points the spike rarely settles, but oscillates about the surface with great rapidity. With steel points, on the other hand, the discharge frequently anchors itself to one spot, and there remains quite steady, only moving about when the field is increased almost to flashover. It is not unusual for the stem to take up a position off, and inclined to, the axis of symmetry. When the point is subsequently examined under the microscope it is usually found that the spot favored by the root of the discharge, coincides with a small crater on the surface. These form more readily on steel than on platinum, the process no doubt being assisted by chemical action, and this may account for the effect referred to.

Discourse on the mechanism of the transition from the Trichel pulse regime to the pulse-free discharge would be little more than speculation at this stage, comment is therefore reserved until a more thorough investigation of the phenomenon has been made. It is perhaps worth stating that too much importance should not be attached to the changes in shape of the induced Trichel pulses as the transition is approached, since these are largely conditioned by the circuit.

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Electronic States in Crystals under Large Over-All Perturbations*

PAULA FEUER
Purdue University, Lafayette, Indiana

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Solutions of the three-dimensional Schrödinger equation are discussed for a potential which is the sum of a potential with the periodicity of the crystal lattice plus a perturbing potential. A general theory of large over-all perturbations, such that the energy lies close to one permitted band in one region of the crystal and close to a second permitted band in another, is developed. The theory is then applied to a one-dimensional crystal in a uniform electric field, using the narrow band approximation; the probability for an electron to cross a forbidden energy band is calculated. These results are considered in connection with the interpretation of the current-voltage characteristic of an $N-P$ junction of germanium at high electric fields.

I. INTRODUCTION

A METHOD for obtaining solutions of the perturbed periodic wave equation

$$-(\hbar^2/2m)\nabla^2\psi-\{E-V_P(\mathbf{r})-V(\mathbf{r})\}\psi=0, \qquad (1)$$

where $V_P(\mathbf{r})$ is a periodic potential associated with a crystal lattice and $V(\mathbf{r})$ is some sort of perturbing potential, has been described by Slater.[1]

The method consists of expanding ψ in terms of localized functions, originally used by Wannier[2] in connection with the theory of the exciton, and defined as follows: Let $\psi_0(\mathbf{p};\mathbf{r})$ represent a solution of the periodic wave equation [Eq. (1) with $V(\mathbf{r})=0$] corresponding to the effective momentum $\mathbf{p}$ and such that

$$\int\psi_0{}^*(\mathbf{p};\mathbf{r})\psi_0(\mathbf{p};\mathbf{r})dV=1,$$

the integration being taken over the volume of the crystal. In a permitted band $\mathbf{p}$ assumes values given by $N_i\mathbf{p}\cdot\boldsymbol{\tau}_i=n_ih$, where the n_i are integers which have values $0, \pm1, \pm2, \cdots$, the $\boldsymbol{\tau}_i$ are the primitive lattice translations, and each N_i is the number of cells of the crystal extending along an axis parallel to $\boldsymbol{\tau}_i$. Now, if the phases of the $\psi_0(\mathbf{p};\mathbf{r})$ are properly chosen,

$$a(\mathbf{r}-\mathbf{r}_k)=N^{-\frac{1}{2}}\textstyle\sum_{\mathbf{p}}\exp[-(i/\hbar)\mathbf{p}\cdot\mathbf{r}_k]\psi_0(\mathbf{p};\mathbf{r}) \qquad (2)$$

represents a function localized around the kth atom of the crystal. (The choice of phases of the ψ_0 is very important and will be discussed in considerable detail in the appendix.) The number of atoms of the crystal is N and the sum is taken over all values of $\mathbf{p}$ in a particular permitted band. Thus, corresponding to each permitted band of the crystal, there is a Wannier function for each atom of the crystal. It is easily shown that

$$\int a^*(\mathbf{r}-\mathbf{r}_k)a(\mathbf{r}-\mathbf{r}_m)dV=\delta_{km}. \qquad (3)$$

It can also be shown that

$$\psi_0(\mathbf{p};\mathbf{r})=\textstyle\sum_k\exp[(i/\hbar)\mathbf{p}\cdot\mathbf{r}_k]a(\mathbf{r}-\mathbf{r}_k), \qquad (4)$$

the sum being taken over all atoms of the crystal.

The solution of Eq. (1) proposed by Slater has the form

$$\psi(\mathbf{r})=\textstyle\sum_k\phi(\mathbf{r}_k)a(\mathbf{r}-\mathbf{r}_k). \qquad (5)$$

Slater shows that if this expansion is valid and if $V(\mathbf{r})$ is so slowly varying as to be considered constant over a distance comparable with the range of the Wan-

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[1] J. C. Slater, Phys. Rev. **76**, 1592 (1949).

[2] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

nier functions, the $\phi(\mathbf{r}_k)$ can be obtained by solving the set of difference equations

$$-E\phi(\mathbf{r}_k)+\sum_s A(\mathbf{r}_k-\mathbf{r}_s)\phi(\mathbf{r}_s)+V(\mathbf{r}_k)\phi(\mathbf{r}_k)=0. \quad (6)$$

The A's depend on the unperturbed problem only and have a simple interpretation. Let $E(\mathbf{p})$ represent the energy of the unperturbed problem as a function of the momentum. If a single permitted band is considered, $E(\mathbf{p})$ can be treated as a periodic function of $\mathbf{p}$, and it can be shown that

$$A(\mathbf{r}_s)=N^{-1}\sum_{\mathbf{p}} \exp[(i/\hbar)\mathbf{p}\cdot\mathbf{r}_s]E(\mathbf{p}) \quad (7)$$

and

$$E(\mathbf{p})=\sum_s \exp[-(i/\hbar)\mathbf{p}\cdot\mathbf{r}_s]A(\mathbf{r}_s). \quad (8)$$

Thus the A's are just Fourier coefficients in the expansion of the energy of the unperturbed problem as a function of the effective momentum.

The following criticism[3] of Slater's theory can be made, however. If Eq. (2) is substituted into Eq. (5), we obtain

$$\psi(\mathbf{r})=\sum_{\mathbf{p}} c(\mathbf{p})\psi_0(\mathbf{p};\mathbf{r}), \quad (9)$$

where

$$c(\mathbf{p})=N^{-\frac{1}{2}}\sum_k \phi(\mathbf{r}_k)\exp[-(i/\hbar)\mathbf{p}\cdot\mathbf{r}_k].$$

Now, all the well-behaved solutions of the periodic problem form a complete set, but those corresponding to one permitted band do not; thus Eq. (9) and Eq. (5) represent an expansion of $\psi(\mathbf{r})$ in terms of an incomplete set of functions. It is a good approximate solution provided that the energy considered lies always close to only one permitted energy band. (The Wannier functions used in Eq. (5) must then be those which correspond to this particular permitted band.) If the energy considered lies close to two overlapping permitted bands or if the energy lies close to one permitted band in one region of the crystal and close to a second permitted band in another, the approximation is no longer a good one.

