

Phase Shifts and Local Charge Neutrality in Semiconductors*

VOLKER HEINE†

Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received 27 December 1965)

We imagine solving the Schrödinger equation in a piece of semiconductor with N atoms containing a dislocation, vacancy, or other defect. There will be some probability density $|\phi|^2$ inside the vacancy and the normalization of each state will be affected by it. The mean charge density of each state far from the vacancy will be $1/N$ electrons per atom minus a term of order $1/N^2$, as occurs in metals and leads to the Friedel phase-shift theorem. Thus when we sum over the whole band, we might expect the vacancy and immediate surroundings to carry a nonintegral net charge γ , which is compensated by a charge-density deficit γ/N over the whole crystal. There can be no screening (at 0°K) and the effect would lead to strong electric fields of the type found in fact around dislocations in semiconductors. However, we find in a one-dimensional calculation that γ is identically zero and the effect does not exist. This comes about because the Bloch states at the band edges are standing waves, and the phase shift tends to a multiple of $\pi/2$. The result may plausibly be extended to three dimensions, so that local charge neutrality appears to be maintained, apart from the usual donor and acceptor states, of course.

I. LOCAL CHARGE NEUTRALITY

IN a metal, charge neutrality around an impurity or defect is maintained by the flow of some charge to make a self-consistent screened potential. In detail, we can integrate radially outwards from the defect or impurity and treat the band of the metal as a free-electron gas, applying some boundary condition such as $\phi=0$ at a large distance R . The normalization integral of the state is altered by a fraction of order $1/N$ where N is the number of atoms in the system, and so is the total charge density. In fact the charge density far away from the defect or impurity is reduced by an amount, equal to $(2/\pi)\sum(2l+1)\delta_l$ electrons subtracted uniformly over the system, where the δ_l are the phase shifts. If an impurity itself contributes an extra Z electrons, we add these to the band. Now in a metal the defect is completely screened so that the metal is locally neutral at large distances, where there can be no change of order $1/N$ in the charge density. The condition for self-consistency is therefore that the potential around the defect or impurity adjusts itself until its phase shifts satisfy the well-known Friedel sum rule¹

$$Z = (2/\pi) \sum (2l+1)\delta_l. \quad (1)$$

In an insulator or semiconductor at absolute zero of temperature, there can be no such flow of charge or screening. The preceding analysis suggests that we could be left with a uniform charge density deficit of γ/N electrons per atom over the crystal as a whole, neutralizing a nonintegral charge γ localized in and around the defect. This situation would lead to electric fields over large distances in the semiconductor, resulting in strong bending of the bands. Wherever the bands bend sufficiently for the valence(conduction)-band edge to dip above (below) the Fermi level, free

holes (electrons) would be produced, and of course at finite temperature and in doped samples there are also some mobile free carriers. These two mechanisms would limit the band bending, which could however still extend over several thousand angstroms. The whole effect would be a property of the full band of $4N$ valence states including any localized states split off the valence band which we assume also to be full. It has nothing to do with the usual filling (emptying) of acceptor (donor) states.

Such bending of the bands is indeed found experimentally around dislocations in semiconductors,² and the author considered for some time whether the effect we are discussing could be the explanation of it, instead of the rather unsatisfactory³ conventional story about dangling bonds. The present effect does not appear to have been discussed in the literature before, and if it existed it would have important consequences for the state of surfaces and any defects in semiconductors. It therefore seems desirable either to confirm its existence or dispose of it.

In fact we shall dispose of it. Exact local electrical neutrality is maintained in a semiconductor far from a defect center, and this in itself is an interesting property of full bands since the mechanism must be quite different from that in metals discussed above. The lack of rotational symmetry about the defect makes any discussion in a three-dimensional solid difficult, but this does not arise in one dimension. We shall therefore discuss the effect in detail in one dimension and give plausible arguments in Sec. III that it carries over into three dimensions. In Sec. II we shall discuss exactly the normalization of the wave functions in terms of phase shifts for Bloch functions,⁴ as a preliminary to calculating the charge density in Sec. III. This has to be done exactly to the order of the small terms in $1/N$

* Supported in part by the National Aeronautics and Space Administration.

