

ELECTRONIC STATES AT THE SURFACES OF CRYSTALS

III. THE APPROXIMATION OF TIGHT BINDING: FURTHER EXTENSIONS

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INTRODUCTION

1. To complete the discussion of the electronic states at the surfaces of crystals we consider in this paper two extensions of the previous work. First, restricting ourselves once again to the interaction of atomic s -states, we determine the wave functions and energies of both the normal and surface states of a simple cubic lattice. The analysis involved is a direct extension of that of paper II for a finite linear chain and can be carried through without difficulty.

The second extension arises from the fact that it is only legitimate to consider the s - and p -states separately, as was done in II, provided that the width of the allowed bands is small compared with the separation $E_1 - E_0$ of the atomic states. Here we consider the case when this is not so and the s - and p -states are accordingly degenerate†. We again restrict ourselves to a linear chain of atoms, but the complexity of the problem is such that we have to take this chain to be semi-infinite. We find accordingly that we can at best indicate how and when surface states are likely to arise rather than obtain explicit formulae for their wave functions and energies.

THE SIMPLE CUBIC CRYSTAL

2. We consider a simple cubic crystal consisting of a block N atomic layers thick in the x -direction but extending to infinity in the perpendicular directions; or more accurately we might say that we neglect the end effects in these directions. The atoms are thus situated at points whose position vectors are

$$\mathbf{r}_{lmn} = [-c(l-1), cm, cn], \quad (1)$$

where m and n are unrestricted integers while l takes the values $1, 2, \dots, N$.

We consider only the s -states of the individual atoms. First let us denote by H_l the Hamiltonian for an electron moving in the field of the l th layer of atoms only, that is, the infinite layer of atoms whose positions are given by \mathbf{r}_{lmn} with

† Cf. M.J. pp. 72 *et seq.* (see reference in paper I, p. 205).

unrestricted integral values of m, n . Then, approximating to the metallic potential field as in II, § 4, equation (23), that is, representing it by the sum of the potential fields of the individual atoms, we find that this Hamiltonian has the form

$$H_l = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{mn} U(|\mathbf{r} - \mathbf{r}_{lmn}|). \quad (2)$$

The corresponding wave functions of electrons moving in the field of such a two-dimensional array of atoms are solutions of the wave equation

$$(H_l - E) \psi = 0. \quad (3)$$

Such solutions are found, as in the usual case of a three-dimensional crystal, to be of the type†

$$\psi_{lk_2k_3} = N_l \sum_{mn} e^{i\alpha(mk_2+nk_3)} \phi(|\mathbf{r} - \mathbf{r}_{lmn}|), \quad (4a)$$

with the corresponding energy, independent of l , given by

$$E_{k_2k_3} = E_0 - \alpha - 2\gamma(\cos ck_2 + \cos ck_3). \quad (4b)$$

The Hamiltonian for the complete system is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + \sum_{lmn} U(|\mathbf{r} - \mathbf{r}_{lmn}|), \quad (5a)$$

and the corresponding wave equation is

$$(H - E) \Psi = 0. \quad (5b)$$

Now two states of the type (4a) but with different k_2, k_3 are non-combining‡. We accordingly approximate to Ψ by a series of the form

$$\Psi = \sum_{l=1}^N a_l \psi_{lk_2k_3}. \quad (6)$$

Substituting (6) and (5a) into (5b) we obtain a series of relations between the coefficients a_l , of the type

$$\sum_{l=1}^N a_l \left[(E - E_{k_2k_3}) - \left\{ \sum_{lmn} U(|\mathbf{r} - \mathbf{r}_{lmn}|) - \sum_{mn} U(|\mathbf{r} - \mathbf{r}_{lmn}|) \right\} \right] \psi_{k_2k_3} = 0. \quad (7)$$

Now if N_l of (4a) is chosen so that, neglecting the overlap integral δ , we have

$$\int \psi_{lk_2k_3}^* \psi_{lk_2k_3} d\tau = 1,$$

then we see that the integrals analogous to II, equations (6), that is, with $\phi(\rho_l)$ replaced by $\psi_{lk_2k_3}$, have exactly the same values as the integrals II (6) themselves. Thus it follows that the new recurrence relations and end conditions only differ from those of II in the replacement of E_0 by $E_{k_2k_3}$. All the succeeding work of II, § 2, can therefore be taken over directly with no modification other than this substitution together with that of $\psi_{lk_2k_3}$ for $\phi(\rho_l)$, and the introduction of \sum_{mn} .

