(z+\frac{\partial\phi}{\partial k_z}\right)\sin[(k_z+G_z)z+\delta]\right], \tag{10}$$

$$\frac{\partial^2\phi}{\partial k_z\,\partial z} = -2^{1/2}\sum_{\bar{G}G_z}\cos(\bar{k}+\bar{G})\cdot\vec{r}\left[\left(\frac{\partial C_{\bar{G}G_z}}{\partial k_z}(k_z+G_z) + C_{\bar{G}G_z}\right)\times\sin[(k_z+G_z)z+\delta] + C_{\bar{G}G_z}(k_z+G_z)\left(z+\frac{\partial\delta}{\partial k_z}\right)\times\cos[(k_z+G_z)z+\delta]\right]. \tag{11}$$

From (4a) we have that $\sin[(k_z+G_z)z+\delta] = 0$ and $\cos[(k_z+G_z)z+\delta] = \pm 1$, and from (4b) that $\sin[(k_z+G_z)z+\delta] = \pm 1$ and $\cos[(k_z+G_z)z+\delta] = 0$ at $z = \frac{1}{2}Nc$. Substituting (3) and (9)–(11) into (8) we obtain in either case

$$\frac{\partial E}{\partial k_z}\int_{z\le Nc/2}\phi^2 d^3r = 2\int_{z=Nc/2}\sum_{\bar{G}G_z\bar{G}'G_z'} C_{\bar{G}G_z}C_{\bar{G}'G_z'}(k_z+G_z)\times\left(\tfrac{1}{2}Nc + \frac{\partial\delta}{\partial k_z}\right)\cos(\bar{k}+\bar{G})\,\vec{r}\times\cos(\bar{k}+\bar{G}')\cdot\vec{r}\,dS. \tag{12}$$

The surface integral yields $\frac{1}{2}A\delta_{\bar{G}\bar{G}'}$, where A is the surface area and $\delta_{\bar{G}\bar{G}'}$ the Kronecker δ. Furthermore, following Heine[6] and using the fact that the current density integrated over any z plane must be a constant, one can easily show that $\sum_{G_z\neq G_z'}(k_z+G_z)C_{\bar{G}G_z}C_{\bar{G}G_z'} = 0$, so that

$$\frac{\partial E}{\partial k_z}\int_{z\le Nc/2}\phi^2 d^3r = A\sum_{\bar{G}G_z} C^2_{\bar{G}G_z}(k_z+G_z)\left(\tfrac{1}{2}Nc + \frac{\partial\delta}{\partial k_z}\right). \tag{13}$$

Using the fact that ϕ is normalized so that $\int_{z\le Nc/2}\phi^2 d^3r = \frac{1}{2}$ and that

$$\frac{1}{2}\frac{\partial E}{\partial k_z} = \frac{-\int\chi^* i\frac{\partial}{\partial z}\chi\, d^3r}{\int\chi^*\chi\, d^3r} = \frac{\sum_{\bar{G}G_z} C^2_{\bar{G}G_z}(k_z+G_z)}{\sum_{\bar{G}G_z} C^2_{\bar{G}G_z}}, \tag{14}$$

one obtains

$$\sum_{\bar{G}G_z} C^2_{\bar{G}G_z} = A^{-1}\left(\tfrac{1}{2}Nc + \frac{\partial\delta}{\partial k_z}\right)^{-1} = \frac{2}{ANc}\left(1 - \frac{2}{Nc}\frac{\partial\delta}{\partial k_z} + O(N^{-2})\right). \tag{15}$$

We now square Eq. (3) to obtain

$$\phi^2 = \sum_{\bar{G}G_z\bar{G}'G_z'} C_{\bar{G}G_z}C_{\bar{G}'G_z'}\cos(\bar{k}+\bar{G})\cdot\vec{r}\cos(\bar{k}+\bar{G}')\cdot\vec{r}\times\{\cos(G_z - G_z')z + \cos[(2k_z + G_z + G_z')z + 2\delta]\}. \tag{16}$$

Performing a volume average, one obtains

$$\langle\phi^2\rangle = \tfrac{1}{2}\sum_{\bar{G}G_z} C^2_{\bar{G}G_z} + \tfrac{1}{2}\sum_{\bar{G}G_zG'_z} C_{\bar{G}G_z}C_{\bar{G}G'_z} \times\langle\cos[(2k_z+G_z+G'_z)z+2\delta]\rangle. \quad (17)$$