This limitation of Slater's theory has also been pointed out by Adams,[4] who has considered the perturbed periodic problem for the general case of a perturbing potential which is a function of both position and momentum. Adams expresses the solution of the perturbed periodic wave equation in the form

$$\psi=\sum_{k,n}\phi_n(\mathbf{r}_k)a_n(\mathbf{r}-\mathbf{r}_k), \quad (10)$$

where the sum over k is taken over all atoms of the crystal [as in Eq. (5)]; $a_n(\mathbf{r}-\mathbf{r}_k)$ are the Wannier functions corresponding to the nth permitted band and the sum over n is taken over all permitted bands of the crystal. The wave function ψ is thus expanded in terms of a complete set of functions. Adams then derives a set of simultaneous differential equations from which the $\phi_n(\mathbf{r}_k)$, considered as continuous functions of $\mathbf{r}$, can be determined.

It is the purpose of this paper to present an alternate formulation of the problem, for the case in which the perturbing potential is a function of position only. The solutions ψ of Eq. (1) will be expressed in the form of Eq. (10) and difference equations will be derived for the $\phi_n(\mathbf{r}_k)$. The general theory will then be used to discuss a special model of a one-dimensional crystal under a uniform electric field, and the probability per unit time for an electron to cross a forbidden energy band will be calculated.

II. THE DIFFERENCE EQUATIONS

Substituting Eq. (10) into Eq. (1), we obtain

$$\{H_0-E+V(\mathbf{r})\}\sum_{k,n}\phi_n(\mathbf{r}_k)a_n(\mathbf{r}-\mathbf{r}_k)=0, \quad (11)$$

where

$$H_0=-(\hbar^2/2m)\nabla^2+V_P(\mathbf{r})$$

is the unperturbed Hamiltonian. To obtain difference equations for the $\phi_n(\mathbf{r}_k)$ we multiply Eq. (11) by $a_l^*(\mathbf{r}-\mathbf{r}_m)$ and integrate over the volume of the crystal. The following integrals are then of interest. It can easily be seen that

$$\int a_l^*(\mathbf{r}-\mathbf{r}_m)a_n(\mathbf{r}-\mathbf{r}_k)dV=\delta_{nl}\delta_{km}. \quad (12)$$

For, according to Eq. (2), $a_n(\mathbf{r}-\mathbf{r}_k)$ is a linear combination of unperturbed wave functions $\psi_{0n}(\mathbf{p};\mathbf{r})$, the subscript n being used to denote the nth permitted band; similarly $a_l(\mathbf{r}-\mathbf{r}_k)$ is a linear combination of unperturbed wave functions $\psi_{0l}(\mathbf{p};\mathbf{r})$ of the lth permitted band. When $n\neq l$, all functions ψ_{0n} and ψ_{0l} are orthogonal and hence the integral above vanishes for all values of k and m. When $n=l$, Eq. (12) is the same as Eq. (3). Consider

$$I_{ln}(\mathbf{r}_m-\mathbf{r}_k)=\int a_l^*(\mathbf{r}-\mathbf{r}_m)H_0a_n(\mathbf{r}-\mathbf{r}_k)dV.$$

Using Eq. (2)

$$I_{ln}(\mathbf{r}_m-\mathbf{r}_k)=N^{-1}\sum_{\mathbf{p},\mathbf{p}'}\exp[(i/\hbar)\mathbf{p}\cdot\mathbf{r}_m]$$
$$\times\exp[-(i/\hbar)\mathbf{p}'\cdot\mathbf{r}_k]\int\psi_{0l}^*(\mathbf{p};\mathbf{r})H_0\psi_{0n}(\mathbf{p}';\mathbf{r})dV.$$

When the unperturbed Hamiltonian operates on $\psi_{0n}(\mathbf{p}';\mathbf{r})$, the wave function is just multiplied by the energy corresponding to the effective momentum $\mathbf{p}'$. Thus

$$I_{ln}(\mathbf{r}_m-\mathbf{r}_k)=N^{-1}\sum_{\mathbf{p},\mathbf{p}'}\exp[(i/\hbar)\mathbf{p}\cdot\mathbf{r}_m]$$
$$\times\exp[-(i/\hbar)\mathbf{p}'\cdot\mathbf{r}_k]E_n(\mathbf{p}')\int\psi_{0l}^*(\mathbf{p};\mathbf{r})\psi_{0n}(\mathbf{p}';\mathbf{r})dV.$$

Since all ψ_{0l} and ψ_{0n} are orthogonal for $n\neq l$, $I_{ln}=0$ for

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[3] The discussion of the limitations of Slater's theory, the general theory of large over-all perturbations, and the application of the general theory to a crystal in a uniform electric field, which follow, were presented on October 27, 1951, at the 308th meeting of the American Physical Society.

[4] E. N. Adams II, Phys. Rev. 85, 41 (1952).

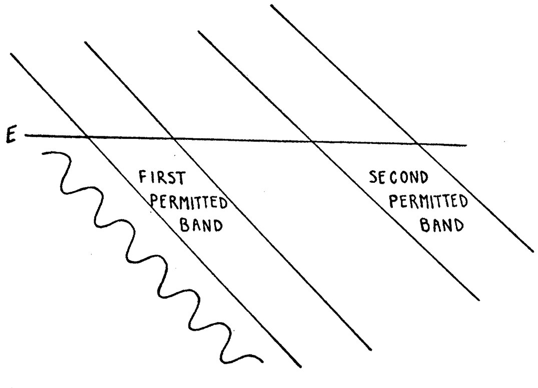

FIG. 1. Potential and energy bands in a periodic potential perturbed by a linear potential.

$n\neq l$. When $n=l$,

$$\int \psi_{0l}^*(\mathbf{p};\mathbf{r})\psi_{0l}(\mathbf{p}';\mathbf{r})dV=\delta_{\mathbf{pp}'}. \tag{13}$$

Thus

$$I_{ll}(\mathbf{r}_m-\mathbf{r}_k)=N^{-1}\sum_{\mathbf{p}}\exp[(i/\hbar)\mathbf{p}\cdot(\mathbf{r}_m-\mathbf{r}_k)]E_l(\mathbf{p}).$$

Comparison of this with Eq. (7) shows that

$$I_{ll}(\mathbf{r}_m-\mathbf{r}_k)=A_l(\mathbf{r}_m-\mathbf{r}_k). \tag{14}$$

Using Eqs. (11), (12), and (14), we then obtain the difference equations

$$-E\phi_l(\mathbf{r}_m)+\sum_k \phi_l(\mathbf{r}_k)A_l(\mathbf{r}_m-\mathbf{r}_k)+\sum_{k,n}\phi_n(\mathbf{r}_k)\times\left\{\int a_l^*(\mathbf{r}-\mathbf{r}_m)V(\mathbf{r})a_n(\mathbf{r}-\mathbf{r}_k)dV\right\}=0, \tag{15}$$

which must be satisfied for all values of $\mathbf{r}_m$. There is a set of such equations corresponding to each permitted band of the crystal, that is, for each value of l. These are the basic equations for further discussion.

