

Quantum Mechanics of Electrons in Crystal Lattices

R. de L. Kronig and W. G. Penney

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diminution of the amount of triple molecules which give rise to the band here. The increase on the short wave-length side is explained as due to increase in single water molecules. Comparison of the work in the infra-red by others has confirmed these observations.

6. The changes in the intensity distribution of the band with addition of electrolytes is also explained by changes in the proportions of triple and single molecules. The development of the second maximum with concentrations higher than 76 per cent. of nitric acid is attributed to formation of hydrates.

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Quantum Mechanics of Electrons in Crystal Lattices.

By R. de L. KRONIG and W. G. PENNEY, University of Groningen.

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Introduction.—Through the work of Bloch our understanding of the behaviour of electrons in crystal lattices has been much advanced. The principal idea of Bloch's theory is the assumption that the interaction of a given electron with the other particles of the lattice may be replaced in first approximation by a periodic field of potential. With this model an interpretation of the specific heat,* the electrical and thermal conductivity,† the magnetic susceptibility,‡ the Hall effect,§ and the optical properties|| of metals could be obtained. The advantages and limitations inherent in the assumption of Bloch will be much the same as those encountered when replacing the interaction of the electrons in an atom by a suitable central shielding of the nuclear field, as in the work of Thomas and Hartree.

* Bloch, 'Z. Physik,' vol. 52, p. 555 (1928).

† Bloch, 'Z. Physik,' vol. 52, p. 555 (1928), vol. 53, p. 216 (1929), and vol. 59, p. 208 (1930); Peierls, 'Ann. Physik,' vol. 4, p. 121 (1930), and vol. 5, p. 244 (1930).

‡ Bloch, 'Z. Physik,' vol. 53, p. 216 (1929).

§ Peierls, 'Z. Physik,' vol. 53, p. 255 (1929).

|| Kronig, 'Proc. Roy. Soc.,' A, vol. 124, p. 409 (1929).

In the papers quoted a number of general results were given regarding the behaviour of electrons in any periodic field of potential. To obtain a clearer idea of the details of this behaviour with a view to the application in special problems, however, it appeared worth while to investigate the mechanics of electrons in periodic fields of potential somewhat similar to those met with in practice and of such nature that the energy values W and eigenfunctions ψ of the wave-equation can actually be computed. It is the purpose of this article to discuss a case where the integration is possible. In Section 1 the energy values and in Section 2 the wave-functions in their dependence on the binding introduced by the potential field are discussed for the one dimensional problem. In Section 3 the matrix elements of the linear momentum, which furnish the electric current associated with the various stationary states as well as the probability of radiative transitions between these states, are evaluated. In Section 4 the results are extended to the three dimensional case and those features considered which one may expect to find in the case of more general periodic fields of potential. Section 5 deals with some applications to physical problems.

1. *The Energy Values.*—The potential field which we shall consider is essentially that shown in fig. 1. Later on we shall pass to the limit $b = 0$

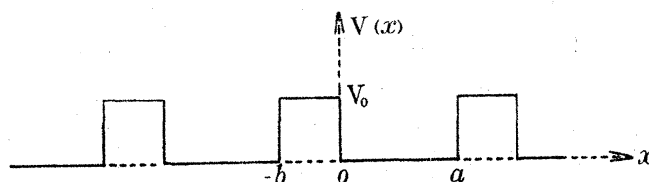


FIG. 1.

and $V_0 = \infty$ as this makes the results mathematically simpler without essentially altering their character, but to begin with we leave both b and V_0 finite. The wave-equation of the problem is given by

$$\frac{d^2\psi}{dx^2} + \kappa^2 [W - V(x)] \psi = 0, \quad \kappa^2 = \frac{8\pi^2m}{h^2}, \quad (1)$$

and following Bloch* we enquire after the solutions ψ which are periodic over a distance $L = G(a + b)$, where G is a large integer. As he has shown, these solutions must be of the form

$$\psi(x) = u(x) e^{i\alpha x}, \quad \alpha = 2\pi k/L, \quad (2)$$

where k is any integer and $u(x)$ a function periodic in x with the period $(a + b)$. To find $u(x)$ we can hence confine ourselves to one period of the lattice, say

* Bloch, 'Z. Physik,' vol. 52, p. 555 (1928).

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from $x = -b$ to $x = a$, and moreover, since we later shall make $V_0 = \infty$, we may assume $0 < W < V_0$. Substituting the expression (2) in equation (1) imposes on u in the range $-b \leq x \leq 0$ the condition

$$\frac{d^2u}{dx^2} + 2i\alpha \frac{du}{dx} - (\alpha^2 + \gamma^2)u = 0$$

with the solution

$$u = Ae^{(-i\alpha+\gamma)x} + Be^{(-i\alpha-\gamma)x}, \quad (3)$$

while in the region $0 \leq x \leq a$ we have

$$\frac{d^2u}{dx^2} + 2i\alpha \frac{du}{dx} - (\alpha^2 - \beta^2)u = 0$$

with the solution

$$u = Ce^{i(-\alpha+\beta)x} + De^{i(-\alpha-\beta)x}. \quad (4)$$

Here β and γ are given by

$$\beta = \kappa \sqrt{W}, \quad \gamma = \kappa \sqrt{V_0 - W}. \quad (5)$$

In particular β and γ are real quantities and may be assumed positive without loss of generality.

