

On the Surface States Associated with a Periodic Potential

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The wave functions and energy levels associated with a finite one-dimensional periodic potential field are investigated. In a plot of the energy spectrum *versus* interatomic distance the surface levels appear only at lattice constants so small that the boundary curves for the allowed energy bands have crossed. The levels appear in the "forbidden" region between allowed bands in pairs one coming from each of the adjoining bands. In three dimensions these surface levels give rise to surface bands. The surface bands probably exist and are half-filled for diamond. They exist for all metals and are entirely unoccupied only for the monovalent metals.

IN dealing with wave functions in solids, the problem is simplified by considering an infinite crystal or else a part of an infinite crystal. This is done so as to deal with wave functions which satisfy simple boundary conditions. However, the simplifications so introduced obscure certain features of interest associated with the surface of the crystal. This defect was apparent to Tamm,¹ who considered the wave functions for an idealized one-dimensional crystal in which the atomic fields were represented by square potential wells (the model of Kronig and Penney²).

Tamm found in this case that it was possible to have energy levels whose wave functions were localized at the surface of the crystal. In this treatment a semi-infinite crystal was used, and Tamm found that one surface level was possible for each energy gap between the ordinary allowed bands of energies. In a later paper Fowler³ discussed Tamm's levels for a finite crystal and pointed out that the levels should occur in pairs because of the two faces of the crystal. They have since been discussed by Rijanow⁴ and Maue⁵ and most recently by Goodwin.⁶ In none of these papers, however, was it found how the surface levels originate from the atomic levels as the crystal is conceived of as being formed by varying the lattice constant from infinity to a finite value.

In the present paper we shall discuss the solution of this problem for a general one-dimensional crystal, Fig. 1(a), containing a finite number of atoms each of which is represented by a potential well whose shape is symmetrical about the center of the atom but is otherwise arbitrary. (This restriction considerably simplifies the mathematical work but is probably not essential.) The particular behavior of the potential beyond the edges of the end cells does not affect our results so long as it stays positive. We shall find that the surface levels exist only under certain particular conditions and shall see how they arise from the bands of allowed levels.

The results may be best understood in terms of a plot of energy *versus* lattice constant. In Fig. 2 such a plot is shown in a qualitative fashion. We see that at large lattice constants we have narrow energy bands such as are to be expected from small overlapping between the atoms. Furthermore, all the wave functions of the band are of the "penetrating type" rather than the surface type. The surface states first appear after the boundary curves of the energy bands have crossed. Postponing for the moment the origin of these boundary curves, we note that after they have crossed, two energy levels have separated, one from each of the bands. These energies correspond to wave functions of the surface type while the other energies correspond to penetrating wave functions. The energy difference between the two surface functions decreases exponentially as the number of atoms increases. The wave functions themselves are of the Tamm type near each surface—that is, they decay exponentially in both directions away

¹ I. Tamm, *Physik. Zeits. Sowjetunion* **1**, 733 (1932).

² R. de L. Kronig and W. G. Penney, *Proc. Roy. Soc.* **A130**, 499 (1931).

³ R. H. Fowler, *Proc. Roy. Soc.* **A141**, 56 (1933).

⁴ S. Rijanow, *Zeits. f. Physik* **89**, 806 (1934).

⁵ A. W. Maue, *Zeits. f. Physik* **94**, 717 (1935).

⁶ E. T. Goodwin, *Proc. Camb. Phil. Soc.* **35**, 205, 221, 232 (1939).