It will now be shown that the type of approximation used by Slater is not sufficiently accurate in the present case. Suppose we approximate the integrals in Eq. (15) by replacing $V(\mathbf{r})$ by $V(\mathbf{r}_m)$. Then, because of the orthogonality properties of the a's, Eq. (15) becomes

$$-E\phi_l(\mathbf{r}_m)+\sum_k \phi_l(\mathbf{r}_k)A_l(\mathbf{r}_m-\mathbf{r}_k)+V(\mathbf{r}_m)\phi_l(\mathbf{r}_m)=0. \tag{16}$$

The above procedure amounts to expanding $V(\mathbf{r})$ in a Taylor series around $\mathbf{r}=\mathbf{r}_m$ and neglecting all terms in the expansion except the first. But Eq. (16) represents the Slater difference equations corresponding to the lth permitted band. There is a set of such difference equations corresponding to each permitted band, that is, corresponding to $l=1, 2, 3, \cdots$. But these sets are, respectively, independent equations in $\phi_1(\mathbf{r}_m)$, $\phi_2(\mathbf{r}_m)$, $\phi_3(\mathbf{r}_m)\cdots$. They would be satisfied by solutions of the type $\phi_2=\phi_3=\cdots=0$ and $\phi_1(\mathbf{r}_m)$ determined by Eq. (16) with $l=1$, or by $\phi_1=\phi_3=\cdots=0$ and $\phi_2(\mathbf{r}_m)$ determined by Eq. (16) with $l=2$, etc. Such solutions correspond to states which would exist if one permitted band were present without the others. In order to obtain a solution which is a good approximation when the energy lies close to one permitted band in one region of the crystal and close to a second permitted band in another, it is thus necessary to consider variation in the potential over a distance comparable with the range of the Wannier functions; that is, it is necessary to include more terms in the Taylor expansion of $V(\mathbf{r})$. (The formulation of Adams[4] leads to a similar conclusion.) The simplest case to consider is that for which the potential energy varies uniformly with distance, as it does when a uniform electric field is applied to the crystal.

III. ELECTRONIC STATES IN A CRYSTAL UNDER AN APPLIED ELECTRIC FIELD

A. General Theory

We now consider the difference equations, Eq. (15), for a one-dimensional crystal when the perturbing potential is $V(x)=eFx$ where F is the electric field strength. Thus, we consider solutions of the one-dimension Schrödinger equation,

$$-(\hbar^2/2m)d^2\psi/dx^2-\{E-V_P(x)-eFx\}\psi=0. \tag{17}$$

The periodic potential and the energy bands under a strong perturbing electric field are sketched in Fig. 1. As indicated there, we will restrict our attention to a region of the crystal such that the energy lies close to the first permitted band in one part of the region and close to the second permitted band in another. In this region, a good approximate wave function will be

$$\psi=\sum_k\{\phi_1(x_k)a_1(x-x_k)+\phi_2(x_k)a_2(x-x_k)\}, \tag{18}$$

which is just the one-dimensional analog of Eq. (10), with contributions from bands other than the first or second neglected. In evaluating the integrals in the difference equations which are the one-dimensional analogs of Eq. (15), it is convenient to use the Taylor expansion $V(x)=eFx_m+eF(x-x_m)$. We have then to evaluate integrals of the type

$$B_{ln}(x_m-x_k)=\int a_l^*(x-x_m)(x-x_m)a_n(x-x_k)dx. \tag{19}$$

These integrals can possess useful symmetry properties. If the periodic potential is symmetric about the cell centers, it can be shown that by proper choice of the phases of the ψ_0 of Eq. (2), the Wannier functions $a(x-x_k)$ can be made real and either symmetric or antisymmetric around $x=x_k$. (This is discussed in detail in the appendix.) It is then easily deduced that

$$B_{nn}(x_i)=B_{nn}(-x_i),\quad B_{ln}(x_i)=B_{nl}(-x_i), \tag{20}$$

$$B_{nn}(0)=0. \tag{21}$$

Moreover, when $a_l(x-x_k)$ and $a_n(x-x_k)$ have opposite symmetries around $x=x_k$, it can be shown that

$$B_{nl}(x_i)=B_{nl}(-x_i). \tag{22}$$

The difference equations for the ϕ_1 and ϕ_2 which correspond, respectively, to Eq. (15) with $l=1$ and $l=2$ (with contributions from permitted bands other than the first and second neglected) then become

$$-E\phi_1(x_m)+eFx_m\phi_1(x_m)+\sum_s A_1(x_s)\phi_1(x_m-x_s) +eF\sum_s B_{11}(x_s)\phi_1(x_m-x_s) +eF\sum_s B_{12}(x_s)\phi_2(x_m-x_s)=0, \quad (23)$$

$$-E\phi_2(x_m)+eFx_m\phi_2(x_m)+\sum_s A_2(x_s)\phi_2(x_m-x_s) +eF\sum_s B_{22}(x_s)\phi_2(x_m-x_s) +eF\sum_s B_{12}(x_s)\phi_1(x_m-x_s)=0. \quad (24)$$

In the sums over k which appear in Eq. (15), k has been set equal to $m-s$, and the sums taken over s. In order to obtain specific expressions for the A's and for the Wannier functions, a particular crystal model must be considered. The difference equations, Eqs. (23) and (24), will now be examined using the so-called narrow band approximation.

B. Unperturbed Wave Functions and Wannier Functions

Katsura, Hatta, and Morita[5] have discussed solutions of the Schrödinger equation, Eq. (17), and have used the narrow band approximation to show that, in this approximation, there is no distortion of the energy bands when a uniform field is applied to the crystal. These authors had not read Slater's paper at the time their work was done. Their method consists of expressing the ψ of Eq. (17) as a sum of atomic orbitals, multiplied by coefficients. Difference equations are then obtained for these coefficients. (The method is similar to but less general than that of Slater. After completing their work, Katsura, Hatta, and Morita[6] became aware that their calculations could be improved by using an expansion in terms of Wannier functions rather than atomic orbitals.) They considered, however, only a range of x such that E lies always close to a particular permitted band; thus interaction between the bands was not discussed and only one set of difference equations was obtained.

