Contribution to the Theory of the Surface Electronic States in the One-Electron Approximation

JAROSLAV KOUTECKÝ

Institute of Physical Chemistry, Czechoslovakian Academy of Sciences, Prague, Czechoslovakia

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A formal treatment has been given of the surface states associated with a semi-infinite crystal. The treatment assumes that the surface states are produced by a potential which is a function only of the distance from the surface but is otherwise unspecified. A formal expansion is made in a complete set of Wannier orbitals, but the conclusions of the paper are based on the assumptions that (a) it is sufficient to use the orbitals of a single band, and (b) the tight-binding approximation is adequate for that band. Some theorems are given on the localization of Wannier orbitals, the localization of surface states, and the number of surface states for a given penetration of the surface potential.

PREVIOUS work on the theory of surface electronic states made use of drastically simplified models and methods. The method of studying the influence of defects in the periodicity of the crystal lattice on the states of electrons, as proposed independently by Lifshitz,[1] Koster and Slater,[2] and Baldock,[3] has made possible a considerably general formulation of the whole problem of surface states. This formulation is subject to only two conditions: (1) the applicability of the one-electron approximation; (2) the Hamiltonian of the electron in the crystal which is confined between two parallel planes can be written in the form

$$H = H_0 + V, \tag{1}$$

where H_0 is the Hamiltonian of the electron in an infinite ideal crystal and V the perturbation potential, which is a function only of the distance from one of these planes representing the surface of the crystal.

It is the primary aim of this paper to present a derivation of the fundamental equations of the state functions and energies of the electrons localized near the crystal surface that is free from arbitrary assumptions and ill-defined logical steps. Furthermore, the applicability of these equations will be shown by calculating a hitherto unsolved case which furnishes some information on the general character of surface states.

GENERAL RELATIONSHIPS

Let us start with an infinite ideal crystal, represented by a "cyclic" crystal, in which any state function is invariant with respect to an N-fold elementary translation in the lattice (Born-Kármán conditions). Let ψ_{ns} be the state function of the electron in the ideal crystal and E_{ns} the corresponding energy. Then let s be defined by the relationship

$$k = 2\pi s |g|/N, \tag{2}$$
$$(\varrho g) = 1,$$

where k is the component of the wave vector in the direction of the elementary translation g of the reciprocal lattice, which corresponds to the elementary translation ϱ of the crystal. ϱ has been chosen in such a manner as to be the only elementary translation in the lattice which is not parallel to a pair of parallel planes S_1, S_2, which in the considerations to follow shall confine the crystal. n contains all the remaining quantum numbers.

Let us define the one-dimensional Wannier functions

$$a_n(\mathbf{r} - m\varrho) = N^{-\frac{1}{2}} \sum_{s=0}^{N-1} e^{-2\pi i sm/N} \psi_{ns}(\mathbf{r}). \tag{3}$$

These functions are suitable for our purposes only on the condition that they are localized. We shall therefore prove the following theorem:

Let N be a very large number. There can then be found a number M such that, if $N > m > M$, then

$$\left| \frac{a_n(\mathbf{r}_1 - m\varrho)}{a_n(\mathbf{r}_1)} \right|^2 < \mu, \tag{4}$$

where $\mu > 0$ is an arbitrarily small number, and the vector $\mathbf{r}_1$ is confined to the elementary cell in which we have placed the coordinate origin.

If we introduce the variable t by the relation

$$t = 2\pi s/N \tag{5}$$

and replace the sum by the integral, we obtain

$$N^{\frac{1}{2}} \psi_n(t, \mathbf{r}_1) = \sum_{m=0}^{N} e^{itm} a_n(\mathbf{r}_1 - m\varrho),$$
$$a_n(\mathbf{r}_1 - m\varrho) = \frac{1}{2\pi} \int_0^{2\pi} e^{-itm} N^{\frac{1}{2}} \psi_n(t, \mathbf{r}_1) dt. \tag{6}$$

Since the integral

$$\int_0^{2\pi} N |\psi_n(t, \mathbf{r}_1)|^2 dt \tag{7}$$

[1] I. M. Lifshitz, Zhur. Eksptl. i Teoret. Fiz. 17, 1017 (1947); 17, 1076 (1947).
[2] G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954); 96, 1208 (1954).
[3] G. R. Baldock, Proc. Cambridge Phil. Soc. 48, 457 (1952).

is limited, all the conditions for

$$\lim_{m \to \infty} |a_n(\mathbf{r}_1 - m\boldsymbol{\varrho})|^2 = 0 \tag{8}$$

are fulfilled, as follows from the theory of the Fourier series. This establishes the localization of the Wannier functions.