We substitute (15) for the first term and note that the second term vanishes except when $G'_z=-G_z$ or $G'_z=-G_z-2\pi/c$. Thus we finally obtain

$$\langle\phi^2\rangle = \frac{1}{ANc}\left(1-\frac{2}{Nc}\frac{\partial\delta}{\partial k_z}\right)+\frac{1}{2}\sum_{\bar{G}G_z} C_{\bar{G}G_z}C_{G,-G_z} \times\langle\cos(2k_zz+2\delta)\rangle+\frac{1}{2}\sum_{\bar{G}G_z} C_{\bar{G}G_z}C_{\bar{G},-G_z-2\pi/c} \times\left\langle\cos\left[\left(2k_z-\frac{2\pi}{c}\right)z+2\delta\right]\right\rangle. \quad (18)$$

III. CHARGE NEUTRALITY

We shall need to know $\delta(k_z)$ only for $k_z=0$ and π/c. Equating the logarithmic derivative of ϕ at $z=0$ to that of the wave function integrated in from $z=-\infty$ automatically satisfies the boundary condition at $z=Nc$ as well because of Eqs. (4a) and (4b). We have

$$\left(\frac{\phi'}{\phi}\right)_{z=0} = -\frac{\sum_{\bar{G}G_z} C_{\bar{G}G_z}(k_z+G_z)\cos(\bar{k}+\bar{G})\cdot\vec{r}}{\sum_{\bar{G}G_z} C_{\bar{G}G_z}\cos(\bar{k}+\bar{G})\cdot\vec{r}}\tan\delta = -\tan\delta\left(\frac{-i\Psi'}{\Psi}\right)_{z=0}. \quad (19)$$

For $k_z=0$ or π/c, the z reflection is a member of the group of the wave vector so that Ψ is either even or odd and $(\Psi'/\Psi)_{z=0}$ is either zero or infinite. Because there is zero probability that the logarithmic derivative of the wave function integrated in from $z=-\infty$ will be *exactly* zero or infinity, we must have $\delta=\frac{1}{2}m\pi$ with m an integer.

Because of the spatial average of the cosine, the second term of (18) will vanish except for $k_z\to 0$ and the third term will vanish except when $k_z\to\pi/c$. Thus we evaluate the δ's in these terms at $k_z=0$ and π/c, respectively. We note that as $k_z\to 0$, $C_{\bar{G},-G_z}=\pm C_{\bar{G}G_z}$, depending upon whether Ψ is even or odd. Also for $k_z=\pi/c$, $C_{\bar{G},-G_z-2\pi/c}$ is the coefficient of the plane wave $\exp[i(\pi/c-G_z-2\pi/c)z] = \exp[-i(\pi/c+G_z)z]$, whereas $C_{\bar{G},G_z}$ is the coefficient of $\exp[i(\pi/c+G_z)z]$, so that $C_{\bar{G},-G_z-2\pi/c}=\pm C_{\bar{G},G_z}$. Summing $\langle\phi^2\rangle$ over all allowed values of $(\bar{k},k_z)$ replacing the sum over k_z by an integral for the second term in the square brackets, one obtains

$$\sum_{\bar{k}k_z}\langle\phi^2\rangle = (N\vec{a}\times\vec{b}\cdot\vec{c})^{-1}\left\{N+\Delta N-\left(\frac{2}{\pi}\right)(\delta_{\pi/c}-\delta_0) \pm\sum_{k_z}\left\langle\cos(2k_zz+2\delta_0) +\cos\left[\left(2k_z-\frac{2\pi}{c}\right)z+2\delta_{\pi/c}\right]\right\rangle\right\}. \quad (20)$$

In evaluating the $\sum_{\bar{G}G_z} C^2_{\bar{G}G_z}$ preceding the cosine terms we used only the leading term of (15) since we are working only to order N^{-1}. ΔN is the deviation from N in the number of allowed positive k_z within the slab-adapted Brillouin zone.