The constants A, B, C, D are to be so chosen that the solutions in the two regions have the same value and the same first derivative for $x = 0$, while from the periodic nature of u it follows that the solution (3) and its first derivative for $x = -b$ shall be equal respectively to the solution (4) and its first derivative for $x = a$. The four linear homogeneous equations resulting for the constants from these requirements are

$$\begin{aligned} A+B &= C+D, \\ (-i\alpha+\gamma)A + (-i\alpha-\gamma)B &= i(-\alpha+\beta)C + i(-\alpha-\beta)D, \\ Ae^{(i\alpha-\gamma)b} + Be^{(i\alpha+\gamma)b} &= Ce^{i(-\alpha+\beta)a} + De^{i(-\alpha-\beta)a} \\ (-i\alpha+\gamma)Ae^{(i\alpha-\gamma)b} + (-i\alpha-\gamma)Be^{(i\alpha+\gamma)b} &= i(-\alpha+\beta)Ce^{i(-\alpha+\beta)a} \\ &\quad + i(-\alpha-\beta)De^{i(-\alpha-\beta)a}, \end{aligned}$$

and can be satisfied only if the quantities β and γ , which according to equation (5) are directly related to the energy value W , satisfy the relation

$$\frac{\gamma^2 - \beta^2}{2\beta\gamma} \sinh \gamma b \sin \beta a + \cosh \gamma b \cos \beta a = \cos \alpha (a + b).$$

Passing now to the limit where $b = 0$ and $V_0 = \infty$ in such a way that $\gamma^2 b$ stays finite and calling

$$\lim_{\substack{b \rightarrow 0 \\ \gamma \rightarrow \infty}} \frac{\gamma^2 ab}{2} = P,$$

this relation becomes

$$P \sin \beta a / \beta a + \cos \beta a = \cos \alpha a, \quad (6)$$

a transcendental equation for βa .

To discuss the roots of this equation we have plotted its left-hand side as a function of βa in fig. 2, assuming for P the value $3\pi/2$. The values of βa

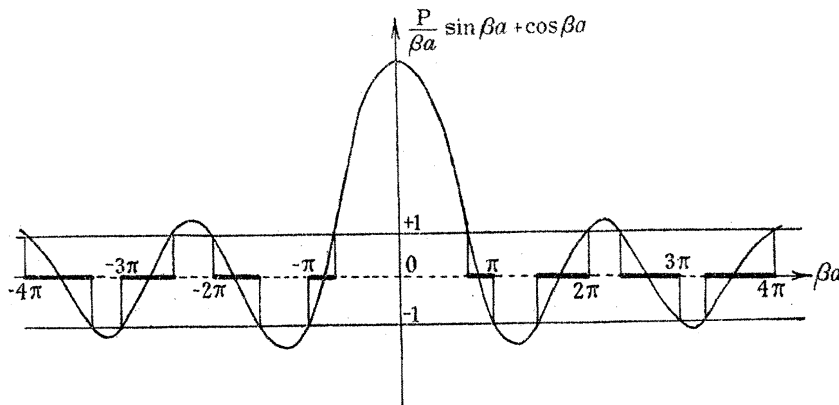


FIG. 2.

satisfying equation (6) are obtained as the projections on the βa -axis of the intersections of the curve with a straight line drawn at the distance $\cos \alpha a$ parallel to this axis. Since $\cos \alpha a$ lies between -1 and $+1$, and since the ordinates of the maxima of the curve have an absolute magnitude greater than 1 , then, upon varying α by giving k different values, the curve is found to consist of the portions between the parallels ± 1 on which there lie intersections and the remaining portions outside these parallels on which there lie no intersections. By projection the βa -axis too is divided into portions containing permissible values of βa (drawn heavily in fig. 2) and portions not containing such values. Letting L approach infinity allows us according to equation (2) to vary α continuously, and the permissible values of βa will then fill the heavily drawn portions of the βa -axis continuously. *The energy values which an electron moving through the lattice may have, hence form a spectrum consisting of continuous pieces separated by finite intervals.*

It is of interest to study the influence of P upon this spectrum. If P vanishes, the curve of fig. 2 goes over into $\cos \beta a$, the forbidden intervals of the βa -axis disappear, and we have one continuous spectrum of all energy values from 0 to ∞ . This is the limiting case of *free electrons*. Increasing P we obtain the forbidden intervals, the ratio of the length of these intervals to that of the adjoining allowed portions decreasing as we pass to large values of βa . We may say that fast electrons have less trouble to pass the potential

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barriers than slow electrons and can be considered more nearly as free. Letting P approach infinity reduces the allowed portions of the βa -axis to the points $n\pi$ ($n = \pm 1, \pm 2, \dots$). The energy spectrum now becomes discrete, the energy values

$$W = n^2 \hbar^2 / 8ma^2, \quad (n = 1, 2, \dots)$$

being those of an electron confined to move between two impenetrable potential barriers at a distance a apart. *The electrons are caught between the potential walls, they have become bound.*

Fig. 3 shows the change in the energy spectrum during the transition from the case of free to that of bound electrons.

