

ELECTRONIC STATES AT THE SURFACES OF CRYSTALS

II. THE APPROXIMATION OF TIGHT BINDING: FINITE LINEAR CHAIN OF ATOMS

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INTRODUCTION

1. The treatment of the electronic states at crystal surfaces given in the preceding paper is based on an assumption that the electrons may be regarded as nearly free. This assumption is not true in practice, of course, the properties of a real crystal being intermediate between those of this extreme case and of the opposite one represented by the approximation of tight binding†. Now Maue‡ deduces that, according to this latter approximation, surface states could not arise, which would make the visualizing of the intermediate case a matter of considerable difficulty. In this paper, however, we attack the problem from this opposite standpoint and we see that Maue's deduction is in error, and that surface states are indeed predicted by the analysis.

The calculations involved in the application of the approximation of tight binding to the electron theory of metals are in general more complicated than those required by the nearly free electron picture. For the sake of simplicity, therefore, we restrict ourselves at first to a finite linear chain of atoms§. We then find that we are able to obtain explicit formulae for the energies and wave functions of the "surface" states in terms of the overlap integrals of the atomic wave functions. We still refer to these states as surface states though in this case "point states" is perhaps a more descriptive name.

ATOMIC *s*-STATES

2. We consider a finite linear chain of N similar atoms. These we take to be situated at the points whose position vectors are

$$\mathbf{r}_l = [-c(l-1), 0, 0] \quad (l=1, 2, \dots, N), \quad (1)$$

and thus c is the internuclear separation or lattice constant. The potential of an electron moving in the field of an isolated atom is then of the form

$$U(|\mathbf{r} - \mathbf{r}_l|) \equiv U(\rho_l),$$

† See, e.g., M.J. pp. 65 *et seq.* (cf. paper I, reference on p. 205.)

‡ *Loc. cit.* (paper I), p. 725.

§ The extension to a three-dimensional crystal is considered in the next paper.

\mathbf{r} being the position vector of the electron and ρ_l its distance from the l th isolated atom considered. The wave equation corresponding to motion in this field is then

$$\nabla^2\phi + \frac{2m}{\hbar^2}[E - U(\rho_l)]\phi = 0. \quad (2)$$

We denote the solution corresponding to an s -state of energy E_0 by $\phi(\rho_l)$, since it is spherically symmetrical.

We write the wave equation of the complete system as

$$\nabla^2\psi + \frac{2m}{\hbar^2}(E - V)\psi = 0. \quad (3)$$

We now apply the perturbation theory for degenerate systems, taking as the zero-order wave function

$$\psi = \sum_{l=1}^N a_l \phi(\rho_l). \quad (4)$$

Thus we are considering only the s -states, the effect of the p -states being dealt with in a later section and in paper III. Then, substituting (4) into (3), we obtain

$$\sum_{l=1}^N a_l [(E - E_0) - \{V - U(\rho_l)\}] \phi(\rho_l) = 0. \quad (5)$$

We now multiply by $\phi^*(\rho_m)$ and integrate over all space, neglecting all interactions except those of nearest neighbours, i.e. we write

$$\left. \begin{aligned} \int \phi^*(\rho_m) \phi(\rho_l) d\tau &= 1 && \text{if } m=l, \\ &= \delta && \text{if } m=l \pm 1, \\ &= 0 && \text{otherwise,} \end{aligned} \right\} \quad (6a)$$

$$\left. \begin{aligned} \int \phi^*(\rho_m) [V - U(\rho_l)] \phi(\rho_l) d\tau &= -\alpha && \text{if } m=l \neq 1 \text{ or } N, \\ &= -\alpha' && \text{if } m=l = 1 \text{ or } N, \\ &= -\gamma && \text{if } m=l \pm 1, \\ &= 0 && \text{otherwise.} \end{aligned} \right\} \quad (6b)$$

α' differs from α in (6b) since it corresponds to the end atoms of the chain, while α is the same in all other cases, since we are only considering the effects of the interaction of nearest neighbours.