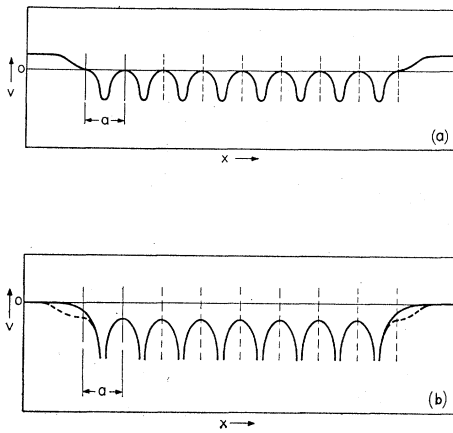


FIG. 1. The potential in the one-dimensional lattice. (a) A periodic potential. (b) The potential corresponding to Goodwin's "tight binding" approximation.

from the surface. The difference between the two surface waves is one of symmetry: The type of crystal envisaged here possesses a center of symmetry and the wave functions are therefore either symmetrical or antisymmetrical, depending upon whether they have the same or opposite signs on the two edges of the crystal.

The equations for the boundary curves of Fig. 2 are similar to those met with by applying Slater's method of finding three-dimensional wave functions.⁷ The wave function in an individual cell is expanded in terms of two functions g and u which are symmetrical and antisymmetrical about the center of the cell. If the wave function is required to be of the form $\psi = \exp(ikx)v(x)$ where $v(x)$ has the period "a" of the lattice, one finds by a familiar process that

$$\tan^2(ka/2) = -(g'/g)/(u'/u),$$

where g and u are the values at the edge of the cell of the functions g and u and g' and u' are corresponding derivatives. The allowed bands of energies occur where only one of the ratios (g'/g) and (u'/u) is negative; the forbidden regions occur where neither or both are negative. Certain crossings of the curves of Fig. 1 are possible; these may occur between $g'/g = \infty$ and $u'/u = 0$ and between $g'/g = 0$ and $u'/u = \infty$; no other crossings are possible. It is, therefore, seen that all possibilities for the occurrence of surface states are represented in Fig. 2.

⁷ J. C. Slater, Phys. Rev. **45**, 794 (1934).

In Goodwin's work surface states have been found to occur for the case of "tight binding"—that is, the case of large lattice constant and uncrossed bands. Goodwin's states arise from his use of a potential which is more realistic than ours; his potential is shown in Fig. 1(b). We see that it is periodic except for the outer edges of the end cells, where it is somewhat higher than in the other cells. If we make his potential periodic as indicated by the dotted lines, then the diagram for the states will be as in Fig. 2. If we now correct the energies of these wave functions by taking as a perturbation the difference between the periodic potential and Goodwin's, we find that two of the wave functions acquire energies above the boundary curves. These two functions will be surface states having wave functions damped towards the interior of the crystal. The origin of these states is essentially different from the origin of the states occurring after the bands have crossed. They will always lie near the band from which they originate. If we had used Goodwin's potential, we should have found these surface states lying just above each energy band in both the case of uncrossed and crossed bands. In the case of crossed bands there would then be four surface states. Goodwin, following the treatment of Maue, has also considered the case of almost free electrons. He uses a^{*} periodic potential without edge effects in the end cells. The surface states he obtains in this way are of the same type as ours, and in Appendix 5 we show that the conditions under which he obtains them are equivalent to the crossing of

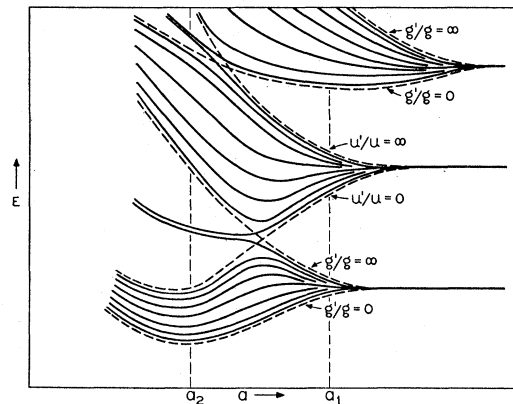


FIG. 2. Energy spectrum for a one-dimensional lattice with eight atoms.

the energy bands. In the remainder of this paper we shall be concerned only with the type of surface states represented in Fig. 2, which arise from the periodic potential.