In the region $0 \leq P \leq 4\pi$, $P/4\pi$ has been chosen as abscissa, while for $4\pi \leq P \leq \infty$ $4\pi/P$ is used. The shaded area represents the allowed values of $(\beta a/\pi)^2$.

2. *The Wave-functions.*—We come now to consider the *wave-functions* of our problem. Since b in the limit is reduced to zero, we are only concerned with the solution (4). Solving the linear equations for the constants A, B, C, D in this limiting case gives us

$$D = -C \frac{1 - e^{-i(\alpha - \beta)a}}{1 - e^{-i(\alpha + \beta)a}}. \quad (7)$$

u is given by equation (4) in the cell extending from 0 to a , while in the cell extending from ra to $(r+1)a$ it will be given by

$$u = Ce^{i(-\alpha + \beta)(x - ra)} + De^{i(-\alpha - \beta)(x - ra)},$$

being periodic with the period a . According to equation (2) ψ in this cell will then be given by

$$\psi = Ce^{i\beta x + ir(\alpha - \beta)a} + De^{-i\beta x + ir(\alpha + \beta)a}, \quad (8)$$

with C and D related by equation (7). If we require that ψ be normalised over a distance equal to its period L , we must have

$$CC^* = \frac{1}{2L} \frac{1 - \cos(\alpha + \beta)a}{1 - \cos \alpha a \cos \beta a + \frac{1}{P}(\cos \alpha a - \cos \beta a)^2}, \quad (9)$$

the asterisk denoting the conjugate.

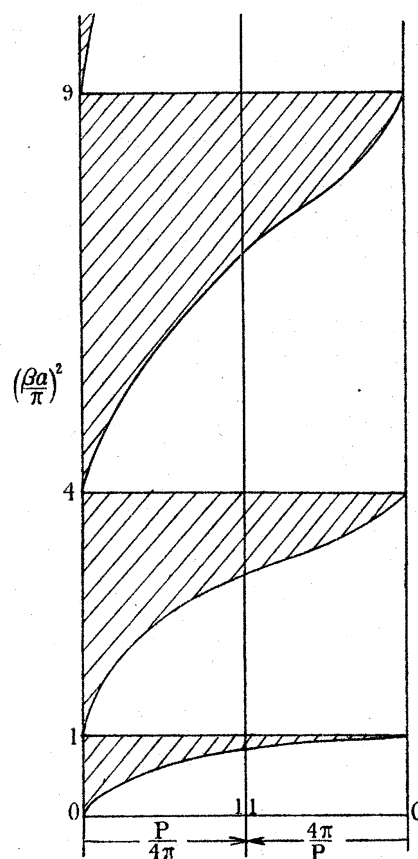


FIG. 3.

From equation (6) it appears that if with a given permissible value of βa a certain value of αa satisfies this equation, then also $\alpha a + 2n\pi$ and $-\alpha a + 2n\pi$ (n an integer) will satisfy it. We see, however, from equations (7) and (8) that by substituting $\alpha a + 2n\pi$ for αa we do not obtain any new wave-functions, while substituting $-\alpha a + 2n\pi$ for αa we get the same wave-function as that belonging to $-\beta a$, $-\alpha a$. We may hence, without loss of generality, accept the convention that if $n\pi \leq \beta a \leq (n+1)\pi$, we shall associate with it that value of αa for which $n\pi \leq \alpha a \leq (n+1)\pi$. In this way there is associated with every permissible value of βa one and only one value of αa , and we may use α to distinguish the stationary states.

We shall next investigate the influence of the value of P on the wave-functions. If we make P vanishingly small, then according to the convention just introduced βa will equal αa , and according to equation (7) D will vanish excepting for $\alpha a = n\pi$, in which case $D = \pm C$. The wave-functions according to equation (8) will go over into $e^{\pm i\alpha x}$ excepting for the special case just mentioned, in which they become equal to $\sin \alpha x$ and $\cos \alpha x$ so that we obtain the *wave-functions of free electrons*. At the same time the significance of α becomes apparent. For P approaching infinity, β takes the values $n\pi$, $D = -C$ according to equation (7), and we get from equation (8) the *wave-functions of electrons confined in their motion between impenetrable potential walls* at a distance a apart.