Thus we obtain a series of N equations which we may write in the form of a recurrence relation

$$a_{n-1}\{(E - E_0)\delta + \gamma\} + a_n(E - E_0 + \alpha) + a_{n+1}\{(E - E_0)\delta + \gamma\} = 0 \quad (N - 1 \geq n \geq 2), \quad (7)$$

together with the end conditions

$$\left. \begin{aligned} a_1(E - E_0 + \alpha') + a_2\{(E - E_0)\delta + \gamma\} &= 0, \\ a_{N-1}\{(E - E_0)\delta + \gamma\} + a_N(E - E_0 + \alpha') &= 0. \end{aligned} \right\} \quad (7a)$$

Now the validity of the approximation of tight binding rests on the smallness of the quantities $\alpha, \alpha', \gamma, \delta$. Thus $E - E_0$ must also be small and $(E - E_0)\delta$ a second-order quantity which may be neglected. Then, if we write

$$E - E_0 + \alpha = \epsilon, \quad \alpha - \alpha' = \epsilon_0, \tag{8}$$

the relations (7) take the form

$$\left. \begin{aligned} \gamma a_{n-1} + \epsilon a_n + \gamma a_{n+1} &= 0 & (N-1 \geq n \geq 2), \\ (\epsilon - \epsilon_0) a_1 + \gamma a_2 &= 0, \\ \gamma a_{N-1} + (\epsilon - \epsilon_0) a_N &= 0. \end{aligned} \right\} \tag{9}$$

We can obtain the general solution of these equations by putting†

$$a_n = (-)^n (Ae^{in\theta} + Be^{-in\theta}). \tag{10}$$

Then the recurrence relation becomes

$$\epsilon = 2\gamma \cos \theta, \tag{11}$$

and, if we substitute this value for ϵ , the end conditions reduce to

$$\left. \begin{aligned} A(\epsilon_0 e^{i\theta} - \gamma) + B(\epsilon_0 e^{-i\theta} - \gamma) &= 0, \\ Ae^{iN\theta}(\epsilon_0 - \gamma e^{i\theta}) + Be^{-iN\theta}(\epsilon_0 - \gamma e^{-i\theta}) &= 0. \end{aligned} \right\} \tag{12}$$

If we eliminate A and B from the equations (12) we obtain

$$\sin(N+1)\theta - 2(\epsilon_0/\gamma) \sin N\theta + (\epsilon_0/\gamma)^2 \sin(N-1)\theta = 0. \tag{13}$$

The root $\theta = 0$ of equation (13) has no physical significance since it leads to the result $a_n = 0$. Accordingly we exclude it and then (13) has N roots for θ and hence, with (11), gives N values of the energy as required.

2.1. *The energies of the electronic states.* Solving the equation (13) for the ratio ϵ_0/γ we have

$$\frac{\epsilon_0}{\gamma} = \frac{\sin N\theta \pm \sin \theta}{\sin(N-1)\theta},$$

whence either
$$\sin \frac{1}{2}(N+1)\theta = \frac{\epsilon_0}{\gamma} \sin \frac{1}{2}(N-1)\theta \tag{14a}$$

or
$$\cos \frac{1}{2}(N+1)\theta = \frac{\epsilon_0}{\gamma} \cos \frac{1}{2}(N-1)\theta. \tag{14b}$$

These equations may be written in the forms

$$\frac{\epsilon_0 - \gamma}{\epsilon_0 + \gamma} = \cot \frac{1}{2}N\theta \tan \frac{1}{2}\theta, \tag{15a}$$

$$\frac{\epsilon_0 - \gamma}{\epsilon_0 + \gamma} = -\tan \frac{1}{2}N\theta \tan \frac{1}{2}\theta. \tag{15b}$$

It is most instructive to consider the variation in the roots of the equations (15) as ϵ_0/γ is increased from the value zero, corresponding to neglecting the end

† The factor $(-)^n$ is included for convenience since we have found that the subsequent results then take a simpler form.

effects, to a value greater than unity. The corresponding variation of the ratio $(\epsilon_0 - \gamma)/(\epsilon_0 + \gamma)$ is from -1 through zero to a positive value and this gives rise to a variation in the roots of (15) which is illustrated for the case of even N by Figs. 1 and 2 and for odd N by Figs. 3 and 4.