If we suppose that there is one electron with each spin per atom then before the crossing of the boundary curves there are just enough states to accommodate all the electrons in the lowest band. After the crossing, however, there are one too few states in the lowest band and one electron is forced into a surface state. Hence after the crossing has occurred, the surface states will be half-occupied.

EXTENSION TO THREE DIMENSIONS

We can visualize to some extent how this last result would be modified in three dimensions by considering a potential equal to the sum of three one-dimensional potentials. For the case where the boundary curves have crossed so much that there is a complete gap in energy between the first and second allowed bands (this occurs when the energy gap in the one-dimensional Fig. 2 is more than twice the width of the lowest band), there are roughly half as many electrons left over as there are surface atoms. This may be seen as follows: For this case the wave functions are the products of three one-dimensional wave functions. For states in the lowest band each factor may run through $(N-1)$ values; hence there are $(N-1)^3$ states in the lowest band. Since there are N^3 electrons there are $N^3 - (N-1)^3 = 3N^2 - 3N + 1 \cong 3N^2$ electrons left over. For the surface states, two possible values are available for one factor and $(N-1)$ for each of the other two. Thus there will be $2(N-1)^2$ surface states for the x faces or $6(N-1)^2$ for all six faces or $6N^2 - 12N + 6 \cong 6N^2$ in all, the same as the number of surface atoms. These surface states form a band corresponding to the variations in energy of the two penetrating factors. Our reasoning indicates that $3N^2$ or half of these states will be occupied and we should therefore expect the surface band to be conducting in two dimensions just as a partially filled three-dimensional band is conducting.

The suppositions upon which the above considerations rest seem to be fulfilled for diamond. The work of Kimball⁸ has shown that for diamond the $2s$ and $2p$ boundary curves have

⁸ G. E. Kimball, *J. Chem. Phys.* **3**, 560 (1935).

crossed to such an extent that there is a wide region of forbidden energies making diamond an insulator. We should, therefore, expect that there would be half-filled surface bands and surface conductivity in diamond. Such a conductivity has not been observed and this may possibly be due to the presence of adsorbed atoms. If a layer of adsorbed atoms is attached to the surface by losing electrons to the vacant levels in the surface band,⁹ so many electrons might be added that the surface band would be completely filled and thus rendered nonconducting. The surface levels can enter into conduction in yet another way by acting as "impurity levels." Electrons in the normally filled states can be excited optically or thermally to the surface levels thus leaving a partially filled and therefore conducting band; similarly electrons can be excited from the surface levels to higher bands and thus enter into the conduction. The number of electrons involved in processes of this sort would depend upon the surface area of cracks in the crystal and would therefore lead to a structure sensitive behavior of the properties of semi-conductors. Considerations of this sort are not new in their general features; however, the fact that the surface levels will normally be half-occupied has not been shown before.

The forbidden regions between the x-ray levels do not arise from the crossing of the energy bands and our theory predicts no surface levels for them. There will be surface states of Goodwin's "tight binding" type in these energy gaps; they will lie very close to the allowed bands from which they originate. A similar situation exists between the highest occupied and lowest unoccupied bands of the alkali halide crystals (calculations for NaCl¹⁰ and LiF¹¹ show that these gaps correspond to uncrossed bands). Even where there are no surface states of the type considered here, it is, of course, still possible for electrons to be trapped on the surface because of polarization forces and resulting distortion of the lattice. However, this is a rather different type of process from the one we have been considering, which is more directly connected with the energy levels of the periodic potential.

⁹ See, for example W. G. Pollard, *Phys. Rev.* **55**, 1147(A) (1939) and also **56**, 324 (1939).

¹⁰ W. Shockley, *Phys. Rev.* **50**, 754 (1936).

¹¹ D. H. Ewing and F. Seitz, *Phys. Rev.* **50**, 760 (1936).