In the narrow band approximation,[7] it is assumed that the crystal atoms are far apart and the solution of the unperturbed periodic wave equation,

$$-(\hbar^2/2m)d^2\psi/dx^2-\{E-V_P(x)\}\psi=0, \quad (25)$$

is written as

$$\psi_0(p;x)=N^{-\frac{1}{2}}c(p)\sum_n \exp[(i/\hbar)px_n]u(x-x_n). \quad (26)$$

The u's are wave functions characteristic of the atoms before they are brought together to form the crystal, and are solutions of

$$-\frac{\hbar^2}{2m}\frac{d^2u(x-x_n)}{dx^2}-\{E_0-U(x-x_n)\}u(x-x_n)=0, \quad (27)$$

where $U(x-x_n)$ is the potential associated with the isolated atom. The constant $c(p)$ is determined by the normalization condition

$$\int\psi_0^*(p;x)\psi_0(p;x)dx=1.$$

Assuming that

$$\begin{aligned}\int u^*(x-x_m)u(x-x_n)dx&=1 \quad \text{for} \quad m=n,\\ &=\delta \quad \text{for} \quad m=n\pm1, \quad (28)\\ &=0 \quad \text{otherwise,}\end{aligned}$$

it easily follows that

$$c(p)=e^{i\theta}[1+2\delta\cos(pa/\hbar)]^{-\frac{1}{2}}, \quad (29)$$

where $e^{i\theta}$ is an arbitrary phase factor.

The energy E as a function of the effective momentum p is then given by

$$E(p)=\int\psi_0^*(p;x)\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_P(x)\right\}\psi_0(p;x)dx.$$

Using Eqs. (27) and (28) and letting

$$\begin{aligned}\int u^*(x-x_m)\{V_P(x)-U(x-x_n)\}u(x-x_n)dx\\ &=-\alpha \quad \text{for} \quad m=n,\\ &=-\gamma_0 \quad \text{for} \quad m=n\pm1, \quad (30)\\ &=0 \quad \text{otherwise,}\end{aligned}$$

it is easily shown that

$$E(p)=\frac{E_0-\alpha+2(\delta E_0-\gamma_0)\cos(pa/\hbar)}{1+2\delta\cos(pa/\hbar)}.$$

Assuming δ is small, we have

$$E(p)\cong E_0-\alpha-2\gamma\cos(pa/\hbar), \quad (31)$$

where $\gamma=\gamma_0-\alpha\delta$. Equation (31) defines a narrow permitted band of width $4|\gamma|$. If $u(x-x_n)$ is a function symmetric around $x=x_n$, $\gamma>0$; if antisymmetric, $\gamma<0$.

The Wannier functions corresponding to such a permitted band are given by the one-dimensional analog of Eq. (2), the sum being taken over values of $p=sh/Na$, $s=0, \pm1, \pm2, \cdots\pm N/2$. Inserting Eq. (26) into Eq. (2) with $p=sh/Na$, using Eq. (29), $x_n=na$,

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[5] Katsura, Hatta, and Morita, Sci. Repts. Tôhuku Imp. Univ., Series I, Vol. XXXIV, No. 1, 19 (1950).

[6] Katsura, Hatta, and Morita, private communication.

[7] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 303–307.

$x_k=ka$, and $\hbar=h/2\pi$, we obtain

$$a(x-x_k)=\sum_n b_{n-k}u(x-x_n), \tag{32}$$

where

$$b_{n-k}=\frac{1}{N}\sum_s \frac{\exp[2\pi i(s/N)(n-k)]}{[1+2\delta\cos(2\pi s/N)]^{\frac{1}{2}}}.$$

In the expression for $c(p)$, θ has been set equal to zero; it will be shown that when this is done, $a(x-x_k)$ has the desired localization around $x=x_k$. The sum over s can be replaced by an integral. Letting $y=2\pi s/N$,

$$b_{n-k}\cong\frac{1}{\pi}\int_0^\pi \frac{\cos(n-k)y}{[1+2\delta\cos y]^{\frac{1}{2}}}dy.$$

This integral can be expressed in terms of the hypergeometric function

$$F=F\left(\tfrac{1}{2};n-k+\tfrac{1}{2};n-k+1;\frac{4\delta^2}{[1+(1-4\delta^2)^{\frac{1}{2}}]^2}\right);$$

it can be shown that

$$b_{n-k}=(-1)^{n-k}\frac{(2n-2k-1)!!}{(2n-2k)!!}$$
$$\times\left\{\frac{2}{1+(1-4\delta^2)^{\frac{1}{2}}}\right\}^{\frac{1}{2}}\left\{\frac{2\delta}{1+(1-4\delta^2)^{\frac{1}{2}}}\right\}^{n-k}F, \tag{33}$$

where $2m!!=(2m)(2m-2)(2m-4)\cdots 2$. The hypergeometric function is rather insensitive to changes in n and, for small values of δ, b_{n-k} decreases with $n-k$ essentially as δ^{n-k}. Thus, in Eq. (32), the term involving $u(x-x_k)$ is the most important; the other $u(x-x_n)$ of the sum are multiplied by coefficients which are smaller the greater the distance of the nth atom from the kth. Thus $a(x-x_k)$ has the desired localization around the kth atom.

C. Solution of the Difference Equations

Consider now a crystal of the type described in Part B, under an applied uniform electric field. Let the first and second permitted bands be characterized by equations of the form of Eq. (31):

$$\begin{aligned}E_1(p)&=E_{01}-\alpha_1-2\gamma_1\cos(pa/\hbar),\\ E_2(p)&=E_{02}-\alpha_2+2\gamma_2\cos(pa/\hbar).\end{aligned} \tag{34}$$

The unperturbed wave functions $\psi_{01}(p;x)$ corresponding to the first permitted band have the form of Eq. (26), with orbitals $u_1(x-x_n)$ symmetric about $x=x_n$; the unperturbed wave functions $\psi_{02}(p;x)$ are similarly constructed from orbitals $u_2(x-x_n)$ which are antisymmetric about $x=x_n$. (This accounts for the opposite signs of the third terms of $E_1(p)$ and $E_2(p)$ where both γ_1 and γ_2 are positive.) The Wannier functions $a_1(x-x_k)$ and $a_2(x-x_k)$ have the form of Eq. (32). The solution of the Schrödinger equation, Eq. (17), is given by Eq. (18) with the $\phi_1(x_k)$ and $\phi_2(x_k)$ determined by the difference equations, Eqs. (23) and (24). The A's of the difference equations satisfy equations which are the one-dimensional analogs of Eqs. (7) and (8). Comparison of Eq. (34) with Eq. (8) indicates that

$$\begin{aligned}A_1(0)&=E_{01}-\alpha_1, & A_1(a)&=A_1(-a)=-\gamma_1,\\ A_2(0)&=E_{02}-\alpha_2, & A_2(a)&=A_2(-a)=\gamma_2,\end{aligned} \tag{35}$$

and that all the other A's are zero. In dealing with the coefficients B in this approximation, integrals involving overlap between Wannier functions associated with atoms further apart than nearest neighbors will be neglected. We thus include terms involving $B(0)$ and $B(a)$ and neglect all other B's. Then, using Eqs. (21) and (35) and setting $x_m=ma$, the difference equations, Eqs. (23) and (24) become

$$\begin{aligned}&\{-E+eFma+E_{01}-\alpha_1\}\phi_1(x_m)\\ &\quad+\{-\gamma_1+eFB_{11}(a)\}\{\phi_1(x_m-a)+\phi_1(x_m+a)\}\\ &\quad+eFB_{12}(0)\phi_2(x_m)+eFB_{12}(a)\\ &\qquad\times\{\phi_2(x_m-a)+\phi_2(x_m+a)\}=0;\end{aligned} \tag{36}$$

$$\begin{aligned}&\{-E+eFma+E_{02}-\alpha_2\}\phi_2(x_m)\\ &\quad+\{\gamma_2+eFB_{22}(a)\}\{\phi_2(x_m-a)+\phi_2(x_m+a)\}\\ &\quad+eFB_{12}(0)\phi_1(x_m)+eFB_{12}(a)\\ &\qquad\times\{\phi_1(x_m-a)+\phi_1(x_m+a)\}=0.\end{aligned} \tag{37}$$