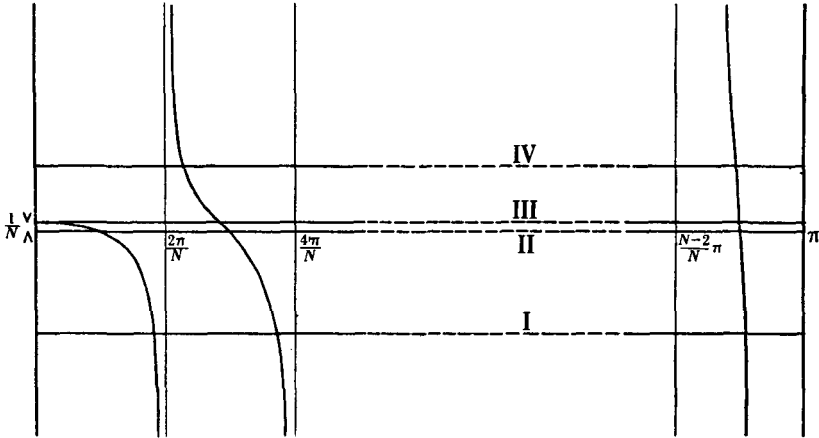


Fig. 1. Diagram showing roots of $(\epsilon_0 - \gamma)/(\epsilon_0 + \gamma) = \cot \frac{1}{2} N \theta \tan \frac{1}{2} \theta$ in the cases I, $\epsilon_0/\gamma = 0$; II, $\epsilon_0/\gamma = 1$; III, $\epsilon_0/\gamma = (N+1)/(N-1)$; IV, $\epsilon_0/\gamma > (N+1)/(N-1)$ (N even).

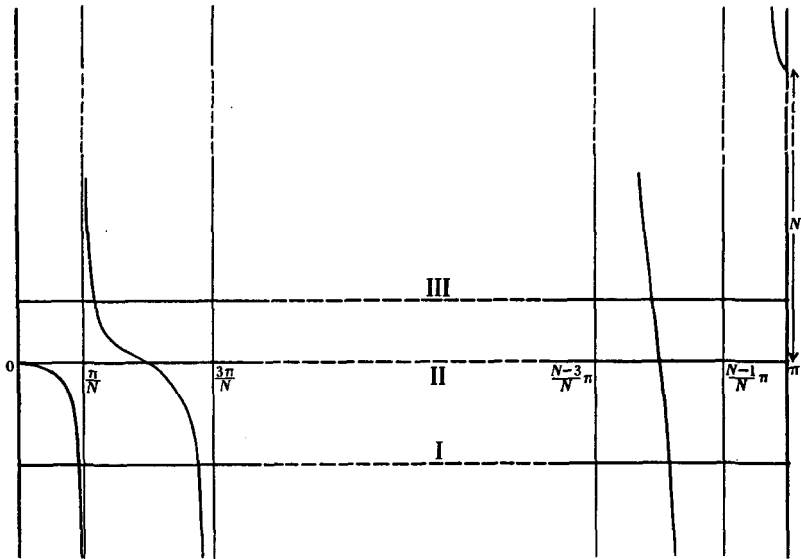


Fig. 2. Diagram showing roots of $(\epsilon_0 - \gamma)/(\epsilon_0 + \gamma) = -\tan \frac{1}{2} N \theta \tan \frac{1}{2} \theta$ in the cases I, $\epsilon_0/\gamma = 0$; II, $\epsilon_0/\gamma = 1$; III, $\epsilon_0/\gamma > 1$ (N even).