The surface states should occur for a number of metals. In the metals there is always a large degree of overlapping of the atomic level boundary curves but not in such a way as to result in a separation of the bands. Instead the bands overlap considerably. For a particular direction of the propagation vector k , for example normal to a 110 crystal face of a body-centered lattice, there will be allowed and forbidden values of energy. In the forbidden regions there will be wave functions corresponding to complex values of k and, since the boundary curves have crossed, these will give rise to surface states. Fig. 3(a) shows the dependence of energy upon k for the 100 plane in k space for sodium.⁷ The surface states correspond to values of k having real components corresponding to the edge of the Brillouin zone and an imaginary component perpendicular to the plane of the surface—the 110 plane in our example. The energy lies in the energy discontinuity at the edge of the zone. Fig. 3(b) shows qualitatively how the energy varies in the surface of the zone for the states of the first zone, the surface states, and the states of the second zone. We see that the lowest energy for the surface states is lower than the lowest energy in the second zone and higher than the lowest energy on the surface of the first zone. For the monovalent elements the first zone is only partially filled and all the electrons occupy states in the interior of the zone;¹² hence none have high enough energies to occupy surface states. In the divalent metals, however, some electrons occupy states in the second zone and therefore have energies higher than the lowest surface levels. On the basis of this reasoning we should expect that all metals save the monovalent ones to have some electrons occupying surface levels. These surface states will affect the charge distribution near the surface of the metal and their contributions must be considered when calculations of work function and contact potential are carried out for polyvalent metals.

The writer would like to express his gratitude to his colleague Mr. R. O. Grisdale and to Professor W. G. Pollard for several stimulating discussions upon the nature of the surface states.

¹² See, for example, N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford, 1936), Chapter V.

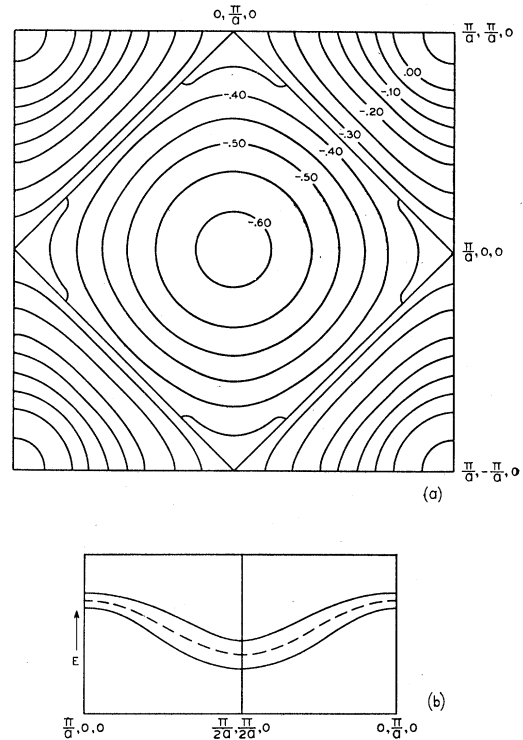


FIG. 3. Energies for surface states and penetrating states.

APPENDIX: MATHEMATICAL ANALYSIS

1. Expressions for the lattice functions

Let the center of the left-hand cell of Fig. 1(a) be $x=0$; then its edges are $x=\pm a/2$. For a given energy E there are only two linearly independent solutions of Schrodinger's equation in the field of this cell; since the potential is symmetrical about $x=0$, these may conveniently be chosen as $g(x)$ and $u(x)$ where g and u are, respectively, even and odd functions of x , i.e., symmetrical and antisymmetrical about $x=0$.