If we let L increase, the energy values, as mentioned before, come closer together, and for very large values of L we may enquire after the *density distribution of the energy values* in the allowed regions of βa . According to equation (2) this is evidently given by

$$\rho(\beta a) = \frac{L}{2\pi} \frac{d\alpha}{d\beta} = \frac{L}{2\pi \sin \alpha a} \left(\frac{P}{(\beta a)^2} \sin \beta a - \frac{P}{\beta a} \cos \beta a + \sin \beta a \right)$$

with $\rho(\beta a)$ so normalised that

$$\int_{(\beta a) \min.}^{(\beta a) \max.} \rho(\beta a) d\beta a = \frac{L}{2},$$

the integration extending over any one of the allowed regions of βa . Fig. 4 shows $\rho(\beta a)/L$ in the first of these for a value $P = 3\pi/2$, while for free electrons ($P = 0$) one obtains instead a horizontal line with an ordinate $1/2\pi$ for all values of βa . The binding has thus the effect of concentrating the stationary states at the limits of an allowed region.

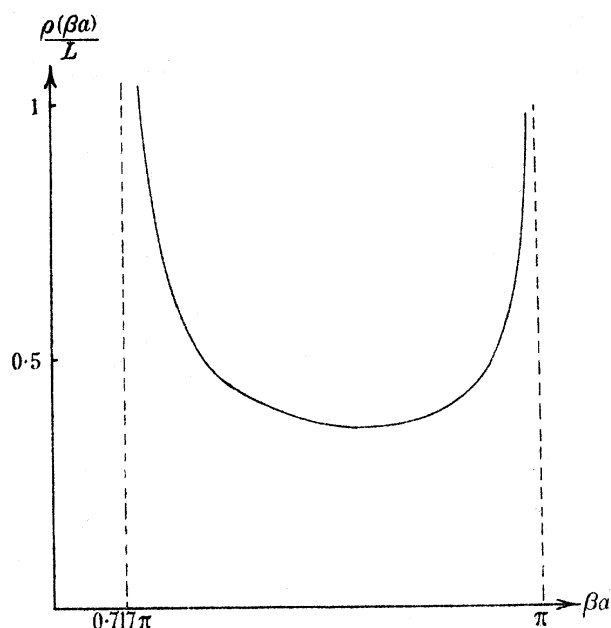


FIG. 4.

3. *The Linear Momentum.*—According to quantum mechanics the matrix elements of the linear momentum of an electron belonging to two stationary states α and α' are given by

$$p(\alpha, \alpha') = \frac{\hbar}{2\pi i} \int \psi_{\alpha}^* \frac{\partial \psi_{\alpha'}}{\partial x} dx,$$

the integration extending over one period L of the functions ψ_{α} and $\psi_{\alpha'}$. Introducing for ψ_{α} and $\psi_{\alpha'}$ their expressions given by equations (7), (8), (9) and performing the integration it is found that $p(\alpha, \alpha')$ vanishes unless αa and $\alpha' a$ differ by an integral multiple of 2π . Thus if the state α lies in the first allowed region of the positive βa -axis, then $p(\alpha, \alpha')$ is different from zero for only one state α' in the first, one in the third, one in the fifth positive allowed region, etc., and one in the second, one in the fourth, one in the sixth negative allowed region, etc., viz., those states for which $\alpha' a = \alpha a + 2n\pi$. A simple calculation gives us for the square of the absolute value of these non-vanishing matrix elements:

$$p(\alpha, \alpha') p(\alpha', \alpha) = \left(\frac{\hbar}{\pi a} \frac{\beta \beta'}{\beta'^2 - \beta^2} \right)^2 \times \frac{\sin^2 \alpha a (\cos \beta a - \cos \beta' a)^2}{\left[1 - \cos \alpha a \cos \beta a + \frac{1}{P} (\cos \alpha a - \cos \beta a)^2 \right] \left[1 - \cos \alpha a \cos \beta' a + \frac{1}{P} (\cos \alpha a - \cos \beta' a)^2 \right]} \quad (10)$$

To make the significance of equation (10) clearer we have computed from it in the first place $\pi a p(\alpha, \alpha)/h$ and plotted it in fig. 5 as a function of βa for the

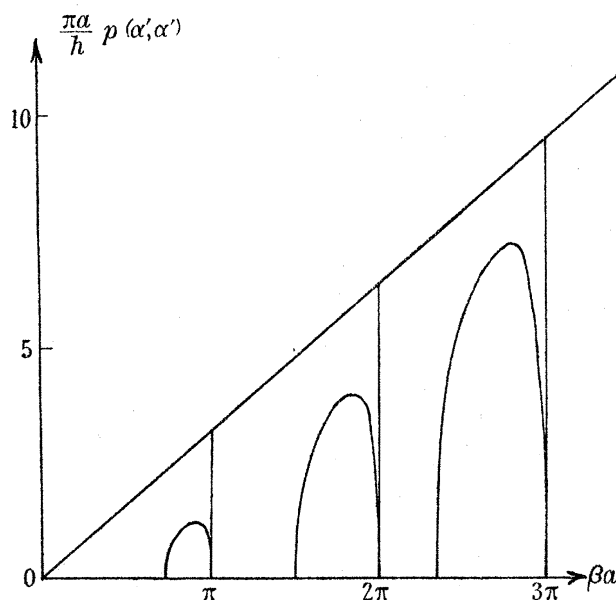


FIG. 5.