If we now change the Hamiltonian of the electron in the sense of Eq. (1), then the state function of the electron, satisfying the characteristic equation

$$(H - W)\Xi = 0, \tag{9}$$

can be represented to any degree of accuracy by the following linear combination of Wannier functions:

$$\Xi = \sum_n \sum_{m=0}^{N-1} e_{nm} a_n(\mathbf{r} - m\boldsymbol{\varrho}). \tag{10}$$

Here the coefficients e_{nm} are given by the following system of equations[4]:

$$\sum_n \sum_{m=0}^{N-1} e_{nm}[\epsilon_{n, m-m'}\delta_{nn'} - W\delta_{nn'}\delta_{mm'} + V_{n'm'; nn}] = 0, \tag{11}$$

where

$$\epsilon_{nm} = N^{-1} \sum_{s=0}^{N-1} e^{-2\pi i sm/N} E_{ns} \tag{12}$$

and

$$V_{nm; n'm'} = \int \bar{a}_n(\mathbf{r} - m\boldsymbol{\varrho}) V a_{n'}(\mathbf{r} - m'\boldsymbol{\varrho}) d\tau. \tag{13}$$

For Wannier functions which belong to the various irreducible representations of the group of translations parallel to S_1, the last integral vanishes.

Proceeding now from the infinite crystal to the finite one, let us assume that

$$V(\mathbf{r}) = V' \gg \sum_{m \neq 0} |\epsilon_{nm}| \tag{14}$$

if

$$M_1 < (\mathbf{r}\boldsymbol{\varrho})/|\rho|^2 < M_2, \tag{15}$$

where V' is a constant. If we choose the difference $M_2 - M_1$ sufficiently large, there will certainly exist a number P such that with a suitably selected origin of coordinates the following relations can be written:

For $M - P < m < N$,

$$\begin{aligned} V_{nm; nm} &= V', \\ V_{nm; n'm'} &< \mu \quad \text{for} \quad m \neq m', \end{aligned} \tag{16}$$

where $P < (M_2 - M_1)$ and μ is an arbitrarily small number. If we assume the existence of a state, the energy W_1 of which is much smaller than the constant potential V',

$$V' \gg W_1, \tag{17}$$

[4] P. Feuer, Phys. Rev. 88, 92 (1952).

then for $N - P < m' \leq N$ it follows from (11) that

$$\sum_{n,m} e_{n'm}[\epsilon_{n'; m-m'} - (W_1 - V')\delta_{mm'}] = 0, \tag{18}$$

which gives

$$\left| \frac{e_{n'm'}}{e_{max}} \right| < (\sum_{m \neq m'} |\epsilon_{n'; m-m'}|)/|V' - W_1 + \epsilon_{n'0}|, \tag{19}$$

where

$$e_{max} = \max_{m \neq m'} (|e_{n'm}|). \tag{20}$$

The right side of Eq. (19), however, is a very small number according to the assumptions (14) and (17). The coefficients in the expansion (10) of the Wannier functions, localized in the region of a high constant potential, will therefore be very small for energies which are not too large. Thus, it is possible to write Eq. (10) with sufficient approximation in the form

$$\Xi = \sum_n \sum_{m=0}^{P} e_{nm} a_n(\mathbf{r} - m\boldsymbol{\varrho}). \tag{21}$$

A suitably chosen potential barrier evidently represents the situation of the electron in the finite crystal quite well. The region of constant high potential lies outside the crystal. Also the indices $m=0$ and $m=P$ belong in general to cells outside the crystal. In the usual approximation these cells have always been placed in the surface of the crystal, so that the expansion (21) with the aid of atomic functions (in the approximation of tight binding) involves only the atoms within the crystal. Since we are interested in a general theory of surface states, we shall not make use of this approximation.