Interaction between the bands is described by the terms containing the B_{12}. To obtain zero-order approximations to the solutions of Eqs. (36) and (37), we consider these equations with the $B_{12}=0$. For a particular value $E=E^0$ of the energy, they can be written in the form

$$\begin{aligned}\phi_1{}^0(x_m-a)+\phi_1{}^0(x_m+a)&=2\left(\frac{eFa}{\gamma_1-eFB_{11}(a)}\right)\\ &\quad\times\left(m-\frac{E^0-E_{01}+\alpha_1}{eFa}\right)\phi_1{}^0(x_m);\end{aligned} \tag{38}$$

$$\begin{aligned}\phi_2{}^0(x_m-a)+\phi_2{}^0(x_m+a)&=-2\left(\frac{eFa}{\gamma_2+eFB_{22}(a)}\right)\\ &\quad\times\left(m-\frac{E^0-E_{02}+\alpha_2}{eFa}\right)\phi_2{}^0(x_m).\end{aligned} \tag{39}$$

These equations are independent equations in $\phi_1{}^0$, and $\phi_2{}^0$ and describe energy states which would exist if one band were present without the other. Each equation is thus of the type obtained by Katsura, Hatta, and Morita, except for γ's defined in a slightly different way and terms in B_{11} and B_{22}, which appear because a better approximation has been used here. They have recognized that such equations have the form of the recursion relations,

$$Z_{m-1}(q)+Z_{m+1}(q)=(2m/q)Z_m(q), \tag{40}$$

of the cylinder functions, $Z_m(q)$. Now $Z_m(q)$ can be written as $CJ_m(q)+DN_m(q)$. Since the $\phi(x_m)$ must approach zero as $|m|\rightarrow\infty$ and since $N_m(q)\rightarrow\infty$ as $|m|\rightarrow\infty$, D must be set equal to zero. Comparison of Eqs. (38) and (39) with Eq. (40) indicates that

$$\phi_1{}^0(x_m)=C_1J_{m+l_1}(-q_1),\quad \phi_2{}^0(x_m)=C_2J_{m+l_2}(q_2), \tag{41}$$

where

$$l_1=\frac{(E^0-E_{01}+\alpha_1)}{|eF|a},\qquad l_2=\frac{(E^0-E_{02}+\alpha_2)}{|eF|a}, \tag{42}$$

$$q_1=\frac{2(\gamma_1-eFB_{11}(a))}{|eF|a},\qquad q_2=\frac{2(\gamma_2+eFB_{22}(a))}{|eF|a}, \tag{43}$$

and where C_1 and C_2 are constants. It has been assumed that the field is applied in the negative x direction. Katsura, Hatta, and Morita have also pointed out that a Bessel function J_{m+l} will not be well behaved as $m\rightarrow\pm\infty$ unless it is of integral order; this condition quantizes the energy.

It is clear that a value of E^0 which corresponds to an integral value of l_1 may not correspond to an integral value of l_2. For such a case, C_2 would have to be set equal to zero and the zero-order solutions would be $\phi_1{}^0(x_m)=C_1J_{m+l_1}(-q_1)$, $\phi_2{}^0(x_m)=0$. Similarly, there could be energy states such that l_2 is integral and l_1 nonintegral, corresponding to solutions of the type $\phi_1{}^0(x_m)=0$, $\phi_2{}^0(x_m)=C_2J_{m+l_2}(q_2)$. On the other hand, for particular values of the field strength F, energy eigenvalues can be such as to make l_1 and l_2 simultaneously integral. This is the degenerate case and the one which will be discussed in detail here. From Eq. (42) it follows that

$$l_2=l_1-n,$$

where

$$n=(E_{02}-\alpha_2-E_{01}+\alpha_1)/|eF|a. \tag{44}$$

Thus, the condition for degeneracy is that n be an integer. In such a case, neither C_1 nor C_2 need be zero, and the zero-order wave function may be written in the form

$$\psi^0=\sum_m\{C_1J_{m+l_1}(-q_1)a_1(x-x_m) +C_2J_{m+l_2}(q_2)a_2(x-x_m)\}. \tag{45}$$

To the approximation considered above, C_1 and C_2 are undetermined; they can be fixed only by considering interaction between the bands—that is, by including the B_{12}'s in the difference equations. Now, provided that the B_{12}'s are small, we can expect Eqs. (36) and (37) to have solutions for eigenvalues E^0+E^1 where E^1 is small and such that the corresponding $\phi_1(x_m)$ and $\phi_2(x_m)$ can be written

$$\phi_1(x_m)=C_1J_{m+l_1}(-q_1)+f_m,$$
$$\phi_2(x_m)=C_2J_{m+l_2}(q_2)+g_m, \tag{46}$$

where f_m and g_m are small. Inserting these expressions for ϕ_1 and ϕ_2 into Eqs. (36) and (37), and recalling that the J's satisfy Eqs. (38) and (39), we obtain

$$\begin{aligned}-E^1J_{m+l_1}(-q_1)&+\{-E^0+eFma+E_{01}-\alpha_1\}f_m\\ &+\{-\gamma_1+eFB_{11}(a)\}f_{m-1}+\{-\gamma_1+eFB_{11}(a)\}f_{m+1}\\ &+eFB_{12}(0)C_2J_{m+l_2}(q_2)+eFB_{12}(0)g_m\\ &+eFB_{12}(a)C_2\{J_{m+l_2-1}(q_2)+J_{m+l_2+1}(q_2)\}\\ &+eFB_{12}(a)\{g_{m-1}+g_{m+1}\}=0.\end{aligned} \tag{47}$$

$$\begin{aligned}-E^1C_2J_{m+l_2}(q_2)&+\{-E^0+eFma+E_{02}-\alpha_2\}g_m\\ &+\{\gamma_2+eFB_{22}(a)\}g_{m-1}+\{\gamma_2+eFB_{22}(a)\}g_{m+1}\\ &+eFB_{12}(0)C_1J_{m+l_1}(-q_1)+eFB_{12}(0)f_m\\ &+eFB_{12}(a)C_1\{J_{m+l_1-1}(-q_1)+J_{m+l_1+1}(-q_1)\}\\ &+eFB_{12}(a)\{f_{m-1}+f_{m+1}\}=0.\end{aligned} \tag{48}$$