We shall require that the wave function be of the form $\psi_k = \exp(ikx)v(x)$ where $v(x+a) = v(x)$. If the function in the cell at $x=0$ is expanded in the form $\psi_k = ag(x) + ibu(x)$, then in the second cell it is $\psi = \exp(ika)(ag(x-a) + ibu(x-a))$ and the conditions that ψ and its derivative be continuous at the cell boundary $x=a/2$ are

$$ag + ibu = e^{ika}(ag - ibu), \quad (1)$$

$$ag' + ibu' = e^{ika}(-ag' + ibu'), \quad (2)$$

where

$$g = g(a/2), \quad u = u(a/2), \\ g' = (dg(x)/dx)_{x=a/2}, \quad u' = (du(x)/dx)_{x=a/2}.$$

These equations can be solved only if their determinant vanishes. This gives the equation

$$\tan^2 ka/2 = -\gamma/\mu, \quad (3)$$

where

$$\gamma = g'/g \quad \text{and} \quad \mu = u'/u.$$

This equation determines k as a function of γ and μ which in turn depend upon the energy. The wave function is multiplied in going from cell to cell by the factor

$$f = \exp 2i\theta \quad \text{where} \quad \theta = ka/2. \quad (4)$$

2. The value of ψ'/ψ for the running waves

We shall next find the value of

$$\frac{\psi'_k(a/2)}{\psi_k(a/2)} = \rho_k \quad (5)$$

for the resulting solution of Eq. (3). This ratio is

$$\frac{ag' + ibu'}{ag + ibu} = i\mu \tan \theta = \rho_k \quad (6)$$

as may be verified by noting that from (1) $b/a = (g/u) \tan \theta$ and by using (3).

3. The boundary conditions for the entire crystal

If $\psi_k(x)$ is a solution in the lattice field then

$$\psi_{-k}(x) = \psi_k(-x) \quad (7)$$

is also a solution for the same energy and, therefore, ψ_k and ψ_{-k} represent a complete set of linearly independent solutions (the pathological case of $\psi_k(-x)/\psi_k(x) = \text{constant}$ occurs only for energies of the boundary curves; it introduces no new features and is formally included in the equations given below.) The general solution in the crystal is

$$\psi = A\psi_k + B\psi_{-k}. \quad (8)$$

This function must join continuously to wave functions for the outside region. These outside wave functions must, of course, be damped exponential waves as we proceed away from the surface. This means that the ratio of $\psi'/\psi = \sigma$ evaluated at $x = -a/2$ (the left edge of the crystal) is a definite single valued function of the energy. For the symmetrical array of n atoms the value of ψ'/ψ at $x = na + a/2$ (the right edge) must be $-\sigma$. For negative energies in Fig. 1, σ must be positive.

We must therefore satisfy the equations

$$\sigma = \frac{A\psi'_k(-a/2) + B\psi'_{-k}(-a/2)}{A\psi_k(-a/2) + B\psi_{-k}(-a/2)} \quad (9)$$

and

$$-\sigma = \frac{A\psi'_k(na + a/2) + B\psi'_{-k}(na + a/2)}{A\psi_k(na + a/2) + B\psi_{-k}(na + a/2)}. \quad (10)$$

Some algebraic manipulation leads to the result that these equations possess solutions if

$$\sigma = \mu \tan \theta \tan n\theta \quad (S), \quad (11)$$

$$\sigma = -\mu \tan \theta \cot n\theta \quad (A), \quad (12)$$

where the expressions (S) and (A) mean that the corresponding solutions are either symmetrical or antisymmetrical functions, i.e., even or odd, about the midpoint of the crystal. The odd and even character can be established by computing the ratio of the denominators of Eqs. (9) and (10). If Eq. (11) is satisfied, this ratio is +1; for (12) it is -1.

4. Determining the allowed solutions

In order to justify all the statements made in the first part of this paper, it is necessary to investigate the solutions of these equations for eight different types of allowed bands and four different types of forbidden bands and to carry this out twice; once for n even and once for n odd. For the purposes of this paper we shall consider only the cases represented by the lattice constants a_1 and a_2 in Fig. 2 and these only for n even. In Fig. 4(a) and (b) are shown the general trend of the γ and μ curves for these two lattice constants. The energy scales have been distorted so that the allowed and forbidden bands correspond for the two cases.