† Permanent address: Cavendish Laboratory, Free School Lane, Cambridge, England.

¹ J. Friedel, *Advan. Phys.* **3**, 446 (1954).

² See Ref. 3 for a convenient brief summary and references.

³ V. Heine, *Phys. Rev.* (to be published).

⁴ This result is unlikely to be novel but I have not been able to find a reference.

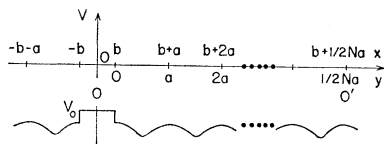


FIG. 1. Potential in a one-dimensional ring with an insertion.

which we are looking for. If we proceed not too carefully, we can prove a phase-shift theorem as in (1) for the net charge localized around the defect. We find the phase shifts (for small perturbations) tend to zero or $\pm\pi/2$ at the band edges, because the Bloch states there become standing waves. Thus application of the sum rule (1) can give a nonzero $\gamma=1$ in the notation above, and in fact does so in the particular case of interest where we have bonding states below the band gap and antibonding ones above. In Sec. III we therefore discuss some further terms in the charge density which in the case considered cancels the previous contribution and gives a total γ of zero. These terms arise as follows. In the usual free-electron analysis, there are in addition to the terms (1) some oscillations in the charge density like $\sin(2kx-2\delta)$, the Friedel wiggles.¹ They are usually discarded on the grounds that they average to zero over a reasonable distance. However, with Bloch states they take the form

$$\sin(2kx-2\delta)v(x), \quad (2)$$

where $v(x)$ is periodic in the lattice displacement a and is related to the periodic part u_k of the Bloch function

$$\psi_k = \exp(ikx)u_k(x). \quad (3)$$

When k approaches the Brillouin-zone boundary π/a , the first factor in (2) can combine with the $2\pi/a$ Fourier component of v to give a term whose wavelength tends to infinity, which can contribute to the mean charge density away from the defect.

For the sake of definiteness we discuss the particular system shown in Fig. 1. It is a one-dimensional ring of N cells (N even) of a periodic potential (period a) with a piece of width $2b$ and potential V_0 inserted between a pair of cells. All the wave functions ϕ_n are real, and either even or odd about the origin $O(x=0)$ in the center of the insertion. We integrate the wave equation from O and demand that the wave functions join up at

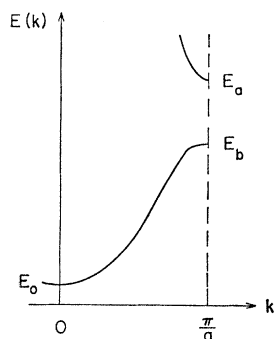


FIG. 2. Nearly free-electron band structure.

the anti-origin $O'(x=b+Na/2)$ halfway round the ring, where the states will automatically be even or odd again, respectively. We treat the potential as weak in the nearly free-electron approximation, using the idea of pseudopotentials as justification.⁵ Let us focus attention on the first band from the bottom $E=E_0$ up to the first band gap at $k=\pi/a$ (Fig. 2). We choose the $2\pi/a$ Fourier component V_1 of the potential to be positive, corresponding to bonding type Bloch state

$$\psi_k \approx \cos(\pi y/a) \quad (4)$$

with energy E_b at the bottom of the gap, where we have referred ψ_k to an origin $y=0$ at the *edge* of a cell (Fig. 1). Similarly we have antibonding states like $\sin(\pi y/a)$ at E_a above the gap (Fig. 2). The situation at the first band gap in our model is closely analogous to the band gap of a group-IV semiconductor. In the latter we have a center of inversion at a point halfway between two atoms, the valence states being even (bonding) about this point, the conduction band antibonding. It is the form of the wave functions halfway between the atoms that counts, because it is there that we cut the solid to form surfaces, etc. Thus we identify the first and second bands of our model with the valence and conduction bands of the semiconductor. We shall retain a completely general analysis where required to demonstrate an exact cancellation, but use the nearly free-electron approximation and the specific model when it is necessary to count states or point to particular terms. For instance we will choose V_0 to be somewhere between the bottom of the band and the band gap, not necessarily a constant. In that case the "valence" band contains the same number of states N (for each spin) in the perturbed case with the insertion,³ as in the unperturbed case $b=0$. There are no localized states split off the band, though there is an extra state in the gap pulled down out of the "conduction" band³ which we are not interested in.