Second-order terms of the form E^1f_m and E^1g_m have been neglected. We now multiply Eq. (47) by $J_{m+l_1}(-q_1)$ and sum over all values of m. The first term can be simplified, using[8]

$$\sum_n J_n{}^2(x)=1 \tag{49}$$

for all values of x. The second, third, and fourth terms become

$$\begin{aligned}\sum_m f_m\{-E^0+eFma+E_{01}-\alpha_1\}J_{m+l_1}(-q_1)&\\ +\{-\gamma_1+eFB_{11}(a)\}\sum_m f_{m-1}J_{m+l_1}(-q_1)&\\ +\{-\gamma_1+eFB_{11}(a)\}\sum_m f_{m+1}J_{m+l_1}(-q_1)&.\end{aligned}$$

By replacing m by $m+1$ in the second sum and m by $m-1$ in the third, these terms combine to yield

$$\begin{aligned}\sum_m f_m[\{-E^0+eFma+E_{01}-\alpha_1\}J_{m+l_1}(-q_1)&\\ +\{-\gamma_1+eFB_{11}(a)\}&\\ \times\{J_{m+l_1+1}(-q_1)+J_{m+l_1-1}(-q_1)\}]&=0,\end{aligned}$$

since $J_{m+l_1}(-q_1)$ satisfies Eq. (38).

Terms involving products of Bessel functions can be simplified using the addition theorem[9]

$$J_n(y+z)=\sum_m J_m(y)J_{n-m}(z),$$

and the relation of Eq. (44), $l_2=l_1-n$. Equation (47) finally becomes

$$\begin{aligned}-E^1C_1&+(-1)^neFC_2[B_{12}(0)J_n(q_1+q_2)\\ &-B_{12}(a)J_{n-1}(q_1+q_2)-B_{12}(a)J_{n+1}(q_1+q_2)]\\ &+eFB_{12}(0)\sum_m J_{m+l_1}(-q_1)g_m\\ &+eFB_{12}(a)\sum_m J_{m+l_1}(-q_1)\{g_{m-1}+g_{m+1}\}=0.\end{aligned} \tag{50}$$

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[8] G. N. Watson, *Bessel Functions* (Cambridge University Press. Cambridge, 1944), p. 31.

[9] See reference 8, p. 30.

Similarly by multiplying Eq. (48) by $J_{m+l_2}(q_2)$, summing over all m and proceeding as above, we obtain

$$-E^1C_2+(-1)^n eFC_1[B_{12}(0)J_n(q_1+q_2)$$
$$-B_{12}(a)J_{n-1}(q_1+q_2)-B_{12}(a)J_{n+1}(q_1+q_2)]$$
$$+eFB_{12}(0)\textstyle\sum_m J_{m+l_2}(q_2)f_m$$
$$+eFB_{12}(a)\textstyle\sum_m J_{m+l_2}(q_2)\{f_{m-1}+f_{m+1}\}=0. \quad (51)$$

Approximate values for C_1, C_2, and E^1 can be obtained by neglecting the terms containing f and g in Eqs. (50) and (51), which then reduce to

$$-E^1C_1+XC_2=0, \quad (52)$$

$$-E^1C_2+XC_1=0, \quad (53)$$

where

$$X=(-1)^n eF[B_{12}(0)J_n(q_1+q_2)$$
$$-B_{12}(a)\{J_{n-1}(q_1+q_2)+J_{n+1}(q_1+q_2)\}]. \quad (54)$$

Consistency of Eqs. (52) and (53) requires that

$$E^1=\pm|X|\,; \quad C_1/C_2=\pm 1.$$

Since the f_m and g_m have been neglected in this approximation, the wave functions have the form of Eq. (45)

$$\psi=C\textstyle\sum_m\{J_{m+l_1}(-q_1)a_1(x-x_m)$$
$$\pm J_{m+l_2}(q_2)a_2(x-x_m)\}. \quad (55)$$

The constant C is chosen so as to normalize ψ. Using Eq. (49) and the orthogonality properties of the a's, it easily follows that $C=1/\sqrt{2}$. Thus the wave functions, corresponding to the energies $E=E^0\pm|X|$ are

$$\psi_{\mathrm{I}}=(1/\sqrt{2})\textstyle\sum_m\{J_{m+l_1}(-q_1)a_1(x-x_m)$$
$$+J_{m+l_2}(q_2)a_2(x-x_m)\}, \quad (56)$$

$$\psi_{\mathrm{II}}=(1/\sqrt{2})\textstyle\sum_m\{J_{m+l_1}(-q_1)a_1(x-x_m)$$
$$-J_{m+l_2}(q_2)a_2(x-x_m)\}. \quad (57)$$

The coefficients $J_{m+l}(q)$ are oscillatory for values of m such that $|m+l|<q$ and behave exponentially elsewhere. Thus ψ_{I} and ψ_{II} are oscillatory within the first permitted band (where m assumes values such that $|m+l_1|<q_1$) and within the second permitted band (where m is such that $|m+l_2|<q_2$).

D. Probability of Penetration of the Forbidden Gap

Consider now a solution of the time dependent Schrödinger equation given by

$$\psi=\psi_{\mathrm{I}}\exp[-iE_{\mathrm{I}}t/\hbar]+\psi_{\mathrm{II}}\exp[-iE_{\mathrm{II}}t/\hbar].$$

From Eqs. (56) and (57), it is seen that at $t=0$, $\psi=\psi_{\mathrm{I}}+\psi_{\mathrm{II}}$ represents a wave function corresponding to an electron localized near the first permitted band. It is easily seen, however, that in a time t such that $(E_{\mathrm{II}}-E_{\mathrm{I}})t=h/2$, $\psi=\psi_{\mathrm{I}}-\psi_{\mathrm{II}}$ corresponding to an electron localized near the second permitted band. Thus the probability per unit time Γ for an electron to cross the forbidden energy band is given by

$$\Gamma=2(E_{\mathrm{II}}-E_{\mathrm{I}})/h=4|X|/h. \quad (58)$$

(The argument used here is similar to that used in the so-called double minimum problem of quantum mechanics[10] to obtain the probability per unit time for an electron to pass from one potential well to another.)