values of βa lying in the first, second and third allowed regions of the positive βa -axis, taking again P equal to $3\pi/2$. $p(\alpha, \alpha)$ represents the *time average of the linear momentum* of an electron in the stationary state α . As one easily sees

$$p(-\alpha, -\alpha) = -p(\alpha, \alpha).$$

Since the energy of the stationary states α and $-\alpha$ is the same, one may enquire if to a linear combination of the wave-functions ψ_α and $\psi_{-\alpha}$ there might correspond a linear momentum of greater absolute value, but from a simple calculation one finds that p lies then between $p(-\alpha, -\alpha)$ and $p(\alpha, \alpha)$. The straight line going through the origin in fig. 5 gives us $\pi a p(\alpha, \alpha)/h$ for the case of free electrons, showing that the potential barriers have the effect of reducing the linear momentum for a given value of the energy. Indeed they make it vanish when P approaches infinity. $p(\alpha, \alpha)$ also furnishes us the *electric current* associated with the stationary state α , whose time average is obtained by multiplying $p(\alpha, \alpha)$ by e/m , the ratio of the charge of the electron to its mass.

Furthermore we have plotted in fig. 6 the values of $\pi^2 a^2 p(\alpha, \alpha') p(\alpha', \alpha)/h^2$ as a function of βa when α is a state in the first allowed region while α' is that state

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in the second negative, third positive and fourth negative allowed region (curves 1, 2 and 3 respectively) for which the above quantity is different from zero. Again P has been taken equal to $3\pi/2$. For vanishing P all the curves are reduced to zero. For infinite P the results agree with those for an electron confined to move between impenetrable walls a distance a apart. The quantities

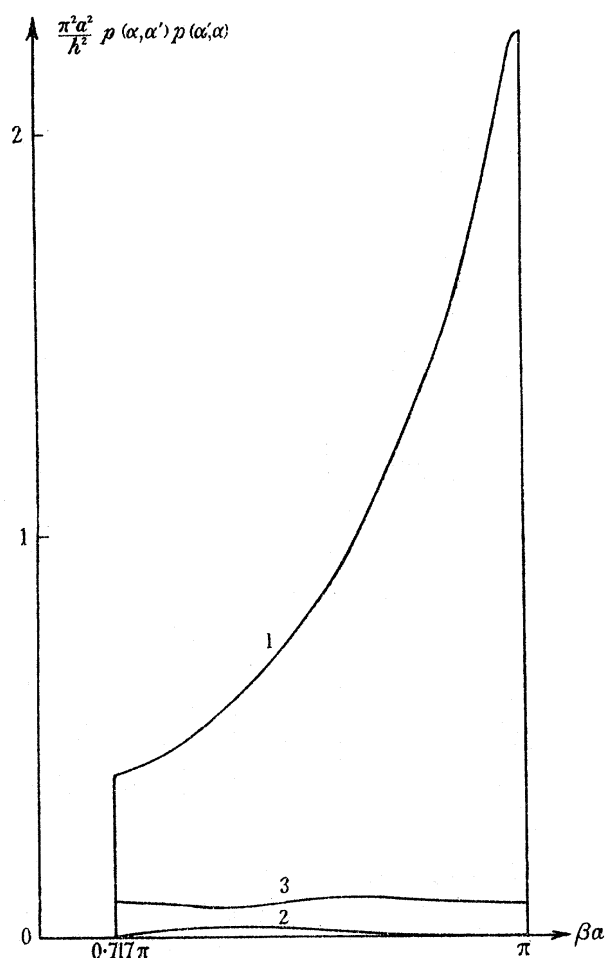


FIG. 6.

$p(\alpha, \alpha')$ determine the probability of radiative transitions between the stationary states, and one sees from fig. 6 that the transitions to the second negative region far outweigh all others.

4. *Extension of the Theory.*—The results just given can be generalised directly so as to apply to the case of a three-dimensional lattice in which the potential is the sum of three terms $V(x)$, $V(y)$, $V(z)$, each of which depends upon its co-ordinate in the same way as $V(x)$ on x in the one dimensional case. This means that the space is divided by infinitely thin potential barriers into cubical cells with an edge a . The wave-equation can then be separated

into three equations of the form (1), each involving only a single co-ordinate, viz.,

$$\left. \begin{aligned} \frac{d^2\psi_1}{dx^2} + \kappa^2[W_1 - V(x)]\psi_1 &= 0 \\ \frac{d^2\psi_2}{dy^2} + \kappa^2[W_2 - V(y)]\psi_2 &= 0 \\ \frac{d^2\psi_3}{dz^2} + \kappa^2[W_3 - V(z)]\psi_3 &= 0 \end{aligned} \right\}, \quad (11)$$

the total energy of the system and its wave-function being given by

$$W = W_1 + W_2 + W_3, \quad (12)$$

$$\psi = \psi_1 \psi_2 \psi_3 \quad (13)$$

respectively. Each of these equations can be treated in exactly the same way as equation (1). The stationary states will now be characterised by three quantities $\beta_1, \beta_2, \beta_3$, related to W_1, W_2, W_3 through equations analogous to equation (5), or by the corresponding quantities $\alpha_1, \alpha_2, \alpha_3$.