Because of definition (21), we shall let the indices m and m' in Eqs. (11) run through all values from 0 to P. If we multiply these equations by $\exp(-2\pi i sm'/N)$ and if we sum by m', we obtain, assuming

$$|E_{n's} - W| \neq 0, \tag{22}$$

after a short rearrangement,

$$\sum_{m'=0}^{P} e_{n'm'} e^{-2\pi i sm'/N} = \left(\frac{1}{W - E_{n's}} \right) \sum_n \sum_{m=0}^{P} e_{nm}$$

$$\times [\sum_{m'=0}^{P} e^{-2\pi i sm'/N} V_{n'm'; nm}$$

$$- \sum_{m'=P+1}^{N-1} e^{-2\pi i sm'/N} \epsilon_{n'; m'-m} \delta_{nn'}]. \tag{23}$$

We multiply these equations by $\exp(2\pi i ps/N)$ and after a further rearrangement we obtain the final

formula for the coefficients in (21):

$$e_{n'p} = \sum_n \sum_{m=0}^{P} e_{nm}$$

$$\times \left[\sum_{m'=0}^{P} \phi_{n';\,p-m'} V_{n'm';\,nm} \right.$$

$$\left. - \sum_{m'=1}^{N-P-1} \phi_{n';\,p+m} \epsilon_{n';\,m'+m} \delta_{nn'} \right], \quad (24)$$

where

$$\phi_{n';\,u} = N^{-1} \sum_s \frac{e^{2\pi i u s/N}}{(W - E_{n's})}. \quad (25)$$

For sufficiently large P there exists a certain number K such that with $K < |m| < P$, there will be

$$|\epsilon_{nm}| < \mu. \quad (26)$$

Because of the localization of the Wannier functions and because of the fact that the perturbation potential V imposed by the limiting pair of parallel boundary planes S_1 and S_2 is negligible in the bulk of a sufficiently extensive crystal, there exist numbers Z and Z' such that

if $\{m > Z$ or $m' > Z\}$, then $|V_{nm;\,n'm'}| < \mu$;

and

if $\{m > Z'$ or $m' > Z'\}$, then $|V_{nP-m;\,n'P-m'}| < \mu$; $\quad$ (27)

$$0 < Z \ll \tfrac{1}{2}P, \quad 0 < Z' \ll \tfrac{1}{2}P.$$

Since for very large values of u the magnitude of $\phi_{n',u}$, as defined by Eq. (25), approaches zero, our problem for a large crystal can be divided into two subproblems: We obtain the surface states localized in the neighborhood of the plane S_1, and states localized in the neighborhood of plane S_2; this can easily be seen, by substituting the conditions (26) and (27) into Eqs. (21). For the states localized in the neighborhood of the plane S_1 which we place near the cells with the index $m = 0$, we obtain Eqs. (24) in the form

$$e_{n'p} = \sum_n \sum_{m=0}^{Z} \sum_{m'=0}^{Z} \phi_{n';\,p-m'} V_{n'm';\,nm} e_{nm}$$

$$- \sum_{m=0}^{K} \sum_{m'=1}^{K-m} \phi_{n';\,p+m'} \epsilon_{n';\,m'+m} e_{n'm}. \quad (28)$$

The energy W is given by the determinant

$$\left| \sum_{m'=0}^{Z} \phi_{n';\,p-m'} V_{n'm';\,nm} \right.$$

$$\left. - \delta_{nn'} \sum_{m'=1}^{K-m} \phi_{n';\,p+m'} \epsilon_{n';\,m'+m} - \delta_{nn'} \delta_{mm'} \right| = 0. \quad (29)$$

If we put $M = \max (Z,K)$, this determinant is of order M.

From this derivation it is evident that Eqs. (28) and (29) are of general validity for very large crystals; if the crystal is a foil it is necessary to start directly from Eq. (24) to determine the energy and state functions of the electrons in such a foil.