We have

$$\pm\sum_{k_z}\langle\cos(2k_zz+2\delta_0)\rangle = \pm\mathrm{Re}^{2i\delta_0}\left(\sum_{m=1}^{M}\langle\exp(4\pi imz/Nc)\rangle +\sum_{m=0}^{M}\langle\exp[2\pi i(2m+1)z/Nc]\rangle\right). \quad (21)$$

Remember that $\delta_0=0,\pm\pi$, etc., when $\Psi(z=0)=0$, i.e., for odd Ψ, and that $\delta_0=\pm\frac{1}{2}\pi,\pm\frac{3}{2}\pi$, etc. for $\Psi'(z=0)=0$, i.e., for even Ψ. Thus $\pm e^{2i\delta_0}$ contributes a factor of -1. Comparing with Eqs. (4) we see that for $\delta_0=0$, etc., the first sum is over even φ and the second over odd, but when $\delta_0=\pm\frac{1}{2}\pi$, etc., the reverse is true. The sums are straightforward and yield

$$\mathrm{Re}\sum_{m=0}^{M}\langle\exp[2\pi i(2m+1)z/Nc]\rangle = \left\langle\frac{\sin4\pi(M+1)z/Nc}{2\sin2\pi z/Nc}\right\rangle = 0, \quad (22)$$

$$\mathrm{Re}\sum_{m=1}^{M}\exp(4\pi imz/Nc) = \left\langle-\frac{1}{2}+\frac{\sin4\pi(M+1/2)z/Nc}{2\sin2\pi z/Nc}\right\rangle = -\frac{1}{2}, \quad (23)$$

Thus the result is independent of the exact value of the upper limit M, and $\pm\sum_{k_z}\langle\cos(2k_zz+2\delta_0)\rangle=\frac{1}{2}$. The second cosine term in (20) can be written in a form identical to (21) and also yields $\frac{1}{2}$. Then replacing the two cosine terms in (20) by unity, dropping the first term $(\vec{a}\times\vec{b}\cdot\vec{c})^{-1}$ which gives the charge density neglecting surface effects, and multiplying by 2 for spin, one obtains

$$\Delta\rho = 2(N\vec{a}\times\vec{b}\cdot\vec{c})^{-1}(1+\Delta N+\delta) \quad (24)$$

as the surface-induced bulk-charge-density discrepancy, where

$$\delta = (2/\pi)(\delta_0-\delta_{\pi/c}). \quad (25)$$

TABLE I. Values of even and odd k_z's as a function of n and δ_n and the resulting ΔN.

n	δ_n	k_{ze}	k_{zo}	ΔN
0	0	0	π/Nc	-1
0	$-\frac{1}{2}\pi$	π/Nc	$2\pi/Nc$	0
0	$\frac{1}{2}\pi$	$-\pi/Nc$	0	-2
$\frac{1}{2}N-1$	0	$\pi/c-2\pi/Nc$	$\pi/c-\pi/Nc$	0
$\frac{1}{2}N-1$	$-\frac{1}{2}\pi$	$\pi/c-\pi/Nc$	π/c	-1
$\frac{1}{2}N-1$	$\frac{1}{2}\pi$	$\pi/c-3\pi/Nc$	$\pi/c-2\pi/Nc$	1

TABLE II. Values of δ and ΔN as a function of $\delta_{\pi/c}$ and δ_0. Note that $\delta_{\pi/c}$ corresponds to $\delta_{n=(N/2)-1}$ in Table I.

$\delta_{\pi/c}$	δ_0	δ	ΔN
0	0	0	−1
$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	−1
$-\frac{1}{2}\pi$	$-\frac{1}{2}\pi$	0	−1
0	$-\frac{1}{2}\pi$	−1	0
$\frac{1}{2}\pi$	0	−1	0
$-\frac{1}{2}\pi$	0	1	−2
0	$\frac{1}{2}\pi$	1	−2
$\frac{1}{2}\pi$	$-\frac{1}{2}\pi$	−2	1
$-\frac{1}{2}\pi$	$\frac{1}{2}\pi$	2	−3