Three ranges of values for γ/μ must be considered I $\gamma/\mu < 0$, II $0 < \gamma/\mu < 1$, III $1 < \gamma/\mu$. For the first of these $\tan^2 \theta$ is positive and θ lies between zero and $\pi/2$. The value of $\gamma/\mu = 1$ cannot occur since it implies that g and u are not linearly independent. For II and III $\tan^2 \theta$ is negative and we write θ in the form

$$\theta = \alpha - i\beta. \quad (13)$$

In Table I we have tabulated the expressions associated

TABLE I.

	I	
$\gamma/\mu < 0, \quad \beta = 0,$		$\tan \alpha = (\gamma/\mu)^{\frac{1}{2}} $
$\tan \theta = \tan \alpha$		$f = e^{2i\alpha}$
$\tan n\theta = \tan n\alpha$		$\cot n\theta = \cot n\alpha$
	II	
$0 < \gamma/\mu < 1, \quad \alpha = 0,$		$\tanh \beta = (\gamma/\mu)^{\frac{1}{2}} $
$\tan \theta = -i \tanh \beta$		$f = e^{2\beta}$
$\tan n\theta = -i \tanh n\beta$		$\cot n\theta = i \coth n\beta$
	III	
$1 < \gamma/\mu, \quad \alpha = \pi/2,$		$\coth \beta = (\gamma/\mu)^{\frac{1}{2}} $
$\tan \theta = -i \coth \beta$		$f = -e^{2\beta}$
$\tan n\theta = -i \tanh n\beta$	n even	$\cot n\theta = i \coth n\beta$
$\tan n\theta = -i \coth n\beta$	n odd	$\cot n\theta = i \tanh n\beta$

with these three cases. The equations have been so written that positive values will be obtained for α and β ; there is no loss in generality in this since both positive and negative values of k occur in (8). In Table II we give the values to

TABLE II.

	I	
$\sigma/\mu = \tan \alpha \tan n\alpha$		(S)
$\sigma/\mu = -\tan \alpha \cot n\alpha$		(A)
	II	
$\sigma/\mu = -\tanh \beta \tanh n\beta$		(S)
$\sigma/\mu = -\tanh \beta \coth n\beta$		(A)
	III	
	n even	
$\sigma/\mu = -\coth \beta \tanh n\beta$		(S)
$\sigma/\mu = -\coth \beta \coth n\beta$		(A)
	n odd	
$\sigma/\mu = -\coth \beta \coth n\beta$		(S)
$\sigma/\mu = -\coth \beta \tanh n\beta$		(A)

which $\tan \theta \tan n\theta$ and $-\tan \theta \cot n\theta$ reduce for these ranges.

The method employed in finding the solutions is a qualitative graphical one. Fig. 4(c) represents the variations

