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ELECTRONIC STATES IN PERTURBED PERIODIC SYSTEMS

BY

H.M. James

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Hubert M. James

Physics Division

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ELECTRONIC STATES IN PERTURBED PERIODIC SYSTEMS

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Hubert M. James

Introduction

The electronic states of crystals (like those of any other system containing very many particles) can be treated only approximately in wave mechanics, by a forced separation of variables. To a good approximation, however, one can treat each electron as moving in a static potential field $W(\vec{r})$ due to the other electrons, and to all other charges in the system. The motion of an electron with energy E is thus described by a solution ψ of a wave equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi + W(\vec{r})\psi = E\psi$$

All physically significant solutions of this wave equation must be continuous, with their first derivatives, and must <u>remain bounded</u>. If for a given value of E there is no bounded solution of this equation, then the electron can never take on that value of the energy.

The wave mechanics of particles in perfectly periodic potentials, such as would exist in ideal crystals, can be regarded as completely understood, at least in principle. Many years before the advent of wave mechanics, Hamel[1] and Haupt[2] discussed, from the mathematicians point of view, an equation essentially identical with the one-dimensional wave equation for a particle of mass m in a periodic potential W (x):

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + W(x)\psi(x) = E\psi(x). \qquad (1.1)$$

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(1) G. Hamel, Math. Ann. <u>73</u>, 371 (1912)

(2) O. Haupt, Math. Ann. <u>76</u>, 67 (1914); ibid <u>79</u>, 278 (1919)

They were particularly concerned with the "oscillation theorems" for this equation, relating to the dependence on E of the existence or non-existence of bounded solutions $\psi(x)$. They showed that all solutions are bounded for certain ranges of E (the "permitted energy bands" for electrons in crystals), separated, in general, by ranges of energy for which no solutions are bounded ("forbidden bands"). This wave equation, and the corresponding three-dimensional one, have since been studied by a number of methods suited to various special purposes; it will suffice to mention here the work of Bloch,[3] Brillouin[4], and Kramers[5].

Recent work on the solid state has directed increasing interest on the motion of electrons in imperfect crystals. Electrons in real crystals move in potential fields which deviate from perfect periodicity for many reasons; imperfections in the crystal, missing or foreign atoms in the lattice, and in any case, termination of the crystal at free surfaces. These deviations from periodicity, if not too extensive, do not greatly disturb the band structure of the permitted energy values. Experiment and theory have, however, made it clear that they may give rise to electronic states with energies outside the permitted bands -- states in which the electron can not move freely through the crystal, but is restricted to a limited range near the surface or crystal cell where the periodicity is disturbed.

The existence of localized surface states in crystals was first suggested by Tamm,[6] on the basis of study of a special one-dimensional model. The latest and most instructive work of this type is that of Shockley, who discussed the solutions of the one-dimensional wave equation for a potential which is perfectly periodic in a finite range of x, representing the crystal, and rapidly approaches a constant value outside. (Fig. 1[7]). In such a case one might write the wave

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(3) F. Bloch, Z. Physik, 52, 555 (1928)
(4) L. Brillouin, Compt. rend. 191, 198, 292 (1930); Jour. Phys., (VII), 1, 377 (1930)
(5) H. A. Kramers, Physica, 2, 453 (1935)
(6) I. Tamm, Phys. Z. Sowj. 1, 733 (1932)
(7) W. Shockley, Phys. Rev. 56, 317 (1939).