We now consider the expression of Eq. (54) for $|X|$. Equations (44) and (34) indicate that n is the ratio of the energy difference between the centers of the permitted bands of the unperturbed crystal to the change of the perturbing potential over a single cell of the crystal; thus for physically interesting cases, n is very large. Equation (43) indicates that q_1+q_2 is of the order of the ratio of the sum of the half-widths of the first and second permitted bands to the change in the perturbing potential over a single cell of the crystal. Since we consider here the case of narrow permitted bands and wide forbidden bands, it follows that the order of the Bessel functions which appear in Eq. (54) is greater than the argument; we may therefore use the asymptotic expression[11]

$$J_n(n\,\mathrm{sech}x)\sim e^{-n(x-\tanh x)}/[2\pi n\tanh x]^{\frac{1}{2}}. \quad (59)$$

From Eqs. (54), (58), and (59) we then obtain

$$\Gamma\sim\frac{eFa}{h}\left(\frac{eFa}{\epsilon}\right)^{\frac{1}{2}}R\exp\left\{-\frac{\epsilon}{eFa}\ln\left[\frac{2\epsilon}{\tau}-\left(1-\frac{\tau^2}{\epsilon^2}\right)^{\frac{1}{2}}\right]\right\}, \quad (60)$$

where

$$R\sim\frac{2^{\frac{3}{2}}}{\pi^{\frac{1}{2}}(1-\tau^2/\epsilon^2)^{\frac{1}{2}}}\left[\frac{B_{12}(0)}{a}-\frac{B_{12}(a)}{a}\right.$$
$$\times\left\{\exp\left[-\ln\frac{2\epsilon}{\tau}+\left(1-\frac{\tau^2}{\epsilon^2}\right)^{\frac{1}{2}}\right]\right.$$
$$\left.\left.+\exp\left[\ln\frac{2\epsilon}{\tau}-\left(1-\frac{\tau^2}{\epsilon^2}\right)^{\frac{1}{2}}\right]\right\}\right],$$

$$\epsilon=E_{02}-\alpha_2-E_{01}+\alpha_1,$$

$$\tau=2[\gamma_1-eFB_{11}(a)+\gamma_2+eFB_{22}(a)].$$

Since we consider narrow permitted bands, ϵ is essentially the width of the forbidden energy gap. The quantity τ is essentially the average width of the permitted bands.

It is of interest to compare Eq. (60) for Γ with the expression obtained by Zener[12] by another method and

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[10] S. Dushman, *Elements of Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1938), p. 214.

[11] See reference 8, p. 243.

[12] C. Zener, Proc. Roy. Soc. (London) **145**, 523 (1934).

using the approximation of nearly free electrons (narrow forbidden bands). Zener's expression is

$$\Gamma=\frac{eFa}{h}\exp\left[-\frac{\epsilon}{eFa}\left\{\frac{\pi^2ma^2\epsilon}{h^2}\right\}\right], \tag{61}$$

where m is the electron mass. In both expressions for Γ, the important factor is the exponential and in particular the quantity ϵ/eFa of the exponent, which is just the number of cells traversed as the forbidden band is crossed. For ordinary fields, this is very large and Γ is negligibly small. In Eq. (61), $\pi^2ma^2\epsilon/h^2$ is essentially $\sim\epsilon/\tau$, the ratio of the forbidden band width to the permitted band width, and Eq. (61) is valid when this ratio $\ll 1$. This is to be compared with $[\ln(2\epsilon/\tau)-(1-\tau^2/\epsilon^2)^{\frac{1}{2}}]$ of Eq. (60), which is valid when $\epsilon/\tau\gg 1$. Thus, if applied to a practical intermediate case, Eq. (60) will predict a smaller field for which penetration of the barrier becomes important than will Eq. (61).

E. Comparison with Experiment

The considerations of the preceding sections imply that for sufficiently high fields applied to a crystal, one should be able to observe a sudden increase in current, associated with the tunneling of electrons from the filled band to the conduction band. This has been observed in experiments carried out at Bell Laboratories by McAfee, Ryder, Shockley, and Sparks[13] on $N-P$ rectifiers formed in single crystals of germanium. They find that for fields $\sim 2\times 10^5$ volts/cm, the current in the back direction of such a rectifier increases suddenly and rapidly. They call this increase in current the Zener current and, assuming the field in the barrier to be uniform, give a theoretical expression for the current density I, which can be written

$$I=(nze/a^2)\Gamma, \tag{62}$$

where z is the number of electrons per cell and n the number of cells in the barrier. Using an expression for Γ derived by Shockley (the method of derivation is not indicated), which has the form $\Gamma=(eFa/h)e^{-\beta/F}$, where $\beta=(\pi^2/eh)(m/2)^{\frac{1}{2}}\epsilon^{\frac{3}{2}}$, they write I as

$$I=Ve^{\alpha-\beta/F}, \tag{63}$$

where $\alpha=\ln(e^2z/a^2h)$ and V is the applied voltage. Using Eq. (63) with appropriate constants for germanium, they find that the predicted slope of the $\ln I-\ln V$ curve is in good agreement with experiment but that the predicted field at which current should become appreciable is too high.

If one now uses Eq. (60) for Γ, one can write I in the form of Eq. (63) with

$$\alpha=\ln(e^2z/a^2h)+\ln R(eFa/\epsilon)^{\frac{1}{2}},$$
$$\beta=(\epsilon/ea)[\ln(2\epsilon/\tau)-(1-\tau^2/\epsilon^2)^{\frac{1}{2}}].$$

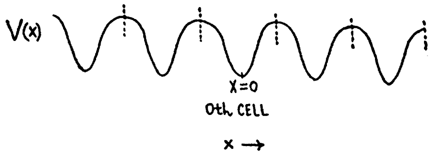

FIG. 2. Periodic potential in a one-dimensional lattice.

In comparing this new expression with the experimental current-voltage characteristic, α could be considered as essentially constant since the observed values of the field varied little. Values of α and β obtained from the experimental curve were found to correspond to $\ln R=0.3$ and $\epsilon/\tau=2.3$. The fairly large value of ϵ/τ is consistent with the assumptions made in deriving Eq. (60) but not with the known band structure of germanium.

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APPENDIX

The Wannier functions $a(\mathbf{r}-\mathbf{r}_k)$ are defined by Eq. (2); it should be emphasized, however, that in Eq. (2), each solution $\psi_0(\mathbf{p};\mathbf{r})$ of the unperturbed problem contains an arbitrary phase factor $e^{if(\mathbf{p})}$. It will be shown here that the $a(\mathbf{r}-\mathbf{r}_k)$ will have the desired localization about the kth atom of the crystal only if the $f(\mathbf{p})$ are appropriately chosen, a point not discussed by Wannier. It will also be shown that the Wannier functions can possess useful symmetry properties.

To obtain a more detailed knowledge of the Wannier functions they will be investigated here using a one-dimensional model originally used by Shockley[14] in discussing surface states, and later considered in more detail by James[15] in discussing solutions of the periodic and perturbed periodic wave equations.