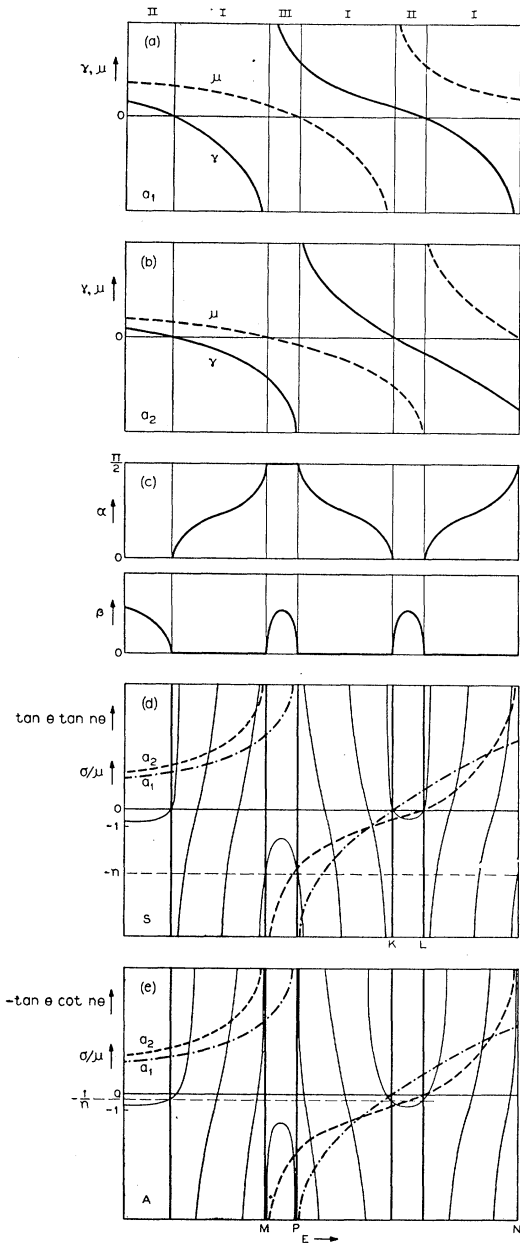


FIG. 4. Graphical results of the analysis. (a) γ and μ vs. E for $a=a_1$. (b) γ and μ vs. E for $a=a_2$. (c) α and β vs. E for $a=a_1$ and $a=a_2$. (d) Plot corresponding to Eq. (11). (e) Plot corresponding to Eq. (12).

of α and β which are qualitatively the same for Fig. 4(a) and (b). In Fig. 4(d) is plotted $\tan \theta \tan n\theta$ for the (S) type functions for the case of six atoms. Also on this figure are shown curves of σ/μ for both a_1 and a_2 lattice constants. For energies below zero on Fig. 1, σ will be a monotonically decreasing positive function of the energy and the variations in σ/μ will arise chiefly from those of μ . Intersections of σ/μ and $\tan \theta \tan n\theta$ on Fig. 4(d) correspond to solutions

of (11) except for two indeterminate cases occurring at the energies marked K and L in Fig. 4(d); these correspond to $\mu = \infty$ and a study of Eq. (11) for them shows that the right side is proportional to $1/n$ and hence that 1 and 2 are not solutions of (11). In Fig. 4(e) are similar curves for the A functions. The curve for a_1 at M and N and the curve for a_2 at P in the figure can be shown to give no solutions of Eq. (12). It is not practical to draw figures corresponding to large values of n as some of the significant features of Fig. 4 would not be apparent. However, in reaching the conclusions given in this paper, it has been supposed that n is very large; this means that $|1/n|$ and $|n|$ are surely lesser and greater than $|\sigma/\mu|$ in Fig. 4(e) and (d), respectively.

From consideration of the significant intersections on Fig. 4(d) and (e), one can establish the results portrayed in Fig. 2 and similar considerations for other values of n render these conclusions general.

The result that no surface states exist for the energy gap at a_1 can be established without recourse to the mathematical methods leading to Eqs. (11) and (12). Since this proof gives a more intuitive notion of the condition for the existence of surface states, it is given here: For any given energy value in the gap between bands in Fig. 2, γ and μ are positive and only damped waves are possible (this follows from Eq. (3)). The two solutions for the crystal are damped waves, one damped to the right and one to the left. Furthermore these waves can be taken as real as may be seen from the equation $b/a = (g/u) \tan \theta$. (Also if the waves could not be made real by multiplying by a constant factor, the real and imaginary parts would be linearly independent and our one-dimensional Schrodinger equation in the lattice would have four linearly independent solutions—an impossibility.) Consider the right edge of the crystal and choose $g(x)$ and $u(x)$ so that $g=u=1$, then $g'=\gamma$, $u'=\mu$. In order to have a surface state at the right edge, the wave function must consist predominantly of a wave damped to the left: if the crystal is large, the wave damped to the right is negligible at the right edge. Hence the wave function must be larger on the right edge than on the left edge of each cell. These various statements together mean that it must be of the form $Ag(x)+Bu(x)$ in the cell where A and B have the same sign (positive for simplicity) so that on the right edge the value $A+B$ is larger in absolute value than $A-B$ on the left edge. This requirement means that the slope on the right edge, $A\gamma+B\mu$, is also positive (since in the gap at a_1 , γ and μ are positive). The above reasoning shows that if a surface state exists on the right edge of the crystal and has a positive value on the right edge of the last cell it has also a positive slope, i.e., $d\psi/dx > 0$ at $x = (n + \frac{1}{2})a$. This wave function must join a wave function from the outside and if the energy is below zero the slope to value ratio for this outside wave function, denoted by $-\sigma$, is certainly negative. It is, therefore, impossible to join the two wave functions with continuous values and slopes and hence no surface states can exist for this energy gap. The situation is different for the gap at a_2 because there γ and μ are both negative and hence the ratio of slope to value for the wave function in the lattice