In the one-dimensional case we have seen that for $P = 0$ the energy W is a continuous function of αa , while for $P \neq 0$ W has discontinuities for $\alpha a = n\pi$ ($n = \pm 1, \pm 2, \dots$). Similarly we shall have here that for $P = 0$, W is a continuous function of $\alpha_1 a, \alpha_2 a, \alpha_3 a$, while for $P \neq 0$ the function becomes discontinuous on the surfaces $\alpha_1 a = n_1\pi, \alpha_2 a = n_2\pi, \alpha_3 a = n_3\pi$ ($n_1, n_2, n_3 = \pm 1, \pm 2, \dots$). The detailed behaviour of the energy values as well as of the wave-functions when P is varied follows directly from equations (12) and (13) and the results of the previous sections. The same remark applies to the matrix elements of the linear momentum. It is interesting to note in this connection that $p_x(\alpha_1, \alpha_2, \alpha_3; \alpha_1', \alpha_2', \alpha_3')$ is different from zero only provided $\alpha_1' a = \alpha_1 a + 2n\pi, \alpha_2' a = \alpha_2 a, \alpha_3' a = \alpha_3 a$ (n integer) with similar results holding for p_y and p_z .

A number of general qualitative features encountered in the special problem discussed may be expected to occur also for other periodic fields of potential. The falling apart of the energy spectrum into continuous regions separated by finite intervals has been met with previously in the case of a potential given by $V(x) = A \cos 2ax$, discussed by Strutt,* who also mentions that a similar

* M. J. O. Strutt, 'Ann. Physik,' vol. 86, p. 319 (1928). Attention may be called here to the fact that the energy regions considered by him as allowed are just the ones excluded for translatory motion through the lattice, and *vice versa*. The energy spectra of the equations corresponding to the potential $A \cos 2ax$ and to a potential as shown in fig. 1 for the particular case $a = b$ have also been discussed in connection with problems

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effect arises for any one dimensional periodic field of potential according to theorems proved by Haupt.† The stationary states, just as in our problem, can be characterised by a value α , the coefficient of the exponent in the function $e^{i\alpha x}$ which results from the wave-function when the potential field is reduced to zero. The energy W of the stationary states again has discontinuities at the points $\alpha a = n\pi$ ($n = \pm 1, \pm 2, \dots$). In an analogous manner the surfaces $\alpha_1 a = n_1\pi$, $\alpha_2 a = n_2\pi$, $\alpha_3 a = n_3\pi$ ($n_1, n_2, n_3 = \pm 1, \pm 2, \dots$) will be surfaces of discontinuity for the function $W(\alpha_1 a, \alpha_2 a, \alpha_3 a)$ in the general three-dimensional case.

Another result, valid for any periodic field of potential, is concerned with the matrix elements of the linear momentum $p(\alpha_1, \alpha_2, \alpha_3; \alpha_1', \alpha_2', \alpha_3')^\ddagger$. It may be shown that these can be different from zero only if $\alpha_1' a = \alpha_1 a + 2n_1\pi$, $\alpha_2' a = \alpha_2 a + 2n_2\pi$, $\alpha_3' a = \alpha_3 a + 2n_3\pi$ (n_1, n_2, n_3 integers). For the wave-functions in the two states $\alpha_1, \alpha_2, \alpha_3$ and $\alpha_1', \alpha_2', \alpha_3'$ according to Bloch (*loc. cit.*) are given by

$$\begin{aligned}\psi_{\alpha_1 \alpha_2 \alpha_3} &= u_{\alpha_1 \alpha_2 \alpha_3} e^{i(\alpha_1 x + \alpha_2 y + \alpha_3 z)}, \\ \psi_{\alpha_1' \alpha_2' \alpha_3'} &= u_{\alpha_1' \alpha_2' \alpha_3'} e^{i(\alpha_1' x + \alpha_2' y + \alpha_3' z)},\end{aligned}$$

where the u 's are periodic in x, y, z with the period a . Introducing these functions in the expression for the matrix element of p_x , say, gives us

$$\begin{aligned}p_x(\alpha_1, \alpha_2, \alpha_3; \alpha_1', \alpha_2', \alpha_3') &= \frac{\hbar}{2\pi i} \int \psi_{\alpha_1 \alpha_2 \alpha_3}^* \frac{\partial \psi_{\alpha_1' \alpha_2' \alpha_3'}}{\partial x} dx dy dz \\ &= \frac{\hbar}{2\pi i} \int u_{\alpha_1 \alpha_2 \alpha_3}^* \left[\frac{\partial u_{\alpha_1' \alpha_2' \alpha_3'}}{\partial x} + i u_{\alpha_1' \alpha_2' \alpha_3'} \right] e^{i[(\alpha_1' - \alpha_1)x + (\alpha_2' - \alpha_2)y + (\alpha_3' - \alpha_3)z]} dx dy dz \\ &= \frac{\hbar}{2\pi i} \int u_{\alpha_1 \alpha_2 \alpha_3}^* \frac{\partial u_{\alpha_1' \alpha_2' \alpha_3'}}{\partial x} e^{i[(\alpha_1' - \alpha_1)x + (\alpha_2' - \alpha_2)y + (\alpha_3' - \alpha_3)z]} dx dy dz,\end{aligned}$$