Figure 2 shows the electronic potential energy as a function of position in the crystal. The potential is symmetric about the center of each cell. The crystal wave functions are expressed in terms of functions $g(E;x)$ and $u(E;x)$ which are solutions of the Schrödinger equation for the single potential well associated with the zeroth cell. $g(E;x)$ and $u(E;x)$ are respectively symmetric and antisymmetric about the cell center $x=0$. Moreover,

$$g(E;0)=1;\ g'(E;0)=0;\ u(E;0)=0;\ u'(E;0)=1, \tag{64}$$

where the primes signify derivatives with respect to x. Within the pass band, corresponding to an energy E, there are two independent crystal wave functions—complex conjugates of each other. In the nth cell, these are

$$\psi_n=\exp\pm(ipna/\hbar)\{\alpha(E)g(E;x-x_n)+\beta(E)u(E;x-x_n)\}, \tag{65}$$

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[13] McAfee, Ryder, Shockley, and Sparks, Phys. Rev. **83**, 650 (1951).

[14] W. Shockley, Phys. Rev. **56**, 317 (1939).

[15] H. M. James, Phys. Rev. **76**, 1602 (1949).

where

$$\frac{\beta(E)}{\alpha(E)} = \mp i \frac{g_0(E)}{u_0(E)} \left| \frac{g_0'(E)u_0(E)}{g_0(E)u_0'(E)} \right|^{\frac{1}{2}} = \mp i\delta(E). \quad (66)$$

The subscript 0 indicates the value of the function at the left edge of the 0th cell. $\alpha(E)$ is determined, except for a phase factor, by normalizing the wave function. For an energy corresponding to a band edge, one of the quantities g_0, u_0, g_0', u_0' vanishes and there is only one well-behaved wave function. Below are listed the various possibilities for band edge wave functions (in the nth cell).

1. If

$$g_0(E_e) = 0, \quad \psi_n(E_e; x) = c(E_e)(-1)^n g(E_e; x - x_n). \quad (67)$$

2. If

$$g_0'(E_e) = 0, \quad \psi_n(E_e; x) = c(E_e) g(E_e; x - x_n). \quad (68)$$

3. If

$$u_0(E_e) = 0, \quad \psi_n(E_e; x) = c(E_e) u(E_e; x - x_n). \quad (69)$$

4. If

$$u_0'(E_e) = 0, \quad \psi_n(E_e; x) = c(E_e)(-1)^n u(E_e; x - x_n). \quad (70)$$

Various bands will now be classified according to their upper and lower edges, and Wannier functions corresponding to these bands will be constructed.

Case 1:—Consider a band with edges E_{e1} and E_{e2} corresponding to $g_0'(E_{e1}) = 0$ and $g_0(E_{e2}) = 0$. The Wannier functions localized around the zeroth cell are then given in the nth cell by [Eqs. (2), (65), (66), (67), (68)]

$$a(x) = N^{-\frac{1}{2}} \sum_{p=0}^{\pi\hbar/a} \{2\cos(pna/\hbar)\alpha(E) g(E; x - x_n)$$
$$+ 2\sin(pna/\hbar)\alpha(E)\delta(E)u(E; x - x_n)\}, \quad (71)$$

where $\alpha(E_{e1}) = \frac{1}{2}c(E_{e1})$ and $\alpha(E_{e2}) = \frac{1}{2}c(E_{e2})$. (Since E is a function of p the quantities α, δ, g, and u are all functions of p.) It will now be shown that by choosing $\alpha(E)$ real and positive, the function $a(x)$ is made real and localized as desired around the zeroth cell of the crystal. In order to carry out the above summation it is necessary to know the specific potential distribution within the zeroth cell, since this determines the g's and u's. One can see qualitatively how the localization comes about, however, by examining $a(x)$ at the center of the zeroth cell, first cell $\cdots$ nth cell. At the center ($x = 0$) of the zeroth cell $a(x)$ is given by Eq. (71) with $n = 0$. Thus

$$a(0) = N^{-\frac{1}{2}} \textstyle\sum_p \alpha(E) g(E; 0) = \sum_p \alpha(E),$$

(since $g(E, 0) = 1$), each term of the sum being positive. On the other hand (since $u(E; 0) = 0$),

$$a(x_n) = N^{-\frac{1}{2}} \textstyle\sum_p \alpha(E) \cos(pna/\hbar).$$

Now $\alpha(E)$ is a smoothly and slowly varying function of E or p. [For the special case of a constant potential, $\alpha(E)$ is constant and equal to $(Na)^{-\frac{1}{2}}$.] Since $\cos(pna/\hbar)$ becomes more and more rapidly oscillatory as n increases, the terms of the sum change sign more and more rapidly and the magnitude of the sum decreases; thus $a(x)$ is attenuated with increasing $|n|$. To get an idea of the rate of attenuation, let us compare $\sum \alpha(E) \cos(pna/\hbar)$ when $n = 0$ and $n = N/2$. When $n = 0$, we obtain a sum of positive terms, which can be written $N\alpha(E)_{\text{Av}}$. We now recall that in the sum, $p = sh/Na$, where $s = 0, 1, 2, \cdots$. Thus, when $n = N/2$, the cosine term behaves as $(-1)^s$ and the series has a value of the order of magnitude of a single term of the series, which in turn is of the order of $\alpha(E)_{\text{Av}}$ or less. Thus, the ratio of the value of the sum in the $(N/2)$th cell to that in the zeroth cell is $\sim 1/\frac{1}{2}N$ at most; attenuation may actually be much more rapid.

It can easily be seen, using the symmetry properties of the g and u, that $a(x)$ is symmetric around $x = 0$.

Case 2:—Consider a band with edges E_{e3} and E_{e4} corresponding to $u_0'(E_{e3}) = 0$ and $u_0(E_{e4}) = 0$. The Wannier functions localized around the zeroth cell can then be written [Eqs. (2), (65), (69), (70)]

$$a(x) = N^{-\frac{1}{2}} \sum_{p=0}^{\pi\hbar/a} \left\{ 2\cos(pna/\hbar)\beta(E)u(E; x - x_n) \right.$$
$$\left. - 2\sin(pna/\hbar)\frac{\beta(E)}{\delta(E)} g(E; x - x_n) \right\}, \quad (72)$$

where $\beta(E_{e3}) = \frac{1}{2}c(E_{e3})$ and $\beta(E_{e4}) = \frac{1}{2}c(E_{e4})$. Since in this case the function is zero at the center of the zeroth cell, we obtain information about the function by considering its slope at the centers of the various cells. At the center of the zeroth cell, $a'(0)$ is the sum of $\beta(E)u'(E; 0)$ over the permitted band. Since $u'(E; 0) = 1$, each term of the sum will be positive if $\beta(E)$ is chosen positive. To obtain $a'(x_n)$, however, it is necessary to sum over products $\beta(E) \cos(pna/\hbar)$ (since $g'(E; 0) = 0$). Using arguments analogous to those applied to the discussion of $a(x)$ in case 1, it is seen that here $a'(x)$ is attenuated with increasing $|n|$.

It can easily be shown that the $a(x)$ of Eq. (72) is antisymmetric about $x = 0$.

Localized Wannier functions which are symmetric or antisymmetric around the cell centers can be similarly constructed for the other types of bands.