is negative at the right edge and a solution is possible. In order to prove that solutions actually do occur, considerations like those of Fig. 4 are needed.

5. Comparison with the case of almost free electrons

For the case of free electrons all the boundary curves have just crossed. This must be true because otherwise one would have the absurd result of forbidden energy ranges for free electrons; it can also be seen by considering the g and u wave functions corresponding to the boundary curves of Fig. 2. In the notation of section 1 of the appendix these are

$$g_m(x) = \cos \pi mx/a, \quad u_m(x) = \sin \pi mx/a. \quad (14)$$

Even values of m including zero give the bottoms of g bands and, except for $m=0$, the tops of u bands; odd values of m give the tops of g bands and bottoms of u bands. For free electrons the energy depends only on the value of m and we see that the bands are just crossed.

Goodwin, following the work of Maue, finds that if a potential of the form

$$V = -V_m(-)^m \cos 2\pi mx/a \quad (15)$$

is present, there will be surface states in the energy gap which appears at the energy corresponding to the unperturbed g_m and u_m if V_m is positive but not if V_m is negative. A first-order perturbation calculation shows that for V_m positive this potential raises the energy of g_m and lowers that of u_m if m is odd; for m odd g_m is the top of a g band and u_m the bottom of a u band. Hence the perturbation causes the bands to cross. A similar crossing occurs for m even. For V_m negative the bands are uncrossed and we have no surface states. Hence the findings of Maue and Goodwin for the case of almost free electrons are in keeping with the results of Fig. 2.

6. Comparison with Tamm's potential

In Fig. 5(a) we show the potential which Tamm used

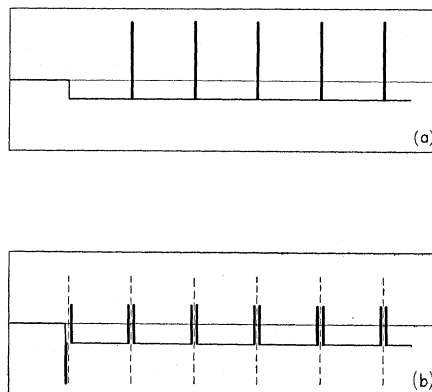


FIG. 5. (a) Tamm's potential. (b) The periodic and symmetrical potential equivalent to Tamm's.

in his original paper on surface states. The heavy lines represent δ -function potentials. Tamm's potential is not periodic for the last cell is incomplete. In Fig. 5(a) we have constructed a periodic potential from Tamm's potential by attributing one-half a δ -function to each edge of each cell. There is a negative half of a δ -function left over at the left edge of the crystal. Now a first-order perturbation calculation using the wave function of Section 4 shows that this potential corresponds to uncrossed bands. The Tamm states arise because of the negative δ -function which is left over. For the case of uncrossed bands we found a negative value of ψ'/ψ at the left edge of the crystal for a wave function which decayed exponentially into the crystal. Since the value of ψ'/ψ was positive for the exponential outside and to the left of the crystal, no surface state could occur. The role of left-over δ -function is to reverse the value of ψ'/ψ before it reaches the edge of the cell and thus permit the existence of a surface state.