† M.J. p. 66.

‡ M.J. pp. 59 and 72.

In this way we obtain two series of states

$$\Psi_{\theta k_2 k_3} = \sum_{s=0}^{N-1} \sum_{mn} \cos(\frac{1}{2}N - \frac{1}{2} - s)\theta e^{i\alpha(mk_2 + nk_3)} \phi(|\mathbf{r} - \mathbf{r}_{s+1, m, n}|), \quad (8a)$$

and $\Psi_{\theta k_2 k_3} = \sum_{s=0}^{N-1} \sum_{mn} \sin(\frac{1}{2}N - \frac{1}{2} - s)\theta e^{i\alpha(mk_2 + nk_3)} \phi(|\mathbf{r} - \mathbf{r}_{s+1, m, n}|),$

the appropriate energy being in each case

$$E = E_0 - \alpha + 2\gamma(\cos \theta - \cos ck_2 - \cos ck_3), \quad (8b)$$

and the values of θ being exactly as before. Thus $0 < \theta < \pi$.

The energies (8b) for the range $0 < \theta < \pi$ clearly give the usual band of energies forming the first Brillouin zone for a simple cubic crystal. Indeed if θ is replaced by $\pi - ck_1$ the forms of the expressions are identical†. This zone now contains only $M(N-2)$ possible states‡, where M is the number of atoms in a monatomic layer parallel to the x -axis, i.e. $M = \sum_{mn} 1$.

The other $2M$ states are now surface states of the form

$$\Psi_{\xi k_2 k_3} = \sum_{mn} e^{i\alpha(mk_2 + nk_3)} \left[\begin{aligned} & [\phi(|\mathbf{r} - \mathbf{r}_{1mn}|) \pm \phi(|\mathbf{r} - \mathbf{r}_{Nmn}|)] \\ & + e^{-\xi} [\phi(|\mathbf{r} - \mathbf{r}_{2mn}|) \pm \phi(|\mathbf{r} - \mathbf{r}_{N-1, m, n}|)] \\ & + \dots \end{aligned} \right], \quad (9a)$$

where either the upper or the lower sign is taken throughout. The energy appropriate to these states is

$$E = E_0 - \alpha + 2\gamma(\cosh \xi - \cos ck_2 - \cos ck_3), \quad (9b)$$

which again lies outside the zone, since $\cosh \xi > 1 > \cos \theta$. The range of k_2, k_3 is as usual from $-\pi/c$ to π/c .

We observe that, if we neglect the electron spin, the number of surface states corresponding to any given surface is equal to the number of atoms in that surface. This result is also true for the case of nearly free electrons discussed in I, as is easily seen if we consider the density of states in phase space§. If we consider a finite cube of metal we obtain "surface states" corresponding to all six surfaces, "line states" corresponding to all twelve edges and finally "point states" corresponding to the eight corners.

DEGENERACY OF THE ATOMIC s - AND p -STATES

3. When the s - and p -states are to be taken as degenerate we consider the case of a semi-infinite linear chain and, as in II, concentrate on the relations between the coefficients of the wave function. We solve these as a set of recurrence relations and hence we are able to predict the existence of a surface state lying

† Cf. M.J. p. 68, equation (58.1).

‡ Here, as in I and II, we neglect the electron spin which has the effect of doubling the number of possible electronic states.

§ Cf. M.J. pp. 56 and 69.

above the higher allowed band with another lying between the two bands but with no such state below the lower band. It is, however, impossible to find the energy of either of these states.

3.1. *The allowed bands.* We take the atoms to be situated at the points

$$\mathbf{r}_l = (-cl, 0, 0) \quad (l=0, 1, \dots, \infty).$$

For such a chain only the p_x -states combine with the s -states. Denoting the p_x -states by $\phi_1(\rho_l)$, we therefore write for the zero-order wave function

$$\Psi = \sum_{l=0}^{\infty} a_l \phi_0(\rho_l) + \sum_{l=0}^{\infty} b_l \phi_1(\rho_l).$$