Consider first the case of even N . When end effects are neglected ($\epsilon_0 = 0$) we see from Fig. 1 that (15a) has $\frac{1}{2}N$ real roots in the interval $0 < \theta < \pi$. As ϵ_0/γ increases, the roots decrease steadily, passing through the values $(2r - 1)\pi/N$

(for $r = 1, 2, \dots, \frac{1}{2}N$) when $\epsilon_0/\gamma = 1$, until when $\epsilon_0/\gamma = (N + 1)/(N - 1)$ the lowest root vanishes. If $\epsilon_0/\gamma > (N + 1)/(N - 1)$ there are only $\frac{1}{2}N - 1$ real roots. Similarly, Fig. 2 shows that (15b) has $\frac{1}{2}N$ real roots if $\epsilon_0/\gamma < 1$ but if $\epsilon_0/\gamma > 1$ only $\frac{1}{2}N - 1$ real

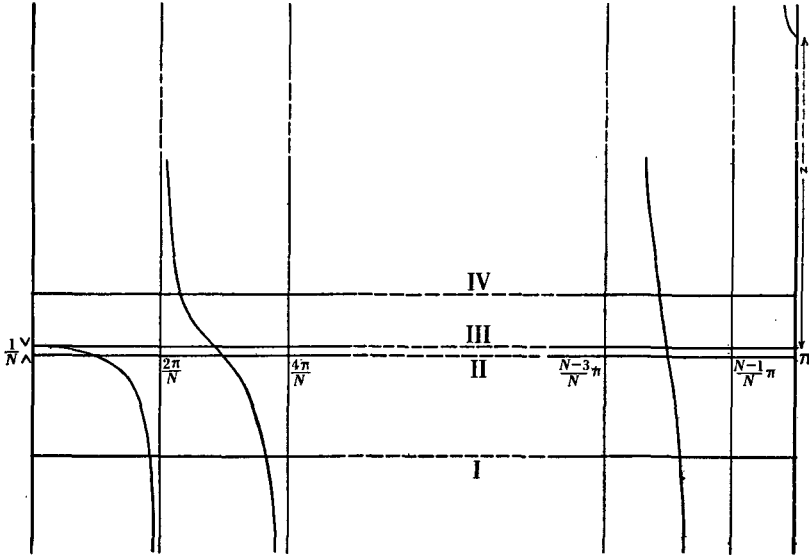


Fig. 3. Same as Fig. 1 (N odd).

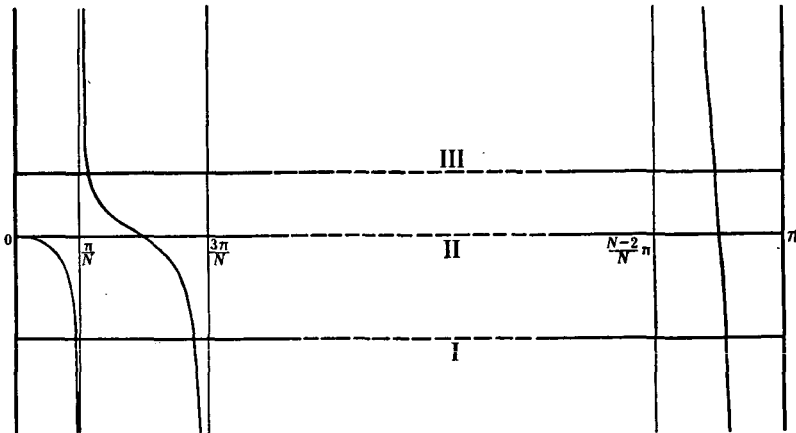


Fig. 4. Same as Fig. 2 (N odd).

roots, the lowest root again disappearing. Since N is very large, the ratio $(N + 1)/(N - 1)$ is very nearly unity and so we may say that, considering both equations (15) together, we have the expected N real roots for (13) provided

that $\epsilon_0/\gamma < 1$ but that if $\epsilon_0/\gamma > 1$ the lowest two roots drop out and leave only $N - 2$ real roots.