II. THE NORMALIZATION THEOREM

We consider the Schrödinger equation

$$[-d^2/dx^2 + V(x)]\phi(x,E) = E\phi(x,E) \quad (5)$$

which we wish to integrate with energy E from the origin $x=0$ to some point $x=X$. From (5) we have

$$[-d^2/dx^2 + V(x)]\partial\phi/\partial E = \phi + E\partial\phi/\partial E. \quad (6)$$

We multiply (6) by ϕ (which is real), also (5) by $\partial\phi/\partial E$ and subtract. Then integrating from 0 to X and using the usual Green's identity, we obtain

$$\int_0^X \phi^2 dx = \left[\frac{\partial\phi}{\partial E} \frac{\partial\phi}{\partial x} - \phi \frac{\partial^2\phi}{\partial E \partial x} \right]_0^X. \quad (7)$$

⁵ See, for example, V. Heine, *Proceedings of the Ninth International Low Temperature Conference, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. V. Edwards, F. J. Milford, and M. Yagou (Plenum Press, Inc., New York, 1965).

Assuming a center of symmetry at $x=0$, we have there either $\phi=0$ for all E and hence $\partial\phi/\partial E=0$ for odd states, or $\partial\phi/\partial x=\partial^2\phi/\partial E\partial x=0$ for even states. In any case the bracket in (7) vanishes at $x=0$, leaving us with

$$\int_0^x \phi^2 dx = \left(\frac{\partial\phi}{\partial E} \frac{\partial\phi}{\partial x} - \phi \frac{\partial^2\phi}{\partial E\partial x} \right)_{x=X} \quad (8)$$

as our basic "normalization theorem."

One possible ambiguity should be dealt with at this point concerning the meaning of $\partial\phi/\partial E$. In the case of odd states for example, if we start integrating with some definite initial condition $\phi=0$, $\partial\phi/\partial x=1$ at all E , then this defines ϕ uniquely as a continuous function of E . We are not applying any quantizing boundary condition at the other boundary at this stage. Moreover if we had chosen some other convention which fixes the amplitude of ϕ differently by a factor $A(E)$, then substituting the new ϕ into (8) simply multiplies each side by $[A(E)]^2$ as it should: All terms involving $\partial A/\partial E$ cancel out.

Considering the situation in Fig. 1, we integrate first from $x=0$ to the edge of the insertion $x=b$, obtaining some value of the logarithmic derivative $\phi^{-1}\partial\phi/\partial x$ there. In the solid $x>b$ our ϕ has to be some linear combination of the Bloch states ψ_k, ψ_{-k} . We will choose the periodic part of the potential to have a center of symmetry so that ψ_k, ψ_{-k} are complex conjugates of one another. Thus their real and imaginary parts may be taken as the linearly independent solutions, and an arbitrary real solution can be written

$$\phi = \Re(e^{i\delta}\psi_k) \quad (9)$$

in terms of a phase shift δ . Matching onto the logarithmic derivative already found at $x=b$ determines δ as a function of k or E .

By way of a brief aside, it is instructive to prove from (8) the phase-shift sum with Bloch waves. We note that

$$\Re(f)\Re(g) = \frac{1}{2}\Re(fg + fg^*) \quad (10)$$

Using (9) and the representation (3) but with variable y instead of x , we find (8) becomes

$$\int_0^x \phi^2 dx = (dk/dE) \{ [v_1 + (x+d\delta/dk)v_2] + [v_3 + (x+d\delta/dk)v_4] \cos(2kx+2\delta) + [v_5 + (x+d\delta/dk)v_6] \sin(2kx+2\delta) \}, \quad (11)$$