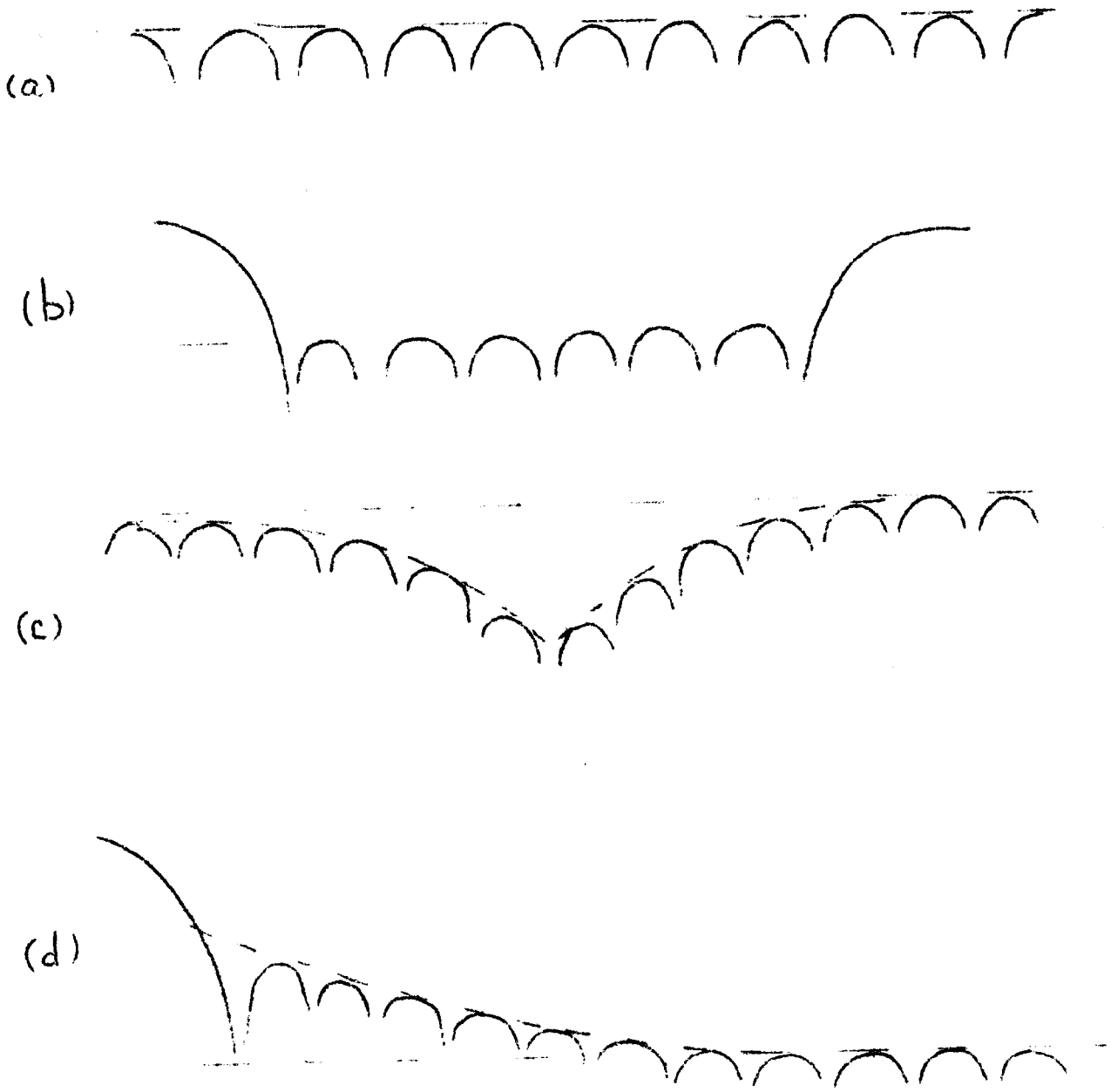

Figure 1.
Modified Periodic Potentials.

equation as

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + W(x)\psi(x) = E\psi(x) \qquad o<x<L, \tag{1.2}$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \quad x<o, x>L,$$

when W(x) is the periodic potential of the crystal, and V(x) a prescribed non-periodic function. An alternative approach to the physical problem is that of Goodwin[8], who used the perturbation method in treating a finite chain of identical atoms. Both methods indicate the existence of surface states, but closer investigation of their nature is required, particularly since experimental evidence as to their existence is not yet conclusive.

A quite different type of deviation from periodicity occurs where there is a foreign atom in a crystal lattice. The potential is profoundly modified in the crystal cell which contains this atom. In addition, if the net charge in this cell (due to all charges except the electron under consideration) is different from that in other cells, then the periodicity of the potential through the whole crystal is modified by the coulomb potential of the excess charge. The corresponding one-dimensional wave equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + [W(x) + V(x)]\psi(x) = E\psi(x), \tag{1.3}$$

where W(x) is again the periodic potential of the ideal crystal, and V(x) is a non-periodic perturbing potential. A similar modification of a periodic potential may arise from charges outside a crystal, or on its surface. Fig. (1c) represents the total potential energy of an electron in the presence of a foreign ion with excess positive charge. Fig. (1d) represents the potential energy of an electron near the surface of a crystal which has a negative surface charge and a corresponding positive Schottky layer, where the negative charge density falls below that existing in the interior of the crystal.