The case of N odd is similar, as is demonstrated by the Figs. 3 and 4. The equation (15a) has $\frac{1}{2}(N - 1)$ real roots if $\epsilon_0/\gamma < (N + 1)/(N - 1)$ but only $\frac{1}{2}(N - 3)$ if $\epsilon_0/\gamma > (N + 1)/(N - 1)$, while (15b) has $\frac{1}{2}(N + 1)$ real roots when $\epsilon_0/\gamma < 1$ and $\frac{1}{2}(N - 1)$ when $\epsilon_0/\gamma > 1$. Again in view of the largeness of N we may combine the results and say that if $\epsilon_0/\gamma < 1$ we have N real roots for (13) but only $N - 2$ if $\epsilon_0/\gamma > 1$, the lowest two roots disappearing.

It is shown later that, in the cases of interest to us, ϵ_0/γ is positive and greater than unity. The existence of surface states is found to depend on the inequality $\epsilon_0/\gamma > 1$ and so, while we defer the proof of this until § 4, henceforth we assume it to be the case. We have therefore $N - 2$ real roots for equation (13) which for N large may be considered to occupy the range $0 < \theta < \pi$, and the corresponding energies are given by (8) and (11) as

$$E = E_0 - \alpha + 2\gamma \cos \theta. \tag{16}$$

This is the same band of energies as for a linear chain neglecting end effects though it now contains two fewer states than before. Moreover these two missing states are those of smallest θ , i.e. those of highest energy.

Now it is clear physically that the total number of roots for the energy cannot be altered by the variation of the ratio ϵ_0/γ . The two real roots for θ that have disappeared must accordingly have become pure imaginary roots, since complex imaginary roots lead to complex values of the energy in view of the relation $\epsilon = 2\gamma \cos \theta$. We therefore put $\theta = i\xi$ in the equations (14) which, since

$$\sin N\theta = \sin Ni\xi = i \sinh N\xi \approx \frac{1}{2}ie^{N\xi}$$

and

$$\cos N\theta = \cos Ni\xi = \cosh N\xi \approx \frac{1}{2}e^{N\xi},$$

for very large N , both reduce to

$$\left. \begin{aligned} e^\xi &= \epsilon_0/\gamma, \\ \xi &= \log \epsilon_0/\gamma. \end{aligned} \right\} \tag{17}$$

i.e.

Thus the two states both have the same energy

$$E = E_0 - \alpha + 2\gamma \cosh \xi, \tag{18}$$

which lies above the band (16) since $\gamma > 0$ (M.J. *loc. cit.*) and $\cosh \xi > 1 > \cos \theta$.

2.2. *The wave functions of the electronic states.* The form of the electronic wave functions is determined by the values of the coefficients a_n . Now from (10) and (11)

$$\begin{aligned} (-)^n a_n &\propto e^{in\theta}(\epsilon_0 e^{-i\theta} - \gamma) - e^{-in\theta}(\epsilon_0 e^{i\theta} - \gamma), \\ &\propto (\epsilon_0/\gamma) \sin(n-1)\theta - \sin n\theta \\ &= \frac{\sin N\theta \pm \sin \theta}{\sin(N-1)\theta} \sin(n-1)\theta - \sin n\theta, \quad \text{by (14)} \\ &\propto \sin(n-N)\theta \pm \sin(n-1)\theta. \end{aligned}$$