Finally we now proceed to show that the state functions described by the relations (28) are actually localized if only relation (23) is valid. From the properties of the functions $\phi_{n';u}$ it can be seen directly that $\lim |e_{n',p}| = 0$; we can, moreover, easily prove the localization in the sense of the validity of the inequality

$$R = \sum_n \sum_{m=0}^{M} |e_{nm}|^2 \Big/ \sum_n \sum_{m=0}^{P} |e_{nm}|^2 > \nu. \quad (30)$$

where ν is a finite number (see Chirgwin and Coulson[5]).

From (28) we obtain by successive use of the Schwarz inequality

$$\sum_{p=0}^{P} |e_{n'p}|^2 \leq \sum_{p=0}^{N} |e_{n'p}|^2$$

$$= \sum_s \Big| \sum_n \sum_{m=0}^{M} \sum_{m'=0}^{M} \frac{e^{-2\pi i s m'/N}}{(W - E_{n's})} V_{n'm';\,nm} e_{nm}$$

$$- \sum_{m=0}^{M} \sum_{m'=1}^{M-m} \frac{e^{2\pi i s m'/N}}{(W - E_{n's})} \epsilon_{n';\,m'+m} e_{n'm} \Big|^2$$

$$\leq \lambda^2 \Big[\sum_n \sum_{m=0}^{M} \sum_{m'=0}^{M} |V_{n'm';\,nm}|^2$$

$$+ \sum_{m=0}^{M} \sum_{m'=1}^{M} |\epsilon_{n';\,m'+m}|^2 \Big] \sum_n \sum_{m=0}^{M} |e_{nm}|^2,$$

where

$$\lambda = \min (|W - E_{n's}|). \quad (31)$$

The definition for e_{np} has been extended also for $p > P$, by defining, for $p > P$, these coefficients again by the relation (28).

Our theorem has thus been proved, since

$$R \geq \nu = \lambda^2 \Big[\sum_{nn'} \sum_{m=0}^{M} \sum_{m'=0}^{M} |V_{nm;\,n'm'}|^2$$

$$+ \sum_{n'} \sum_{m=0}^{M} \sum_{m'=1}^{M} |\epsilon_{n';\,m'+m}|^2 \Big]^{-1}.$$

APPROXIMATION OF TIGHT BINDING

As an illustration of the method elaborated in this paper, we shall discuss in detail the surface states for a case when it is possible to consider one energy band only and where the energy of the defectless infinite crystal

[5] B. H. Chirgwin and C. A. Coulson, Proc. Roy. Soc. (London) A201, 196 (1949).

is given by

$$E_{ns} = \epsilon_{n0} + 2\epsilon_1 \cos(2\pi i s/N). \tag{32}$$

This approximation corresponds to the approximation of tight binding. If it is sufficient to consider one band of permitted energies in an ideal crystal, then the number n involves only those components of the wave vector k which are parallel to the plane S_1. According to the note following Eq. (13), the derived procedure can be applied to the state functions, characterized by a single value of n.

We shall now attempt to ascertain the number and character of the states localized in the neighborhood of the plane limiting the semi-infinite crystal, for the case in which the perturbation potential is not confined only to the elementary cells in the immediate neighborhood of the plane S_1, as it is usually supposed to be.

If the energy of the electron in an infinite crystal depends on the parameter s according to Eq. (32), then

$$\phi_u = \frac{1}{2\pi} \int_0^{2\pi} \frac{e^{iu\alpha} d\alpha}{(W - \epsilon_{n0} - 2\epsilon_1 \cos\alpha)} = \frac{1}{\epsilon_1} \left(\frac{z_1^{|u|}}{z_2 - z_1} \right), \tag{33}$$

where

$$z_{1,2} = \tfrac{1}{2}\beta[1 \mp (1 - 4/\beta^2)^{\frac{1}{2}}] \tag{34}$$

and

$$\beta = (W - \epsilon_{n0})/\epsilon_1, \tag{35}$$

as can easily be found by integration in the complex plane $[z = \exp(i\alpha)]$. The equation for the coefficients e_{np} can then be written in the form

$$e_{n'p} = \frac{1}{z_2 - z_1} \left[\sum_{m=0}^{Z} \sum_{m'=0}^{Z} z_1^{|p-m'|} U_{m'm} e_m - z_1^{p+1} e_0 \right], \tag{36}$$