Applying the perturbation theory and neglecting the interactions of all but nearest neighbours, we obtain an infinite number of relations between the coefficients a_l and b_l . These we write in the form of the recurrence relations

$$\left. \begin{aligned} -\beta b_{l-1} - \gamma a_{l-1} + (E - E_0) a_l - \gamma a_{l+1} + \beta b_{l+1} &= 0, \\ \beta a_{l-1} + \gamma_1 b_{l-1} + (E - E_1) b_l + \gamma_1 b_{l+1} - \beta a_{l+1} &= 0, \end{aligned} \right\} \quad (10)$$

together with the end conditions

$$\left. \begin{aligned} (E - E_0 - \epsilon_0) a_0 - \gamma a_1 + \alpha_{01} b_0 + \beta b_1 &= 0, \\ (E - E_1 - \epsilon_1) b_0 + \gamma_1 b_1 + \alpha_{01} a_0 - \beta a_1 &= 0. \end{aligned} \right\} \quad (11)$$

In these equations for simplicity of writing we have replaced $E - E_0 - \alpha$, $E - E_1 - \alpha_1$ by $E - E_0$, $E - E_1$ respectively. The new quantities α_{01} , β are given by the formulae

$$\left. \begin{aligned} \int \phi_1^*(\rho_m) [V - U(\rho_l)] \phi_0(\rho_l) d\tau &= 0 & \text{if } m=l \neq 0, \\ &= -\alpha_{01} & \text{if } m=l=0, \\ &= \mp \beta & \text{if } m=l \pm 1, \\ &= 0 & \text{otherwise,} \end{aligned} \right\}$$

all other quantities being defined as in II, equations (6), for s -states and the corresponding integrals for p -states.

To solve the equations (10) we put

$$a_l = A e^{il\theta}, \quad b_l = B e^{il\theta}. \quad (12)$$

Then each pair of relations (10) reduces to the form

$$\left. \begin{aligned} A(E - E_0 - 2\gamma \cos \theta) + B 2i\beta \sin \theta &= 0, \\ -A 2i\beta \sin \theta + B(E - E_1 + 2\gamma_1 \cos \theta) &= 0, \end{aligned} \right\} \quad (13)$$

whence, eliminating A and B , we obtain

$$\cos \theta = \frac{\left[\begin{aligned} &[\gamma_1(E - E_0) - \gamma(E - E_1)] \\ &\pm \sqrt{\{[\gamma_1(E - E_0) - \gamma(E - E_1)]^2 + 4(\gamma\gamma_1 - \beta^2)[(E - E_0)(E - E_1) - 4\beta^2]\}} \end{aligned} \right]}{4(\gamma\gamma_1 - \beta^2)}. \quad (14)$$

The roots of equation (14) for θ are of the form $\pm\theta_1, \pm\theta_2$. Moreover, a detailed consideration shows that if E is greater than $E_1 + 2\gamma_1$, less than $E_0 - 2\gamma$, or lies between $E_1 - 2\gamma_1$ and $E_0 + 2\gamma$, then both θ_1, θ_2 are complex of the form $i\mu$ or $\pi + i\mu$. If, however, E lies within either of the bands

$$\left. \begin{aligned} E_1 + 2\gamma_1 > E > \max(E_1 - 2\gamma_1, E_0 + 2\gamma), \\ \min(E_1 - 2\gamma_1, E_0 + 2\gamma) > E > E_0 - 2\gamma, \end{aligned} \right\} \quad (15)$$

then one of the roots θ_1 is real and the other is complex of the form $i\mu$ or $\pi + i\mu$.

The general solution of the equations (10) is

$$\left. \begin{aligned} a_l &= A_1^+ e^{i\theta_1 l} + A_1^- e^{-i\theta_1 l} + A_2^+ e^{i\theta_2 l} + A_2^- e^{-i\theta_2 l}, \\ b_l &= B_1^+ e^{i\theta_1 l} + B_1^- e^{-i\theta_1 l} + B_2^+ e^{i\theta_2 l} + B_2^- e^{-i\theta_2 l}. \end{aligned} \right\} \quad (16)$$

Now let us consider first the case when E lies within either of the bands (15). Then the term $e^{-i\theta_2 l}$ increases exponentially with l and so for a physically possible state we must have $A_2^- = B_2^- = 0$. The expressions (16) thus contain effectively two arbitrary constants, namely the ratios $A_1^+ : A_1^- : A_2^+$, since θ_1, θ_2 and the ratios $A : B$ are determined by (13). The end conditions (11) then afford the necessary two equations to determine these ratios. Actual substitution shows that the equations have a unique solution for any value of E which lies within one of the bands (15). These bands are, therefore, completely occupied by electronic states and are seen to correspond exactly to the allowed bands obtained for the infinite metal in the case when the s - and p -states are degenerate, being, in fact, their one-dimensional counterpart.