where the v_j are periodic functions related to u_k and do not involve δ . We first throw away the oscillating Friedel wiggles as of no interest, which is valid if we sum only up to some point in the middle of the first band as discussed in Sec. I. We then apply (11) at some finite distance X from the defect, assuming the states to be quantized by some boundary condition at some point Na where N can be made arbitrarily large. The

k vectors and normalization constants of the allowed states then differ by order $1/N$ from those of the unperturbed system with $b=0$, this difference being negligible in the present circumstances because we are calculating the charge in a finite region. We take the difference of (11) between perturbed and unperturbed states. The left side gives the extra charge attracted inside X by the perturbation. The right side is

$$(dk/dE)(d\delta/dk)v_2. \quad (12)$$

Turning back to (8) and seeing where v_2 comes from, we find it is just

$$\Re(-\psi_k^* i \partial\psi/\partial x). \quad (13)$$

We want the mean value of this, say over one atomic cell, which is

$$\bar{v}_2 = (2/Na)dE/dk, \quad (14)$$

when (9) is normalized over N cells. Now the quantized k values are equally spaced (to order $1/N$) with a density $Na/2\pi$ even and odd states per unit of k space. After substituting (14) into (12), we can therefore sum (12) up to some energy E and over both spin directions, to obtain the total charge

$$(2/\pi)(\delta_{\text{even}} + \delta_{\text{odd}}) \quad (15)$$

attracted by the perturbation. Even and odd correspond in one dimension to different angular momenta in 2 and 3 dimensions. This formula assumes we have chosen the states such that both δ 's are zero for the unperturbed case and tend to zero at the bottom of the band with the perturbation (which may be difficult to arrange).

We return to the question of the exact determination and normalization of the allowed states. It is convenient to work with the new variable

$$y = x - b, \quad (16)$$

with origin at the edge of the first cell (Fig. 1). We can write a Bloch function as

$$\psi_k = \sum_{\sigma} C_{\sigma} \exp i(k+g)y, \quad (17)$$

where the g 's are reciprocal lattice vectors. We note that the C_{σ} can be chosen all real because the cell edge is a center of symmetry for the periodic potential and the secular equation in terms of plane waves is then completely real. Thus (9) becomes

$$\phi = \sum C_{\sigma} \cos[(k+g)y + \delta]. \quad (18)$$

The allowed energy and k values are determined by applying the boundary condition $\partial\phi/\partial y=0$ for even states at $y=Na/2$. We have

$$\partial\phi/\partial y = -\sum C_{\sigma}(k+g) \sin[(k+g)y + \delta], \quad (19)$$

and the boundary condition is satisfied if

$$k_n Na/2 + \delta_n = n\pi \quad (\text{even states}). \quad (20)$$

We also have

$$\begin{aligned} \partial^2\phi/\partial E\partial y = & -(y+d\delta/dk)(dk/dE) \\ & \times \sum C_g(k+g) \cos[(k+g)y+\delta] \\ & - \sum dC_g/dE(k+g) \sin[(k+g)y+\delta]. \end{aligned} \quad (21)$$

We wish to apply (8) at the point $y=Na/2$, and note from (20) that all sine terms in (19), (21) are zero and all cosine terms $(-1)^n$. Equation (8) therefore becomes

$$\begin{aligned} \int_{-b}^{Na/2} \phi^2 dy = & \frac{dk}{dE} \left(\frac{Na}{2} + \frac{d\delta}{dk} \right) \\ & \times [\sum_g \sum_{g'} C_g C_{g'}(k+g)]. \end{aligned} \quad (22)$$

In order to simplify (22) we shall prove that the terms with $g' \neq g$ sum to zero, so that the term in square brackets is related to the expectation value of the momentum operator for ψ_k , which is proportional to dE/dk and cancels with the first factor of (22). Consider the Bloch state ψ_k . Its current density is, apart from the normalization factor,

$$\begin{aligned} J(y) = & -(i/2)[\psi^*(\partial\psi/\partial y) - (\partial\psi^*/\partial y)\psi] \\ = & \sum C_g^2(k+g) + \sum_{g' \neq g} \sum' C_g C_{g'}(k+g) \\ & \times \cos(g-g')y. \end{aligned} \quad (23)$$