If we allow n to take values between zero and $\frac{1}{2}N-1$ (for even N) we obtain N values of k_z from Eqs. (4a) and (4b). Then ΔN is determined by counting the number of k_z which are not allowed. In Table I we list the values of k_{ze} and k_{zo} obtained from (4a) and (4b) for $n=0$ and $n=\frac{1}{2}N-1$ and three values of δ_n. We see for $n=0$, $\delta_n=\frac{1}{2}\pi$ that $k_{ze}=-\pi/Nc$. Since negative values of k_z are not allowed this contributes -1 to ΔN. We also see three cases where $k_z=0$ or π/c; for these cases one cannot satisfy the boundary condition (19), so they also contribute -1 to ΔN. For example, consider the case $n=\frac{1}{2}N-1$, $\delta_n=-\frac{1}{2}\pi+\epsilon$, corresponding to even Ψ, where ϵ is an infinitesimal. Then from (4b) $k_{zo}=\pi/c-2\epsilon/Nc$. Now for even Ψ one has $(-i\Psi'/\Psi)_{z=0}$ proportional to $(\pi/c-k_{zo})$ so that

$$-\tan\delta(-i\Psi'/\Psi)_{z=0}\propto(2\epsilon/Nc)\cot\epsilon\to 2/Nc\,. \qquad (26)$$

It would be a coincidence of zero probability if the logarithmic derivative of the wave function integrated in from $z=-\infty$ should be equal to that obtained from (26). If one repeats the calculation for $n=\frac{1}{2}N-2$ one finds $-\tan\delta(-\Psi'/\Psi)_{z=0}\propto(2\pi/Nc)\cot\epsilon$, so that in this case the boundary condition can be fitted by ϵ taking on a value of order N^{-1}. Finally, for the case $n=\frac{1}{2}N-1$ and $\delta_n=\frac{1}{2}\pi$ in Table I one finds $k_{ze}=\pi/c-3\pi/Nc$. This means that n can take on the value $\frac{1}{2}N$, yielding $k_{ze}=\pi/c-\pi/Nc$, still within the slab-adapted Brillouin zone. This then contributes $+1$ to ΔN. In Table II for each of the nine possible pairs of $\delta_{\pi/c}$ and δ_0 values we list δ calculated from (25) and ΔN, which is the sum of the two ΔN's taken from Table I for $n=0$ and $n=\frac{1}{2}N-1$. Note that $\delta+\Delta N=-1$ in every case, so that $\Delta\rho$ in Eq. (22) vanishes to order N^{-1} in every case.[8] One can easily see that this result holds for any pair of $\delta_0=\frac{1}{2}m_1\pi$, $\delta_{\pi/c}=\frac{1}{2}m_2\pi$. Therefore every band in the slab-adapted Brillouin zone contributes to order N^{-1} exactly two electrons per bulk slab-adapted unit cell. The total electronic charge of the filled valence bands then exactly cancels the ionic charge to order N^{-1} in the bulk unit cells. Q. E. D.

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Note added in manuscript. It has been suggested that a more general proof of charge neutrality might be based upon Eq. (2.22) of Appelbaum and Blount.[9] The quantity $N(z-d)-N(z)$ is indeed the charge of a single electron between a pair of planes separated by a lattice constant, although not in a very convenient form for our purposes. Note that we were forced to invoke a reflection plane in order to sum over k_z, but not to get the charge of a single electron. Therefore applying the methods of this paper to Eq. (2.22) will not yield a result more generally valid. In fact, we have been able to extend the validity of these results to the case of cubic crystal slabs with only inversion symmetry such as (100) and (111) silicon.[10]

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[1]J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 32, 225 (1974).

[2]They state that there are three surface-state bands but one of the bands is twofold degenerate at the points in the two-dimensional Brillouin zone which they sampled.

[3]E. T. Goodwin, Proc. Cambridge Philos. Soc. 35, 205 (1939).

[4]L. Kleinman, Phys. Rev. B 6, 1142 (1972).

[5]J. A. Appelbaum and D. R. Hamann (private communication).

[6]V. Heine, Phys. Rev. 145, 593 (1966).

[7]The (110) rotation in diamond requires a nonprimitive translation. Since this may be taken to be $\vec{\tau}=(\frac{1}{4}a)(1,-1,-1)$, which lies in the plane of the slab, this is a valid operation for the slab. We have made a translation of origin of $\frac{1}{2}\vec{\tau}$ in Eq. (2) since the combination of Bloch states actually contains the factor $\cos(\vec{k}+\vec{G})\cdot(\vec{r}+\frac{1}{2}\vec{\tau})$.

[8]For odd N one can allow n to take values between zero and $\frac{1}{2}(N-1)$, yielding $N+1$ values of k_z. Then the ΔN appearing in the table corresponding to Table II is one plus the sum of the two ΔN's taken from the table corresponding to Table I. One again obtains $\delta+\Delta N=-1$ in every case.

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

[10]L. Kleinman (unpublished).