3.2. *The forbidden bands.* We proceed now to the case when E does not lie in either of the bands (15). Then both $e^{-i\theta_1 l}$ and $e^{-i\theta_2 l}$ increase exponentially with l , and thus for the solution to be physically significant we must have

$$A_1^- = A_2^- = B_1^- = B_2^- = 0.$$

a_l, b_l accordingly take the simpler forms

$$\begin{aligned} a_l &= A_1 e^{i\theta_1 l} + A_2 e^{i\theta_2 l}, \\ b_l &= B_1 e^{i\theta_1 l} + B_2 e^{i\theta_2 l}. \end{aligned}$$

Though θ_1 and θ_2 are both complex we prefer to leave them in this form, since we thereby avoid discussing whether they are of the form $i\mu$ or $\pi + i\mu$, which would involve a consideration of the signs and relative magnitudes of the quantities involved in the expression (14) for $\cos \theta$. The recurrence relations then reduce to

$$\left. \begin{aligned} A_1(E - E_0 - 2\gamma \cos \theta_1) + B_1 2i\beta \sin \theta_1 &= 0, \\ -A_1 2i\beta \sin \theta_1 + B_1(E - E_1 + 2\gamma_1 \cos \theta_1) &= 0, \\ A_2(E - E_0 - 2\gamma \cos \theta_2) + B_2 2i\beta \sin \theta_2 &= 0, \\ -A_2 2i\beta \sin \theta_2 + B_2(E - E_1 + 2\gamma_1 \cos \theta_2) &= 0, \end{aligned} \right\}$$

while the end conditions become

$$\left. \begin{aligned} A_1(E - E_0 - \epsilon_0 - \gamma e^{i\theta_1}) + B_1(\alpha_{01} + \beta e^{i\theta_1}) \\ + A_2(E - E_0 - \epsilon_0 - \gamma e^{i\theta_2}) + B_2(\alpha_{01} + \beta e^{i\theta_2}) = 0, \\ A_1(\alpha_{01} - \beta e^{i\theta_1}) + B_1(E - E_1 - \epsilon_1 + \gamma_1 e^{i\theta_1}) \\ + A_2(\alpha_{01} - \beta e^{i\theta_2}) + B_2(E - E_1 - \epsilon_1 + \gamma_1 e^{i\theta_2}) = 0. \end{aligned} \right\}$$

From these equations we can eliminate A_1 , A_2 , B_1 , B_2 and obtain the determinantal equation

$$\begin{vmatrix} E - E_0 - \epsilon_0 - \gamma e^{i\theta_1} & \alpha_{01} + \beta e^{i\theta_1} & E - E_0 - \epsilon_0 - \gamma e^{i\theta_2} & \alpha_{01} + \beta e^{i\theta_2} \\ \alpha_{01} - \beta e^{i\theta_1} & E - E_1 - \epsilon_1 + \gamma_1 e^{i\theta_1} & \alpha_{01} - \beta e^{i\theta_2} & E - E_1 - \epsilon_1 + \gamma_1 e^{i\theta_2} \\ \epsilon_0 - \gamma e^{-i\theta_1} & -(\alpha_{01} + \beta e^{-i\theta_1}) & \epsilon_0 - \gamma e^{-i\theta_2} & -(\alpha_{01} + \beta e^{-i\theta_2}) \\ -(\alpha_{01} - \beta e^{-i\theta_1}) & \epsilon_1 + \gamma_1 e^{-i\theta_1} & -(\alpha_{01} - \beta e^{-i\theta_2}) & \epsilon_1 + \gamma_1 e^{-i\theta_2} \end{vmatrix} = 0. \quad (17)$$

If we write

$$e^{i\theta_1} + e^{i\theta_2} = S, \quad e^{i\theta_1} e^{i\theta_2} = (\gamma\gamma_1 - \beta^2) \Pi,$$

the equation (17) can be reduced to the simpler form

$$\begin{vmatrix} E - E_0 - \epsilon_0 + [(\gamma\gamma_1 + \beta^2)\epsilon_0 - 2\beta\gamma\alpha_{01}]\Pi - \gamma S \\ \alpha_{01} + [2\beta\gamma\epsilon_1 - (\gamma\gamma_1 + \beta^2)\alpha_{01}]\Pi + \beta S \\ \alpha_{01} + [2\beta\gamma_1\epsilon_0 - (\gamma\gamma_1 + \beta^2)\alpha_{01}]\Pi - \beta S \\ E - E_1 - \epsilon_1 + [(\gamma\gamma_1 + \beta^2)\epsilon_1 - 2\beta\gamma_1\alpha_{01}]\Pi + \gamma_1 S \end{vmatrix} = 0. \quad (18)$$