Now ψ_k is a stationary state and $J(y)$ has to be divergenceless, i.e., in one dimension a constant. Thus the second term of (23) vanishes which means all the terms in (22) with $g' \neq g$ also sum to zero, and the square bracket of (22) reduces to

$$[\dots] = \sum C_g^2(k+g). \quad (24)$$

We also note that dE/dk is twice the expectation value of the momentum for state ψ_k :

$$\frac{1}{2} \frac{dE}{dk} = \frac{\int \psi^*(1/i)(\partial/\partial y)\psi dy}{\int \psi^*\psi dy} = \frac{\sum C_g^2(k+g)}{\sum C_g^2}, \quad (25)$$

where the factor of one-half comes in because we have omitted it from the kinetic-energy operator in (5). Now we want the left side of (22) to be just $\frac{1}{2}$ because we are integrating halfway around the ring, and from (22), (24), (25) this determines the amplitude of the C_g by

$$\begin{aligned} \sum C_g^2 = & \frac{2}{Na} \left[1 + \frac{2}{Na} \frac{d\delta}{dk} \right]^{-1} \\ = & \frac{2}{Na} \left[1 - \frac{2}{Na} \frac{d\delta}{dk} + O(N^{-2}) \right]. \end{aligned} \quad (26)$$

We obtain the same formula for the odd states starting with the other boundary condition $\phi=0$.

III. THE CHARGE DENSITY

At this point we focus attention on the particular model of Sec. I with V_0 in the range mentioned. The exact number of states $N+0$ or ± 1 in the band, the possibility of localized states split off, and the value $\pm\pi/2$ of the phase shifts at the band edges, these all depend on the particular situation, and it is not convenient to develop a general formalism.

For the even states, ϕ in the insertion behaves like

$$\begin{aligned} \phi \approx & \cosh(V_0 - E_0)^{1/2}x \quad \text{at } E \approx E_0, \\ \approx & \cos(E_b - V_0)^{1/2}x \quad \text{at } E \approx E_b, \end{aligned} \quad (27)$$

so that the logarithmic derivative ϕ'/ϕ at $y=0$ ($x=b$) is positive at the bottom of the band, passes through zero, and becomes negative at the top [Fig. 3(a)]. From (18) it has to be equal to

$$\begin{aligned} \frac{\phi'}{\phi} = & -\tan\delta \left[\frac{\sum C_g(k+g)}{\sum C_g} \right] \\ = & -\tan\delta \left[\frac{-i\psi_k'(y=0)}{\psi_k(y=0)} \right]. \end{aligned} \quad (28)$$

We have bonding type of functions both at the top and bottom of the valence band. For both of these the numerator of (28) vanishes whereas the denominator remains finite. Thus the factor in (28) in square brackets tends to zero at the band edges, and it is easy to verify with the nearly free electron (NFE) approximation that it does so from the positive side in our case. We have $\tan\delta \rightarrow \pm\infty$, and the phase shift varies as shown in Fig. 3(b). For the odd states ϕ'/ϕ is positive throughout the band and the phase shift has the form also shown in Fig. 3(b).

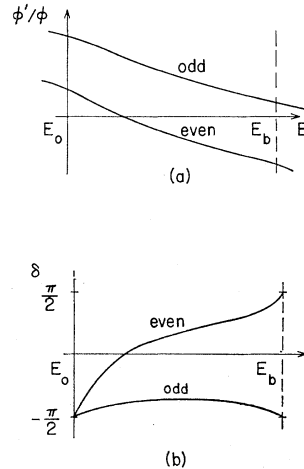


FIG. 3. (a) Logarithmic derivative ϕ'/ϕ , and (b) phase shift δ , for even and odd states.