the second term in the bracket not contributing anything on account of the orthogonality of the two wave-functions. From the periodicity of the u 's it follows that we may write

$$u_{\alpha_1 \alpha_2 \alpha_3}^* \frac{\partial u_{\alpha_1' \alpha_2' \alpha_3'}}{\partial x} = \sum_{n_1 n_2 n_3 = -\infty}^{\infty} A_{n_1 n_2 n_3} e^{\frac{2\pi i}{a}(n_1 x + n_2 y + n_3 z)},$$

of classical physics by van der Pol and Strutt, "Phil. Mag.," vol. 5, p. 18 (1928). The advantage of the potential field considered in our article as compared with the field $A \cos 2ax$ lies in the fact that only elementary functions occur, making the evaluation of the various matrix elements very easy.

† O. Haupt, 'Math. Ann.,' vol. 79, p. 281 (1919).

‡ See also Kronig, *loc. cit.*

and introducing this in p_x leads immediately to the conclusion stated above. For two stationary states not separated by a surface of discontinuity of W the matrix element p hence always vanishes.

5. *Applications.*—A problem which we shall investigate here with the help of the one-dimensional model is the reflection of electrons of a given velocity falling from vacuum on to the lattice. The potential will then be as shown in fig. 7, for if our model is to represent an actual lattice, the potential of the

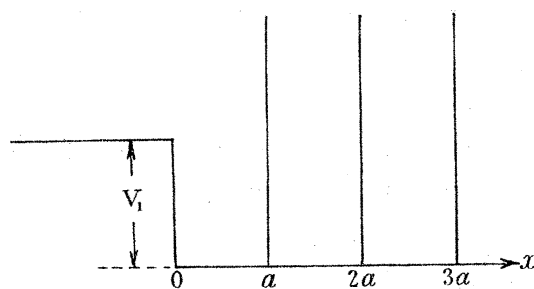


FIG. 7.

bottom of the lattice must be assumed to lie below that outside by a certain amount V_1 . We enquire after a solution representing an incident and a reflected beam of electrons for negative values of x and a transmitted beam for positive values of x . For $x < 0$ we shall have thus:

$$\psi = e^{i\alpha_0 x} + A e^{-i\alpha_0 x}, \quad (14)$$

while for $x > 0$ the solution is given by equation (8). α_0 and β are related by

$$\alpha_0^2 + \kappa^2 V_1 = \beta^2,$$

since the right and left-hand sides of this equation represent respectively the energies of the electron on the left and right of the point $x = 0$, which must be equal. The requirement that the function and its first derivative shall be continuous for $x = 0$ gives us the values of A in equation (14) and of C in equation (8).

AA^* measures the intensity of the reflected beam, that of the incident beam being equal to 1, and is hence equal to the coefficient of reflection R . We find that

$$R = \frac{(\cos \alpha a - \cos \beta a)^2 + (\sin \alpha a - \frac{\alpha_0}{\beta} \sin \beta a)^2}{(\cos \alpha a - \cos \beta a)^2 + (\sin \alpha a + \frac{\alpha_0}{\beta} \sin \beta a)^2} \quad (15)$$

in the allowed regions of βa , while $R = 1$ for the forbidden regions of βa . The

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quantity α in equation (15) is the one associated with β in the manner described in the earlier sections. In fig. 8 R is represented as a function of the velocity

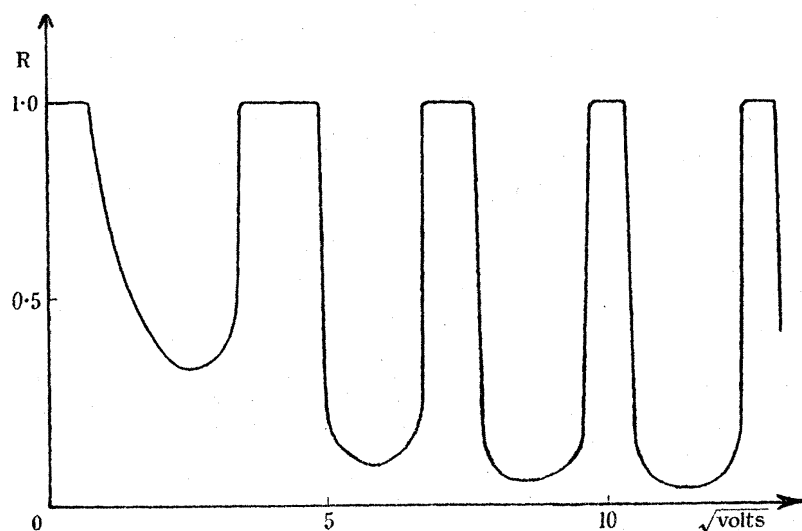


FIG. 8.