If this equation (18) has a root lying outside the energy bands (15), that root corresponds to a state in which, in view of the complex form of θ_1 and θ_2 , the coefficients a_l , b_l decrease exponentially with increasing l . Such a state is a surface state.

The expressions Π , S are exceedingly complex and in their complete form would render further analysis intractable. However, the three quantities γ , γ_1 , β are all of the same order of magnitude while, in view of the greater overlap of the p -states, $\gamma_1 > \beta > \gamma$. Thus from a consideration of the integrals defining these quantities it seems reasonable to suppose that β^2 and $\gamma\gamma_1$ are approximately equal and that accordingly $\gamma\gamma_1 - \beta^2$ may be taken as small. With this approximation, equation (18) becomes

$$\begin{vmatrix} E - E_0 - \epsilon_0 + 2\Pi\{\gamma\gamma_1\epsilon_0 - \gamma\alpha_{01}\sqrt{(\gamma\gamma_1)}\} - \gamma S \\ \alpha_{01} + 2\Pi\{\gamma\epsilon_1\sqrt{(\gamma\gamma_1)} - \gamma\gamma_1\alpha_{01}\} + \sqrt{(\gamma\gamma_1)} S \\ \alpha_{01} + 2\Pi\{\gamma_1\epsilon_0\sqrt{(\gamma\gamma_1)} - \gamma\gamma_1\alpha_{01}\} - \sqrt{(\gamma\gamma_1)} S \\ E - E_1 - \epsilon_1 + 2\Pi\{\gamma\gamma_1\epsilon_1 - \gamma_1\alpha_{01}\sqrt{(\gamma\gamma_1)}\} + \gamma_1 S \end{vmatrix} = 0,$$

that is,

$$\begin{aligned} & (E - E_0 - \epsilon_0)(E - E_1 - \epsilon_1) - \alpha_{01}^2 \\ & + \left[2\Pi\gamma\gamma_1 \left(\epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) + \gamma_1 S \right] \left[E - E_0 - \epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right] \\ & + \left[2\Pi\gamma\gamma_1 \left(\epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) - \gamma S \right] \left[E - E_1 - \epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right] = 0, \end{aligned}$$

which on slight rearrangement becomes

$$\begin{aligned} & (E - E_0 - \epsilon_0 - \gamma S)(E - E_1 - \epsilon_1 + \gamma_1 S) - \alpha_{01}^2 \\ & + 2I\gamma\gamma_1 \left[\left(\epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) \left(E - E_0 - \epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) \right. \\ & \left. + \left(\epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) \left(E - E_1 - \epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) \right] = 0. \quad (19) \end{aligned}$$

3.3. *Approximations to S and II.* Before we can proceed any further we must consider the approximate forms taken by *S* and *II* when $\gamma\gamma_1 - \beta^2$ is small. From (14) we obtain immediately the approximate roots

$$\begin{aligned} \cos \theta_1 &= \frac{\gamma_1(E - E_0) - \gamma(E - E_1)}{2(\gamma\gamma_1 - \beta^2)}, \\ \cos \theta_2 &= -\frac{(E - E_0)(E - E_1) - 4\gamma\gamma_1}{2[\gamma_1(E - E_0) - \gamma(E - E_1)]}, \end{aligned}$$

whence, since $|e^{i\theta_1}| < 1$, $|e^{i\theta_2}| < 1$, we obtain

$$\begin{aligned} e^{i\theta_1} &= \frac{\gamma\gamma_1 - \beta^2}{\gamma_1(E - E_0) - \gamma(E - E_1)}, \\ e^{i\theta_2} &= -\frac{(E - E_0)(E - E_1) - 4\gamma\gamma_1}{2[\gamma_1(E - E_0) - \gamma(E - E_1)]} \pm \sqrt{\left\{ \left[\frac{(E - E_0)(E - E_1) - 4\gamma\gamma_1}{2[\gamma_1(E - E_0) - \gamma(E - E_1)]} \right]^2 - 4 \right\}} \\ &= \frac{\left[\begin{aligned} & -[(E - E_0)(E - E_1) - 4\gamma\gamma_1] \\ & \pm \sqrt{[(E - E_0 - 2\gamma)(E - E_1 + 2\gamma_1)(E - E_0 + 2\gamma)(E - E_1 - 2\gamma_1)]} \end{aligned} \right]}{2[\gamma_1(E - E_0) - \gamma(E - E_1)]}. \end{aligned}$$