We wish to calculate the total charge density in the solid a large distance from the perturbation. We simply use (18) with the normalization (26) which takes into account exactly the amount of charge contained in and around the insertion. With the aid (9), (10), (17) we can write down

$$\phi^2 = \frac{1}{2} \left\{ \sum C_\sigma^2 + \sum_{\sigma' \neq \sigma} \sum C_\sigma C_{\sigma'} \cos(g-g')y + \sum \sum C_\sigma C_{\sigma'} \cos[(2k+g+g')y+2\delta] \right\}. \quad (29)$$

Here we drop the second term completely because it gives identically zero contribution to the charge in one unit cell. The third term represents the Friedel wiggles. As mentioned in Sec. I, each term in it averages to zero over a reasonable distance, but we must for the present retain those terms for which $2k+g+g'$ can become zero. In fact it will be obvious from our evaluation of these special terms that the others are negligible. The relevant terms are $g' = -g$ which can become dangerous at the bottom of the band, and $g' = -g-G$ at the top of the band, where we have written G as an abbreviation for $2\pi/a$. We also substitute from (26) for the first term in (29) which therefore becomes

$$\phi^2 = \frac{1}{Na} \left\{ 1 - \frac{2}{Na} \frac{d\delta}{dk} \right\} + \left(\frac{1}{2} \sum C_\sigma C_{-\sigma} \cos[2ky+2\delta] + \left(\frac{1}{2} \sum C_\sigma C_{-\sigma-G} \cos[(2k-G)y+2\delta] \right). \quad (30)$$

We now sum (30) for all the even states in the band. From (20) and Fig. 3(b), we note the allowed values k_n in the band are given by

$$n=0, 1, 2, \dots, N/2 \quad (31)$$

in (20), i.e. $N/2+1$ values in all, so the first term of (30) sums to

$$(Na)^{-1}(N/2+1). \quad (32)$$

With the usual density (20), (31) of points in k space, the second term of (30) becomes an integral over dk , and gives

$$-(Na)^{-1} \pi^{-1} [\delta(E_b) - \delta(E_0)] = -(Na)^{-1} \quad (33)$$

with the phase shifts of Fig. 3(b). The sum of the next term in (30) we write as

$$\Re \sum_n f(k_n) \exp i[2k_n y + 2\delta_n], \quad (34)$$

where the coefficient $\frac{1}{2} \sum C_\sigma C_{-\sigma}$ is a slowly varying function of k . It is a typical "stationary phase" summation, where we get an important contribution from near the limit $n=0$ where the argument in square brackets is near zero, and a rapidly oscillating component like $\cos(2\pi y/a)$ from near the upper limit $n=N/2$. The

latter again gives zero contribution to the net charge in one unit cell and we ignore it. Without affecting the component we are interested in, we can replace $f(k_n)$ and δ_n in (34) by their values at the point of zero phase, i.e., $k=0$. There $C_\sigma = C_{-\sigma}$, so that with (26) and (20) we make the replacements

$$f(k_n) = (Na)^{-1}, \quad 2\delta_n = -\pi, \quad (35)$$

$$2k_n y = (2n+1)2\pi y / (Na).$$

Equation (34) becomes

$$-(Na)^{-1} \Re \sum_{n=0}^{N/2} \exp i(2n+1)2\pi y / (Na)$$

$$= -(Na)^{-1} \left[O + \frac{\sin[(N+2)2\pi y / Na]}{2 \sin(2\pi y / Na)} \right]. \quad (36)$$

We see that the constant term which we are interested in happens to be zero: In another case studied by the author where V_0 was set equal to the bottom of the band E_0 , this term contributed $(2Na)^{-1}$. We turn to the last term in (30) for which the point of zero phase is $k=\pi/a$ and we evaluate the slowly varying functions there. C_σ and $C_{-\sigma-G}$ are the coefficients of the plane waves

$$\exp i(\pi/a + g)y,$$

and

$$\exp i(\pi/a - g - G)y = \exp -i(\pi/a + g)y, \quad (37)$$

so that C_σ and $C_{-\sigma-G}$ are equal at $k=\pi/a$ and the coefficient in (30) becomes $\sum C_\sigma^2$ which is evaluated in (26) as before. It is convenient to define $m = N/2 - n$ so that $(2k-G)y$ becomes $-(2m+1)(2\pi y / Na)$. We therefore get the same series as in (36), and zero contribution to the mean charge density. Collecting everything, we have the charge density (not counting spin degeneracy)