In the work to be reported here, attention has been centered on the development of a more satisfactory method for the solution of Eq. (1.3). Basically, the method involves

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(8) E. T. Goodwin, Proc. Camb. Phil. Soc. 35, 205 (1939)

constructing solutions for a single period of the periodic part of the potential, and piecing them together to form a solution of the wave equation through the whole domain of x. The same general idea has been used, in the case of perfectly periodic potentials, by Kronig and Penney[11], who studied square-well potentials, and by Shockley [7], who considered potentials symmetrical about the center of the cells, but otherwise unrestricted in form. The new formulation of this idea employed in the present work has proved to be especially convenient, being suited for discussions of the general features of the problem, and equally so for the study of special details; it appears also to be ideal when numerical calculations are to be made. Here it will be necessary to discuss its application to perfectly periodic potentials, in preparation for the later discussion of imperfectly periodic systems. A proof will be given (one-dimensional case only!) for the existence of a band structure in the permitted energies of particles moving in a periodic potential; some features of the wave functions, essential for later applications, will be derived.

It may be mentioned that the differential equation to be considered appears in quite different problems. The equation for a mechanical oscillator of mass M, displacement x, and spring constant k is

$$\frac{d^2x}{dt^2} = -\frac{k}{M}x.$$

If

$$k = k_0 + k_1(t),$$

where $k_1(t)$ is a small periodic change, this equation has the same form as Eq. (1.1), with the time variable t replacing the spatial variable x, and x playing the role of ψ. The band structure theorem to be proved then has the following significance: in the presence of a periodic perturbation of k, the oscillations of the system will remain bounded for values of ko (that is for frequencies of the oscillator) in certain ranges, but not for values of ko in other ranges. In these ranges of instability most oscillations will increase without limit as $t \to \infty$. Exceptional oscillations will increase without limit as $t \to -\infty$, but will approach 0 as $t \to \infty$. However, these oscillations are still unstable, for the smallest perturbation will convert them into exponentially increasing oscillations.

The same relations hold in LC circuits. In the presence of a given periodic perturbation of L or C the system will oscillate stably in certain ranges of LC or frequency, but will become unstable in other ranges of LC.

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(11) R. de L. Kronig and W. G. Penney, Proc. Roy. Soc., 130, 499 (1931)

The rings of Saturn give visual evidence of such stability phenomena. They consist of many tiny satellites rotating almost independently about Saturn, with frequencies greater the smaller the radius of their orbits. They are subject to periodic perturbations due to Saturn's major planets. Orbital motions of such satellites are stable for certain ranges of orbital frequency or radius; these radii are those for which the rings exist. For other frequencies, other radii, the motions are unstable; the satellites have long since moved out of such orbits, leaving the gaps between the rings. There is thus a close analogy in origin in the band structures of Saturns rings and of electronic energies in crystals.

§2. Preliminary Considerations and Definitions.

Let W(x) be a periodic function with period a:

$$W(x) = W(x+na), \quad x = \pm 1, \pm 2, \ldots \tag{2.1}$$

The range of x will be divided into periods or <u>cells</u> of length a, such that in the nth cell

$$na \leq x \leq (n+1)a. \tag{2.2}$$

The potential has then the same form in each cell. It is often convenient to choose the origin of coordinates so that the potential in each cell is symmetrical about the center (Fig. 2a); this is not always possible (Fig. 2b), nor is it necessary for application of the method to be described. Attention will, however, here be restricted to the symmetrical case.

We now fix attention on the 0<u>th</u> cell, $0 \leq x \leq a$. The wave equation

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + W(x)\psi = E\psi \tag{2.3}$$

is, for any fixed value of E, a linear second-order differential equation with two linearly independent solutions. In particular, there will always exist independent real solutions g and u such that

$$g(E;\tfrac{a}{2}) = 1, \quad g'(E;\tfrac{a}{2}) = 0, \tag{2.4}$$
$$u(E;\tfrac{a}{2}) = 0, \quad u'(E;\tfrac{a}{2}) = 1.$$

These basic solutions can be determined, if necessary, by numerical integration, beginning with the indicated initial conditions at $x = a/2$; they will be defined, and need by computed, only within the 0<u>th</u> cell. It is obvious that g(x) will be symmetrical about the center of the cell, whereas u(x) will be antisymmetrical. One will have then