of the incident beam measured in $\sqrt{\text{volts}}$, which is proportional to α_0 . For the binding constant P we have again taken $3\pi/2$, while for V_1 and a we have assumed the values $V_1 = 15$ volts, $a = 2.2 \cdot 10^{-8}$ cm. (suggested by the work of Rupp quoted below). The most essential feature of the diagram is, that regions of partial reflection alternate with regions of total reflection, and that these latter have a finite breadth, decreasing as the velocity of the particles gets greater. For very large values of the velocity total reflection takes place only when the lattice constant a is very nearly an integral multiple of the de Broglie wave-length of the incident particles, the regions of total reflection then becoming quite narrow.*

Measurements of the reflection and transmission of electrons in crystal lattices have been performed by various observers.† A quantitative comparison of their results with those obtained here is made difficult by the following circumstances: (1) If we had made our calculation with the three-dimensional

* Morse, 'Phys. Rev.', vol. 35, p. 1310 (1930) has investigated the reflection and scattering of electrons by a crystal in which the potential depends upon the three co-ordinates through terms of the type $A \cos 2ax$. He obtains for the reflection coefficient at perpendicular incidence a curve essentially of the same type as that shown in fig. 8.

† Davisson and Germer, 'Phys. Rev.', vol. 30, p. 705 (1927); 'Proc. Nat. Acad.', vol. 14, pp. 317, 619 (1928); Rupp, 'Ann. Physik,' vol. 85, p. 981 (1928), vol. 1, p. 801 (1929), vol. 3, p. 497 (1929), and vol. 5, p. 453 (1930); 'Z. Physik,' vol. 61, p. 587 (1930); Thomson, 'Proc. Roy. Soc.,' A, vol. 117, p. 600 (1928), vol. 119, p. 651 (1928), and vol. 125, p. 352 (1929).

lattice, we would have obtained, besides the reflected and transmitted beams, diffracted beams which reduce the intensities of the former; (2) the periodic field of potential considered here differs from that actually present in a metal; (3) in the experiments it is found that some of the incident electrons suffer energy losses due to inelastic collisions with the electrons in the lattice, a phenomenon not provided for in our model. This effect also reduces the intensities of the reflected and transmitted beams. Nevertheless the principal features which appeared in our investigation, viz., the finite breadth of the reflection maxima, the decrease of this breadth with increasing velocity of the incident electrons and the decrease in the ordinates of the reflection minima, can be recognised in the experimental data (see in particular the work of Rupp).

An explanation can be given here also of a phenomenon recently observed by Rupp.* He finds that when the velocity of the incident electrons is gradually increased, new radiations appear in the soft X-ray spectrum of the substance bombarded at about the same velocities at which the reflection coefficient has a maximum. This can be understood if it be remembered that when the velocity begins to exceed that corresponding to the upper limit of a forbidden interval in the energy spectrum of the crystal, the impinging electron can enter into a new region of allowed energy values, giving it new possibilities for radiative transitions. According to this view the excitation threshold should differ from the reflection maximum by an amount equal to half the top-breadth of the maximum (lying toward higher velocities), but since in Rupp's measurements the maxima are already rather sharp the difference is probably obliterated by effects such as the inhomogeneity in the velocities, the imperfections of the crystal, etc. Perhaps, also, the constant energy losses of electrons impinging upon incandescent metals as observed by Rudberg† may be interpreted as corresponding to the transfer of the conduction electrons to the higher allowed regions of energy.

It is hoped to investigate later other physical properties of the model discussed as they appear in the phenomena mentioned at the beginning of this article.

Summary.

1. It is shown that the wave-equation representing the motion of an electron in a periodic field of potential can be integrated in terms of elementary functions when the potential takes the form of a series of equidistant rectangular barriers.

* 'Naturwiss.,' vol. 18, p. 880 (1930).

† Rudberg, 'Proc. Roy. Soc.,' A, vol. 127, p. 111 (1930).

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When the breadth b of these barriers is made infinitely small and their height V_0 infinitely large, the results become particularly simple, the influence of the barriers depending then only on the product bV_0 .

2. In the one dimensional problem for this limiting case the spectrum of permissible energy values is found to consist of continuous regions separated by finite intervals. By varying the quantity bV_0 from zero to infinity we pass from the case of free to that of bound electrons, and can thus study the changes in the allowed and forbidden ranges of the energy and in the wave-functions during this transition.

3. An investigation of the matrix elements of the linear momentum shows that the electrons can pass through the lattice and that there exists for them the possibility of transition to other stationary states under emission or absorption of radiation, the electrons thus having at the same time the characteristic properties of free and of bound electrons.

4. An investigation of the reflection of electrons by a crystal represented by the field of potential considered leads to results in qualitative agreement with the experimental facts. An explanation of a phenomenon recently observed by Rupp is given, and the possible connection of the theory with measurements of Rudberg is pointed out.