Thus if the plus sign is taken

$$a_n \propto (-)^n \sin(\frac{1}{2}N + \frac{1}{2} - n)\theta, \quad (19a)$$

and if the minus sign is taken

$$a_n \propto (-)^n \cos(\frac{1}{2}N + \frac{1}{2} - n)\theta. \quad (19b)$$

(19a) corresponds to (14a) and hence, as a consideration of Figs. 1 and 3 shows, to a value of θ lying in one of the ranges $(2r+1)\pi/N > \theta > 2r\pi/N$. Similarly (19b) corresponds to (14b) and hence (see Figs. 2 and 4) to a value of θ lying in one of the ranges $2r\pi/N > \theta > (2r-1)\pi/N$. Omitting the normalization factor, we obtain for the corresponding wave functions

$$\psi_\theta = \sum_{n=1}^N \phi(\rho_n) (-)^n \sin(\frac{1}{2}N + \frac{1}{2} - n)\theta, \quad (2r+1)\pi/N > \theta > 2r\pi/N, \quad (20a)$$

$$\psi_\theta = \sum_{n=1}^N \phi(\rho_n) (-)^n \cos(\frac{1}{2}N + \frac{1}{2} - n)\theta, \quad 2r\pi/N > \theta > (2r-1)\pi/N, \quad (20b)$$

the appropriate energy being, in each case

$$E = E_0 - \alpha + 2\gamma \cos \theta, \quad (20c)$$

and the $N-2$ roots being given for even N by $r=1, 2, \dots, \frac{1}{2}N-1$, there being similar ranges for N odd.

For the other two roots we put $\theta = i\xi$ and obtain, since N is large, the wave functions in the form†

$$\psi_\xi = [\phi(\rho_1) + \phi(\rho_N)] - e^{-\xi}[\phi(\rho_2) + \phi(\rho_{N-1})] + \dots, \quad (21a)$$

or
$$\psi_\xi = [\phi(\rho_1) - \phi(\rho_N)] - e^{-\xi}[\phi(\rho_2) - \phi(\rho_{N-1})] + \dots, \quad (21b)$$

the appropriate energy being

$$E = E_0 - \alpha + 2\gamma \cosh \xi. \quad (21c)$$

These clearly represent surface states since, ξ being positive, the electron density falls off exponentially from the ends of the chain. Since $\xi = \log \epsilon_0/\gamma$, alternative forms for the expressions (21) are

$$\psi_\xi = [\phi(\rho_1) \pm \phi(\rho_N)] - (\gamma/\epsilon_0)[\phi(\rho_2) \pm \phi(\rho_{N-1})] + \dots, \quad (22a), (22b)$$

$$E_\xi = E_0 - \alpha + \gamma \left(\frac{\epsilon_0}{\gamma} + \frac{\gamma}{\epsilon_0} \right). \quad (22c)$$

ATOMIC p -STATES

3. Just as the s -states of the individual atoms of a chain give rise to a band of electronic levels for the chain as a whole so do the p -states, d -states, etc., interact to give bands of electronic levels. It may well happen also that the s - and p -states (say) lie close enough to one another for their mutual interaction to be important. This case, however, we consider in the next paper, restricting ourselves

† N.B. (21a) corresponds to (20a) if N is even but to (20b) if N is odd.

here to the interaction of atomic states of the same type only. In order to show that there is no loss of generality in considering the s -states in the preceding paragraph we now indicate briefly the results of the interaction of the atomic p -states.

There are three types of p -states classified according to their symmetry as p_x , p_y , p_z -states. However for a linear chain, and, indeed, for a simple cubic lattice, states of different types do not "combine"†. This implies that the relations corresponding to (9) separate into three groups involving respectively the p_x , p_y or p_z -states only, which may accordingly be treated independently. It is sufficient to consider the p_x -states and we find that the treatment runs parallel to that of § 2 for the s -states. $E_0, \alpha, \gamma, \epsilon_0$ are replaced by $E_1, \alpha_1, -\gamma_1, \epsilon_1$, the negative sign being placed before the third term in order that γ_1 should be positive‡. This change of sign, which is due to the functions p_x having opposite signs where their overlap is greatest, is the only modification of the subsequent work. We obtain, exactly as in § 2, two surface states of energy

$$E = E_1 - \alpha_1 + 2\gamma_1 \cosh \xi_1,$$

which again lie above the allowed band

$$E = E_1 - \alpha_1 + 2\gamma_1 \cos \theta.$$

The wave functions are given by expressions corresponding to (20) with the factor $(-)^n$ removed and to (21) with a similar modification of sign.