Here the upper sign is to be taken if $\cos \theta_2 < 0$ and the lower if $\cos \theta_2 > 0$. Thus

$$\begin{aligned} S &= e^{i\theta_1} + e^{i\theta_2} \cong e^{i\theta_2} \\ &= -\frac{\sqrt{[(E - E_0 - 2\gamma)(E - E_1 + 2\gamma_1)]} \mp \sqrt{[(E - E_0 + 2\gamma)(E - E_1 - 2\gamma_1)]}}{\sqrt{[(E - E_0 - 2\gamma)(E - E_1 + 2\gamma_1)]} \pm \sqrt{[(E - E_0 + 2\gamma)(E - E_1 - 2\gamma_1)]}}, \end{aligned}$$

and $II = e^{i\theta_1}e^{i\theta_2}/(\gamma\gamma_1 - \beta^2)$

$$= -4/\{\sqrt{[(E - E_0 - 2\gamma)(E - E_1 + 2\gamma_1)]} \pm \sqrt{[(E - E_0 + 2\gamma)(E - E_1 - 2\gamma_1)]}\}^2.$$

In these expressions the upper signs are to be taken if $E > E_1 + 2\gamma_1$ or $< E_0 - 2\gamma$, the lower if E lies between $E_1 - 2\gamma_1$ and $E_0 + 2\gamma$. These ranges are not quite the same as $\cos \theta_2 < 0$ and $\cos \theta_2 > 0$, since $\cos \theta_2 > 0$ if $E < E_0 - 2\gamma$ and

$$\gamma_1(E - E_0) - \gamma(E - E_1) < 0.$$

This case is, however, taken care of by the fact that the denominator of the square root term in the expression for $e^{i\theta_2}$ is then $|\gamma_1(E - E_0) - \gamma(E - E_1)|$, which gives rise to a further compensating change of sign.

3.4. *The existence of surface states.* A consideration of the expressions just obtained for S and Π shows that, within the ranges of E to be considered, the variation in the first term of (19) outweighs in importance that of the succeeding terms. The expression is thus effectively monotonic within these ranges and the existence of roots of the equation (19) should be indicated by the sign at the extremities of the ranges. We now consider the three ranges separately.

(i) $E \geq E_1 + 2\gamma_1$.

S and Π both tend steadily to zero as $E \rightarrow \infty$, and so, for large E , (19) is positive. Moreover, if

$$E = E_1 + 2\gamma_1,$$

$$S = -1, \quad \Pi = -1/(\gamma_1 d), \quad \text{where } d = E_1 + 2\gamma_1 - E_0 - 2\gamma,$$

and the left-hand side of (19) is thus equal to

$$(d + 3\gamma - \epsilon_0)(\gamma_1 - \epsilon_1) - \alpha_{01}^2 - \frac{2\gamma}{d} \left[(d + 2\gamma) \left(\epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) + 2\gamma_1 \left(\epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) + \alpha_{01}^2 - \epsilon_0 \epsilon_1 \right]$$

Since $\epsilon_1 > \gamma_1$ and d is fairly large, this expression is negative. Thus the sign of (19) changes as E increases from $E_1 + 2\gamma_1$ to ∞ and there is accordingly one root, that is, one surface state, with energy lying above the upper band.

(ii) $E \leq E_0 - 2\gamma$.

Again S and Π tend to zero as $E \rightarrow -\infty$. (Observe, however, that there is a region where $\gamma_1(E - E_0) - \gamma(E - E_1)$ is approximately zero and where accordingly the approximations employed in the determination of S and Π are invalid. $|E|$ is then so large, however, that only the first term of (19) is relevant.) Thus, for E large and negative, (19) is positive. Also if $E = E_0 - 2\gamma$ then $S = -1$, $\Pi = -1/(\gamma d')$, where $d' = E_1 - 2\gamma_1 - E_0 + 2\gamma$. The left-hand side of (19) is then equal to

$$(\epsilon_0 + \gamma)(d' + 3\gamma_1 + \epsilon_1) - \alpha_{01}^2 + \frac{2\gamma_1}{d'} \left[2\gamma \left(\epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) + (d' + 2\gamma_1) \left(\epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) + \epsilon_0 \epsilon_1 - \alpha_{01}^2 \right],$$

which is positive.