and the energy is given by equation

$$\left| \sum_{m'=0}^{Z} z_1^{|p-m'|} U_{m'm} - \delta_{m0} z_1^{p+1} - \delta_{pm}(z_2 - z_1) \right| = 0, \tag{37}$$

where we have put

$$U_{m'm} = V_{m'm}/\epsilon_1. \tag{38}$$

For a general discussion, it is more suitable to put Eq. (37) into a different form. Thus, if, for instance, we multiply (37) by the determinant $|S|$, where the matrix S is defined as follows:

$$S_{00} = S_{ZZ} = z_2/(z_2 - z_1);$$
$$S_{jj} = (z_1 + z_2)/(z_2 - z_1) \quad \text{for} \quad j \neq 0, Z; \tag{39}$$
$$S_{jj+1} = S_{jj-1} = 1/(z_1 - z_2),$$

and for all other cases

$$S_{jk} = 0, \tag{39'}$$

we obtain the relation

$$|U' - A| = 0, \tag{40}$$

where the matrices U' and A are defined as

$$U_{pm}' = U_{pm} + \delta_{p+1,m} + \delta_{p-1,m},$$
$$A_{pm} = (z_1 + z_2)\delta_{pm} - z_1 \delta_{p0} \delta_{m0}. \tag{41}$$

From this it can be seen immediately that the energy of the surface state is determined by an equation of the order $(2Z+1)$. The form of (40) is suitable for a direct calculation of the energy of the surface states, or for the determination of the number of states in the case where the numerical values of U_{pm} are given.

It is worth noting that the energy of the electron in a foil with a thickness of Z-elementary cells is given by the equation [see relations (24) and (33)]:

$$|U' - (W/\beta)I| = 0, \tag{42}$$

where I is the unit matrix. The determinant is of the order Z.

For a general discussion of the number of roots, a further rearrangement is helpful. Since U' is a Hermitian matrix, there exists a unitary matrix Q such that

$$QU'Q^\dagger = K, \tag{43}$$

where

$$K_{ij} = K_i \delta_{ij}, \tag{44}$$

and the dagger represents the Hermitian conjugate. Equation (40) can also be rearranged into the following form:

$$|Q| |U' - A| |Q^\dagger|$$
$$= |(K_i - z_1 - z_2)\delta_{ij} + z_1 Q_{iz} Q_{jz}{}^*|$$
$$= \prod_{i=0}^{Z} \rho_i [K_i - z_1 - z_2] z_1 \left\{ z_2 + \sum_{j=0}^{Z} \frac{\rho_j}{(K_j - z_1 - z_2)} \right\} = 0,$$

where

$$\rho_j = |Q_{jz}|^2, \tag{45}$$

and the asterisk denotes the complex conjugate. From the definition of z_1, z_2, and β in Eqs. (34) and (35), we finally obtain

$$\psi(\beta) = \phi(\beta), \tag{46}$$

where [see (34)]

$$\psi(\beta) \equiv z_2(\beta) \tag{47}$$

and

$$\phi(\beta) = \sum_{j=0}^{Z} \frac{\rho_j}{(K_j - \beta)}. \tag{48}$$

$\phi(\beta)$ is a decreasing function, composed of $(Z+2)$ branches. Only on Z branches do there exist the points β such that $\phi(\beta) > 0$ and at the same time points β such that $\phi(\beta) < 0$. For one branch there is $\phi(\beta) > 0$ and for the other one $\phi(\beta) < 0$. If we now assume that $K_0 \cdots K_{p'} < -2$ and $K_{p'+1} \cdots K_Z > -1$, then the branch between $K_{p'}$ and $K_{p'+1}$ does not intersect the negative branch ψ, since $\phi(-2) \geq -1$. By the same argument, if $K_0 \cdots K_p < 1$ and $K_{p+1} \cdots K_Z > 2$, then the root of Eq. (46) does not lie between K_p and K_{p+1}. Having