The p_y, p_z -states may be treated in an exactly similar manner to that employed for the s -states, there being no sign modification such as occurred for the p_x -states. We may observe that in each case the occurrence of the surface states depends on an inequality of the type $\epsilon_0/\gamma > 1$. Accordingly we include an investigation of the magnitude of this ratio.

THE MAGNITUDE OF THE RATIO ϵ_0/γ

4. It is the purpose of this paragraph to indicate that, at least in the case of the s -states, the ratio ϵ_0/γ is positive and greater than unity, as has been assumed in the foregoing analysis. An extension could presumably be made to p -states if required, but this is hardly worth while in view of the additional labour involved and the fact that the result is at best only indicative of the value of ϵ_0/γ .

Before we can determine the relative magnitudes of the integrals (6*b*) representing the quantities ϵ_0, γ we must specify the potential function V of the crystal-line field. We can at best give only an approximate form and the error should be of the same order as that inherent in the approximation of tight binding if we

† M.J. pp. 59 and 70.

‡ M.J. p. 71.

represent V by the simple sum of the potential fields due to the individual atoms. Thus we take

$$V = \sum_{i=1}^N U(\rho_i). \quad (23)$$

Then, if we neglect the interaction of all but nearest neighbours,

$$\begin{aligned} \gamma &= - \int \phi^*(\rho_{i+1}) [V - U(\rho_i)] \phi(\rho_i) d\tau \quad \text{by definition (6b)} \\ &= - \int \phi^*(\rho_{i+1}) U(\rho_{i+1}) \phi(\rho_i) d\tau \quad \text{in view of (23)} \\ &= - \int \phi^*(\rho_2) U(\rho_2) \phi(\rho_1) d\tau \end{aligned} \quad (24)$$

say, being independent of l .

Similarly, applying (23) to the definition of (6b), we have

$$\begin{aligned} \epsilon_0 = \alpha - \alpha' &= - \int \phi^*(\rho_1) [U(\rho_0) + U(\rho_2)] \phi(\rho_1) d\tau + \int \phi^*(\rho_0) U(\rho_1) \phi(\rho_0) d\tau \\ &= - \int \phi^*(\rho_1) [U(\rho_0) + U(\rho_2)] \phi(\rho_1) d\tau + \int \phi^*(\rho_1) U(\rho_0) \phi(\rho_1) d\tau \\ &= - \int \phi^*(\rho_1) U(\rho_2) \phi(\rho_1) d\tau. \end{aligned} \quad (25)$$

Now $U < 0$ and hence $\gamma > 0$ and $\epsilon > 0$. Also the integral (25) for ϵ_0 is of the form of the Coulomb interaction for an electron in the field of two atoms a distance c apart. Similarly the integral (24) for γ represents the exchange interaction. In general metal atoms do not form a stable diatomic molecular ion and this suggests that the Coulomb interaction should exceed that due to exchange, that is, that $\epsilon_0 > \gamma$. This argument is only tentative, however, for we have here specified the internuclear separation c of the metal atoms and it may well be that the curves for the Coulomb and exchange energies of the two metal atoms cross for some value of their separation.

In some particular cases we can obtain an idea of the relative magnitudes of ϵ_0 , γ by estimating the integrals using simplified wave functions of the type

$$\phi(\rho) = N_n \rho^{n-1} e^{-a\rho},$$

where

$$a = \frac{Z-s}{na_0}, \quad N_n = \sqrt{\frac{(2a)^{n+1}}{4\pi n!}},$$

which are due to Slater†. Z is the nuclear charge, s the screening constant estimated as in Slater's paper and a_0 the radius of the first Bohr orbit. Tables for the calculation of the integrals are given by Rosen‡.