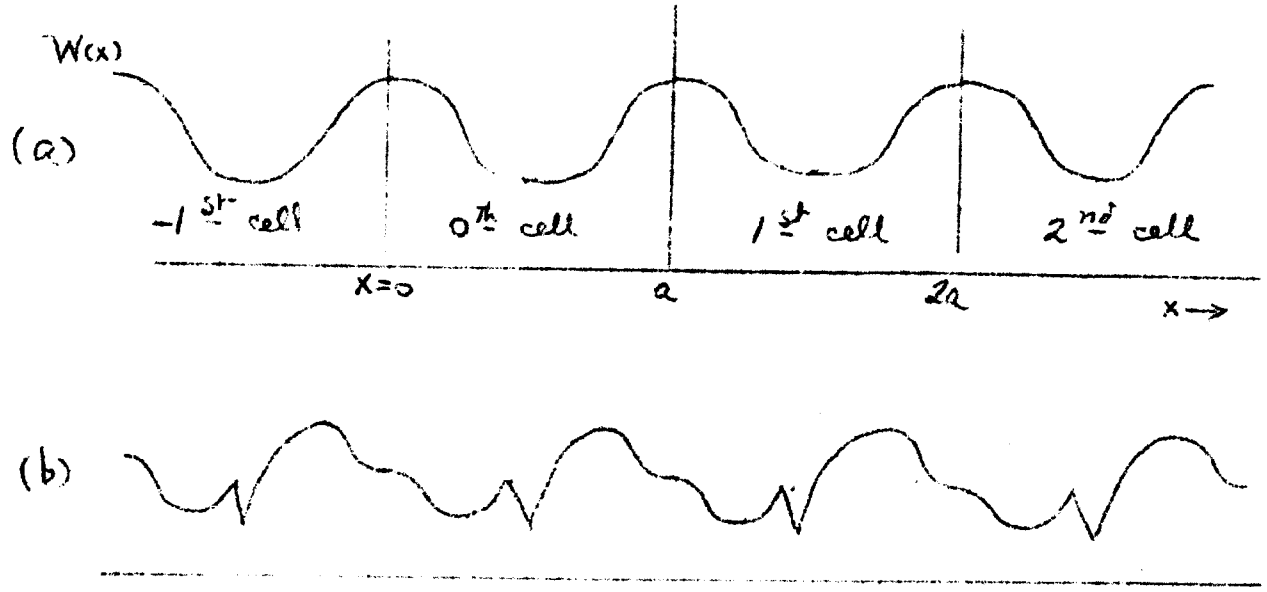

Figure 2. Periodic Potentials.

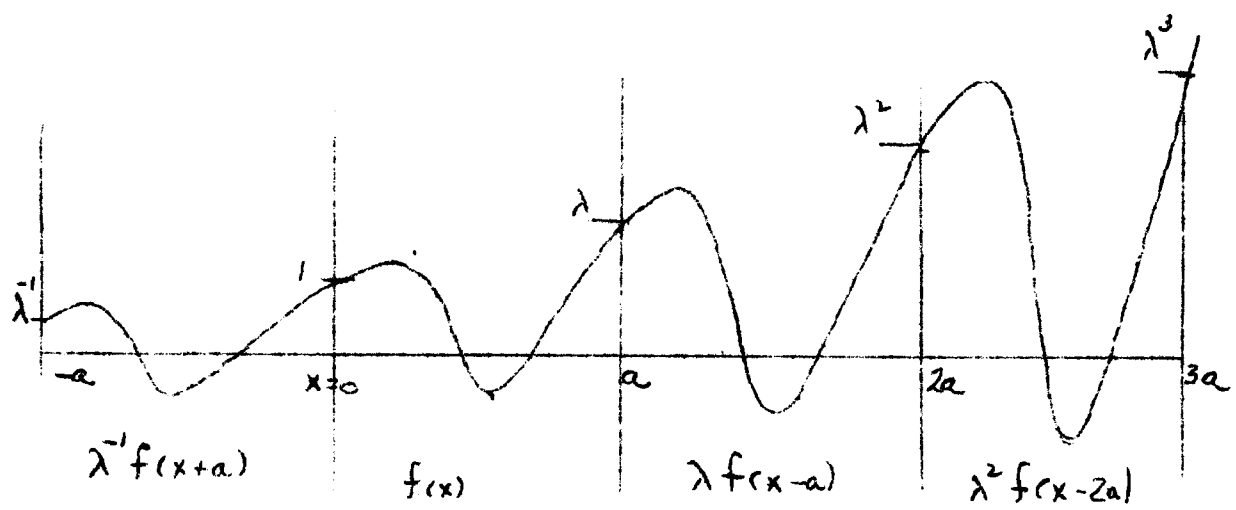

Figure 3. Construction of Crystal Solution from Self-matching Cell Solution.

$$g(E;0) = g(E;a) = g_0 \quad , \quad g'(E;0) = -g'(E;a) = g_0' \, ,$$

$$u(E;0) = -u(E;a) = u_0 \quad , \quad u'(E;0) = u'(E;a) = u_0' \, ,$$

The dependence of these quantities on E will be understood but not indicated hereafter.