derived these auxiliary theorems, we proceed now to the determination of the maximal possible number of roots of Eq. (46). Let us assume that $K_0 \cdots K_p < -2$, noting that the considerations to follow are still valid if there does not exist any $K_i < -2$. If K_{p+1} is in the interval $(-2, -1)$, there may exist a solution of Eq. (46) lying between K_p and K_{p+1}. If $K_{p+2} < 2$, there exists one branch of the function ϕ that does not intersect with ψ (i.e., the branch between K_{p+1} and K_{p+2}). If, on the contrary, $K_{p+2} > 2$, there again does not exist any intersection on the branch, between K_{p+1} and K_{p+2}, with the positive branch of the function ψ, since in that case $K_{p+1} \leq -1 < 1$. If K_{p+1} is in the interval $(-1, 2)$ there will not be any solution of Eq. (46) between K_p and K_{p+1}. If, finally, $K_{p+1} > 2$, the branch of ϕ lying between K_p and K_{p+1} does not intersect with the positive branch of ψ since in that case $K_p \leq -2 < 1$. Thus, in any case, at least one of the $(Z+2)$ branches of the function ϕ does not intersect with ψ. There then follow the theorems:

(1) There exist at most $Z+1$ surface states.

(2) If there are s values K_j such that $|K_j| < 1$, there exist at most $Z-s$ surface states.

(3) If there are s values K_j such that $|K_j| > 2$, there exist at least s surface states.

(4) If $s' > 0$ and there are s' values K_j such that $|K_j| < 2$, there exist at most $(Z-s'+2)$ surface states.

APPROXIMATION OF TIGHT BINDING FOR THE CASE $Z=0$

The solution of this case, the one usually considered, which is characterized by the condition

$$U_{m'm} = U\delta_{m0}\delta_{m'0} = (V/\epsilon_1)\delta_{m0}\delta_{m'0}, \tag{49}$$

follows from the derived relationships in an extremely simple manner. According to (40),

$$z_2 = U. \tag{50}$$

Since $z_2 > 1$, there exists a surface state only if

$$V/\epsilon_1 > 1, \tag{51}$$

and then the energy and the state function of the surface state are given by

$$W = \epsilon_{n0} + V + (\epsilon_1^2/V),$$
$$e_p/e_0 = (\epsilon_1/V)^p, \tag{52}$$

which are the well-known formulas.

APPROXIMATION OF TIGHT BINDING FOR THE CASE $Z=1$

In this more general case it is possible to determine some properties of surface states, where the perturbation potential is not confined to the elementary cells in the immediate neighborhood of the surface of the crystal.

The matrix U' has now the form

$$U' = \begin{pmatrix} U_{00} & U_{01}+1 \\ U_{10}+1 & U_{11} \end{pmatrix}. \tag{53}$$

Furthermore,

$$K_{1,2} = \tfrac{1}{2}(U_{00}+U_{11}) \mp [\tfrac{1}{4}(U_{00}-U_{11})^2 + |U_{01}+1|^2]^{\frac{1}{2}} \tag{54}$$

and

$$\phi(\beta) = \frac{\beta - U_{00}}{(\beta - U_{00})(\beta - U_{11}) - |U_{01}+1|^2}. \tag{55}$$

For the sake of illustration, we shall now consider the case in which U_{00}, U_{01}, and U_{11} are real positive quantities. The positive branch of the function ψ [see (47)] is an increasing function of β and $\psi(\beta) > 1$ for $\beta > 2$. Therefore, if Eq. (46) has to have two positive solutions, one must have $\beta_1 > 2$, $\beta_2 > 2$, where

$$\beta_{1,2} = \tfrac{1}{2}(U_{00}+U_{11}+1)$$
$$\pm [\tfrac{1}{4}(1+U_{11}-U_{00})^2 + |U_{01}+1|^2]^{\frac{1}{2}} \tag{56}$$

are the roots of the equation

$$\phi(\beta) = 1. \tag{57}$$

Hence, we obtain as a condition for the existence of two surfaces states with energies lying above the band of permitted energies of the infinite defectless crystal, the simultaneous validity of the following two inequalities:

$$U_{00} + U_{11} > 3,$$
$$(U_{00}-1)(U_{11}-1) - U_{11} \geq {}'U_{01}|^2 + U_{01} + U_{10}. \tag{58}$$

Similarly, the sufficient and necessary condition for the existence of one surface state is

$$U_{00} + U_{11} > 1. \tag{59}$$

Two localized states may thus exist if the defect caused inside the crystal by its surface is sufficiently strong and essentially affects the second cell under the surface, and finally, if the value of U_{01} is not too large. From the condition (59) it is evident that the formation of a surface state does not require as strong a defect on the surface as in the case considered in the last paragraph; the surface intensity of the defect may be compensated by a deeper penetration into the crystal.