There is, therefore, no change of sign and hence no surface state with an energy lying below the lower band.

(iii) E lying between $E_1 - 2\gamma_1$ and $E_0 + 2\gamma$.

If $E = E_1 - 2\gamma_1$, then $S = 1$, $\Pi = 1/(\gamma_1 d')$, where again $d' = E_1 - 2\gamma_1 - E_0 + 2\gamma$. The left-hand side of (19) is then

$$-(d' - 3\gamma - \epsilon_0)(\epsilon_1 + \gamma_1) - \alpha_{01}^2 + \frac{2\gamma}{d'} \left[(d' - 2\gamma) \left(\epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) - 2\gamma_1 \left(\epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) + \alpha_{01}^2 - \epsilon_0 \epsilon_1 \right].$$

If $E = E_0 + 2\gamma$, then $S = 1$, $\Pi = 1/(\gamma d)$, where again $d = E_1 + 2\gamma_1 - E_0 - 2\gamma$, and the left-hand side of (19) becomes

$$(\epsilon_0 - \gamma)(d + \epsilon_1 + 3\gamma_1) - \alpha_{01}^2 + \frac{2\gamma_1}{d} \left[2\gamma \left(\epsilon_1 - \alpha_{01} \sqrt{\frac{\gamma_1}{\gamma}} \right) - (d - 2\gamma_1) \left(\epsilon_0 - \alpha_{01} \sqrt{\frac{\gamma}{\gamma_1}} \right) + \alpha_{01}^2 - \epsilon_0 \epsilon_1 \right].$$

The signs of these expressions cannot in general be determined without a detailed knowledge of the magnitudes of the quantities involved therein. However, when d , d' are fairly large the expressions are negative and positive respectively and we have one root and therefore one surface state with energy lying between the upper and lower bands. If, on the other hand, d and d' are fairly small, then the energy gap between the bands is fairly small. This implies that the electrons are nearly free, so that our present method of approach is inapplicable, and we must return to the treatment of paper I.

To summarize, therefore, we have established the existence of surface states for the extreme cases of nearly free and tightly bound electrons. It is accordingly reasonable to suppose that they will still be present in the actual intermediate case afforded by real crystals.

CONCLUSION

4. If the results of the three papers of this series are summarized we find that there is some difficulty in coordinating those obtained by the different approximations employed therein. In I, § 2.4, it is shown that, according to the free electron picture, the surface states arise from a falling out of an equal number of states from the lower and upper allowed bands respectively. It is not possible to see whence they come on the approximation of tight binding discussed here, but, in the extreme case when the s -states can be considered independently, the work of paper II shows that the same number of states arises entirely from the lower band. In the actual case afforded by a real metal it is accordingly not possible to decide whence the states arise, whether all from the lower band or in equal numbers from the bands on either side.

This situation is unfortunate since an attempt to consider the effect of these states on any phenomenon would naturally require a knowledge of whether at the absolute zero of temperature the states are to be regarded as full, partly full, or empty. In such a case it would be necessary to consider both possibilities of derivation of the states to see which, if either, leads to results compatible with experiment. However, this position is perhaps no less satisfying than it is in problems in which the possible overlapping or non-overlapping of the zones has to be considered. Here again the distribution of the electronic states is deduced from an attempted correlation with experiment; the experimental results are not predicted from a known electron distribution.

The number of electronic surface states, if we neglect the spin, is equal to the number of atoms in the surface, just as the number of normal states is equal to the total number of atoms in the lattice (here considering, of course, just one band of levels). They are thus greatly outnumbered by the normal electronic states and their effect can only be expected to be appreciable in what are essentially surface phenomena or in crystals in which the number of electrons available for an interaction has for some reason been drastically cut down.

SUMMARY

The method of the previous paper is extended to determine the surface states of a simple cubic crystal on the approximation of tight binding. It is also applied to the case of a semi-infinite linear chain when the atomic s - and p -states are to be regarded as degenerate, the existence of surface states being again predicted.

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