† Slater, *Phys. Rev.* 36 (1930), 57.

‡ Rosen, *Phys. Rev.* 38 (1931), 255.

In this way we find for copper with an internuclear separation of 2.54 Å. (nearest neighbours in the metallic lattice) that $\gamma = 0.8\epsilon_0$. This ratio is hardly small enough to be convincing but we observe that, according to (24) and (25),

$$\gamma = \delta \times (\text{the average value of } -U(\rho_2) \text{ taken with respect to the product of the wave functions } \phi(\rho_1), \phi(\rho_2)),$$

$$\epsilon_0 = \text{the average value of } -U(\rho_2) \text{ taken with respect to the square of the wave function } \phi(\rho_1).$$

We may thus expect the ratio ϵ_0/γ to increase with decreasing δ and so be larger the better the approximation of tight binding, since the validity of this rests on the smallness of the overlap integral. In the examples cited above $\delta = 0.6$, the approximation is accordingly very poor, and it is hardly surprising that the ratio ϵ_0/γ only slightly exceeds unity. For the next nearest neighbours in the copper lattice the internuclear separation is 3.6 Å. and the overlap integral has the somewhat smaller value of 0.47. In this case we find that $\gamma = 0.57\epsilon_0$.

It would appear, therefore, that if the approximation which we use, namely that of tight binding, is valid then in general ϵ_0/γ will be appreciably greater than unity and the existence of surface states is accordingly predicted.

4.1. *Concluding remarks.* The equations (22) show that ϵ_0/γ is also a measure of the rate at which the electron density falls off as we proceed inwards from the end of the chain. In fact the magnitudes of the successive maxima of the wave functions, which occur once every interatomic distance, decrease by a factor γ/ϵ_0 . For the case just considered of copper with an internuclear separation $c = 3.6$ Å. this is 0.57. The falling off in the opposite direction, i.e. outwards from the end of the chain, is much more rapid, being equal to that of the wave function of the end atom. If we represent this by its simplified Slater form, the factor decrease per interatomic distance is not constant. However, the wave function has a maximum when $\rho = 1/(3a)$ and in the next 3.6 Å. falls off by a factor 0.025, while for all succeeding intervals c the decrease is even greater approaching 0.0007 in the limit.

It is interesting to observe that this more rapid decay of the surface state outside the crystal is also predicted by the approximation of nearly free electrons. Equations (28) of paper I show that the factor decrease of the wave function per interatomic distance c inwards is e^{-qc} while outwards it is $e^{-qcV_0/V}$, and V_0 is necessarily appreciably greater than V . Taking as reasonable estimates the values $V_0 = 12$ e.V., $V = 0.5$ e.V., with $c = 3.6$ Å., we find that $q = (0.065) 10^8$ cm.⁻¹ and thus the above factors are 0.79 and 0.005 respectively. These are of roughly the same order as those predicted on the tightly bound electron approximation, being in as close agreement as could be expected of the results of two extreme approximations.

Finally Maue, as we have already observed, argued that surface states could not arise if the electrons were taken to be tightly bound. He reasoned that in this case the quantity q of paper I would be large and that accordingly the boundary condition at the surface, namely equation (23) of I, could not be satisfied. This is, however, an attempted application of data appertaining to tightly bound electrons to a result that can only be relevant when the electrons are nearly free. Such a procedure is unjustifiable, and herein would appear to lie the error in Maue's reasoning. The present paper indicates that even when the electrons are to be considered as tightly bound surface states will in general occur.

SUMMARY

The wave functions and energies of both the normal and surface electronic states of a finite linear chain are determined in terms of the overlap integrals by the approximation of tight binding, it being assumed that the interaction of atomic s -states with p -states can be neglected. It is shown that the existence of surface states depends on the ratio of two overlap integrals being greater than unity, and reasons are given for expecting this to be so.

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