To clarify the character of the surface states further, we shall now calculate the ratios e_i/e_0. According to (36), we have

$$e_1/e_0 = (\beta - U_{00})/(1+U_{01}),$$
$$i \geq 1: \quad e_i/e_1 = z_1^{(i-1)}, \tag{60}$$

so that

$$i > 1: \quad |e_i/e_1| < 1, \tag{61}$$

and according to (56)

$$\frac{e_1}{e_0} < \frac{(1+U_{11}-U_{00}) \pm [(1+U_{11}-U_{00})^2 + 4(U_{01}+1)^2]^{\frac{1}{2}}}{2(1+U_{01})}. \tag{62}$$

If

$$U_{00} > U_{11} + 1, \qquad (63)$$

then for the state with the higher energy there follows

$$e_1/e_0 \leq 1, \qquad (64)$$

whereas for the state with the lower energy

$$e_1/e_0 < -1. \qquad (65)$$

If condition (63) is valid, the amplitudes of the surface state with the higher energy, monotonically decrease with increasing distance from the crystal surface. The amplitudes of the state with the lower energy have a maximum in the second cell below the surface and then monotonically decrease. It is necessary to point out that the existence of these states can be expected from general considerations of the "tearing" of the cyclic crystal by a high potential [see relations (14)]. The surface states usually considered are, from the point of view of this high potential barrier, subsurface states: it depends on what energies we still consider to be admissible, that is how far outside the crystal we shift the plane characterized by the relationship $m=0$ [see the inequality (17)]. If there did not exist "subsurface" states, this procedure would not be self-consistent.

CONCLUSION

The results of this investigation can be summarized as follows.

(1) The state function of an electron in a crystal, which is limited by a pair of parallel planes, can be approximated to any desired degree of accuracy in the one-electron approximation by a linear combination of one-dimensional Wannier functions, having a maximal amplitude within the crystal, and one-dimensional Wannier functions having a maximal amplitude at not too great a distance from the crystal surface.

(2) After having proved in a general way that the Wannier functions are localized, we have shown that the energy of the surface states is determined, for a sufficiently extensive crystal, by a determinant with M rows and columns, where M is the larger of the numbers Z and K, defined by (26) and (27) and $M \ll P$, where

$P+1$ is the number of elementary cells between the planes limiting the crystal.

(3) The localization of the surface states, the energy of which does not fall into the band of permitted energies of an infinite crystal, has been proved generally.

(4) To the approximation in which the energy of the electron in the defectless crystal is given by Eq. (32) and if the considerations can be confined to a single band of energies of the nonperturbed infinite crystal, there exist at most $(Z+1)$ surface states, if the perturbation potential penetrates into a depth of $Z+1$ cells below the crystal surface.

(5) The case of $Z=0$, which is usually considered, follows very readily from the general procedure.

(6) For the case $Z=1$, criteria for the existence of one or two states localized in the neighborhood of the surface can easily be given.

(7) For the case $Z=1$, the existence of "subsurface" states can be demonstrated, the wave functions of which do not have a maximum amplitude at the surface, but below it. These states may have lower energies than the true surface states. If the perturbation potential is positive, volume states will be occupied first, followed by subsurface states, and finally by the surface states. At this point it is necessary to point out the usual confusion with respect to the surface charge caused by the surface states. In the one-electron approximation, if we do not take into account electron interaction, the wave functions of the volume states have lower amplitudes near the surface. By filling the subsurface and surface states, an even distribution of electrons in the entire crystal is attained, as follows from the general theory of the molecular orbital method[6] (see Artmann[7]).

To sum up, it has been possible to show that the number and distribution of energetic levels, corresponding to the states localized in the neighborhood of the crystal surface, depend essentially on the depth of penetration of the perturbation potential into the interior of the crystal.

[6] C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. 36, 193 (1940).
[7] K. Artmann, Z. Physik 131, 244 (1952).