$$\sum \phi^2(y) = \frac{1}{2} a^{-1} \quad (\text{even states}). \quad (38)$$

For the odd states, (20) and (31) are replaced by

$$k_n Na/2 + \delta_n = (n+1/2)\pi, \quad n=1, 2, \dots, 1/2(N-1), \quad (39)$$

with $\frac{1}{2}N-1$ states in all. The phase-shift term in (30) sums to zero since $\delta(E_b) = \delta(E_0)$. The first cosine sum becomes

$$-(Na)^{-1} \sum_{n=1}^{N/2-1} \cos(4n\pi / Na)$$

$$= -(Na)^{-1} \left[-\frac{1}{2} + \frac{\sin[(N-1)2\pi y / Na]}{2 \sin(2\pi y / Na)} \right], \quad (40)$$

where this time we get a nonzero contribution. The second cosine sum gives the same quantity again and

we have the total charge density

$$\sum \phi^2 = \frac{1}{2} a^{-1} \quad (\text{odd states}). \quad (41)$$

Combining (41) with (38), we see that the total charge density in distant cells is exactly 1 electron per unit cell, not counting spin degeneracy. The same result is obtained if we consider $V_0 < E_0$: then there is a bound state with only a localized charge density pulled out of the bottom of the band, and one less even state in the band, but the change in the phase shift from $-1/2\pi$ to $+1/2\pi$ restores the same charge density. The result also remains true when we take $V_0 = E_0$, but the term $n=0$ has to be handled specially. The lowest even state now has $k \equiv 0$ and becomes like A.1 instead of $A \sin(\pi y/Na)$, with consequent changes of a factor of 2 in the normalization and elsewhere for this particular term. The same applies to the state at $k = \pi/a$ if we consider the limit of the perfect solid with zero insertion.

Finally it is necessary to inquire whether these results are likely to carry over to three dimensions. No complete proof seems possible at present because of the lack of symmetry, but several thoughts make it very plausible. The present result is essentially due to the "pulling" of the wave function at the band edges. One can only talk about phase shifts when one has two independent solutions of the Schrödinger equation which one can combine with some arbitrary phase. But at a band edge the two solutions coincide: The wave function can only be a certain standing wave. It is this which pulls the phase shifts to $\pm\pi/2$ in one dimension. Suppose we have in three dimensions a band edge with isotropic effective mass. We can write the wave functions as

$$\exp(i\mathbf{K} \cdot \mathbf{r}) u(\mathbf{r}), \quad (42)$$

where K is measured from the band extremum, and near the band edge do a separation into angular momenta in the usual effective-mass approximation. In this way one gets back to a one-dimensional radial equation for the

envelope function χ , where

$$\psi = \chi u(\mathbf{r}), \quad (43)$$

and one expects to find the local-neutrality phenomenon.

Alternatively we note that the even and odd states each give exactly a charge of $\frac{1}{2}$ per unit cell, even though there are different number of even and odd states. We have here an example of the "back-body radiation" theorem, also known as the Von Laue theorem.⁶ In the case of black-body radiation, it is well known that the spectral density of radiation per unit volume in a closed volume is independent of the shape or boundary condition provided one is not within a few wavelengths of the edge. The quantum analog is

$$\rho(E, \mathbf{r}) = \sum_{E_n > E} |\psi_n(\mathbf{r})|^2, \quad (44)$$

the total charge density in states with energy less than E . We can apply this to a perturbation by integrating outwards from the center until we are in a region of perfect solid, which gives us a definite radial derivative ϕ'/ϕ there as a function of E . We then have to solve the Schrödinger equation in the perfect solid with this complicated but well-defined boundary condition. In the present one-dimensional example the theorem applies separately to even and odd states since parity is conserved by the perturbation. What is not obvious from the usual proofs⁶ is that the theorem is universally valid even to terms of order $1/N$, yet this appears so from the behavior of the even and odd states where one might expect different charge densities because of the different number of states. In that case one would certainly expect the result to extend to three dimensions, where the density of levels is higher (the effect of the discreteness of the energy levels lower) and the disturbance of a boundary decays more rapidly as one moves away from it.

⁶ C. Kittel, *Quantum Theory of Solids* (John Wiley & Sons, Inc., New York, 1963), p. 339.