An arbitrary solution of the wave equation in this cell (a "cell solution") can be expressed as an appropriate linear combination of g and u:

$$\psi(E;x) = \alpha_0 g(E;x) + \beta_0 u(E;x) \, . \tag{2.5}$$

Since the potential has the same form in the 1st cell as in the 0th cell, the solutions of the wave equation will have also identical forms. In particular, $g(E;x-a)$ and $u(E;x-a)$ will be special solutions, and an arbitrary solution in this cell can be expressed as

$$\psi(E;x) = \alpha_1 g(E;x-a) + \beta_1 u(E;x-a) \quad , \quad a \leq x \leq 2a. \tag{2.6}$$

In the same way, an arbitrary solution in the nth cell can be written as

$$\psi(E;x) = \alpha_n g(E;x-na) + \beta_n u(E;x-na) \, , \quad na \leq x \leq (n+1)a. \tag{2.7}$$

Now let ψ denote a solution of the wave equation continuous through the whole range of x, specified by giving its magnitude and slope at x=o. If the special solutions $g(x)$ and $u(x)$ are known in the 0th cell, one can gain a convenient and complete description of ψ by determining the corresponding values of α_n and β_n in all cells. This can be done, starting from the known values of α_0 and β_0, by the familiar process of joining cell solutions at the cell boundaries, in the following way.

If the functions of Eqs. (2.5) and (2.6) represent different portions of the same continuous solution of the wave equation, they must have the same magnitude and slope at x=a, where they join:

$$\begin{aligned} \alpha_0 g(a) + \beta_0 u(a) &= \alpha_1 g(0) + \beta_1 u(0) \, , \\ \alpha_0 g'(a) + \beta_0 u'(a) &= \alpha_1 g'(0) + \beta_1 u'(0) \, , \end{aligned} \tag{2.8}$$

or

$$\begin{aligned} \alpha_0 g_0 - \beta_0 u_0 &= \alpha_1 g_0 + \beta_1 u_0 \, , \\ -\alpha_0 g_0' + \beta_0 u_0' &= \alpha_1 g_0' + \beta_1 u_0' \, . \end{aligned} \tag{2.9}$$

Given α_0 and β_0, one can solve these equations to determine α_1, and β_1. Similar relations exist between (α_1, β_1) and (α_2, β_2) ; solving them, one can then determine α_2 and β_2. By continuing this process one can determine any α_n, β_n for n positive or negative. The calculation can, in fact, be given a convenient matrix form:

$$\begin{pmatrix} \alpha_n \\ \beta_n \end{pmatrix} = \begin{pmatrix} g_0 u_0' + g_0' u_0 & -2 u_0 u_0' \\ -2 g_0 g_0' & g_0 u_0' + g_0' u_0 \end{pmatrix}^n \begin{pmatrix} \alpha_0 \\ \beta_0 \end{pmatrix}, \qquad (2.10)$$

valid for all n, positive or negative.

This matrix formulation of the connection problem can be made the basis of a full discussion of the periodic potential problem, and its generalization to non-periodic potentials has proved to be useful. For most purposes, however, the method next to be described is preferable.

§.3 "Self-Matching" (σ) Cell Solutions.

The problem of connecting cell solutions can be made still simpler by the use of basic cell solutions, $f(E; x)$, with the special property of having the same slope-to-magnitude ratio at the two ends of the cell:

$$\frac{f'(E;0)}{f(E;0)} = \frac{f'(E;a)}{f(E;a)} = \sigma(E). \qquad (3.1)$$

To normalize these functions, it will be required that

$$f(E;0) = 1. \qquad (3.2)$$

In passing from the left end of the cell to the right, the solution will increase in magnitude by the factor

$$f(E;a)/f(E;0) = \lambda(E). \qquad (3.3)$$

Such solutions will here be called self-matching or, for brevity, σ cell solutions.

Self-matching solutions derive their name, and their importance, from the following property: given a <u>single</u> self-matching solution in the 0th cell, one can construct from it a continuous solution of the wave equation through the whole range of x. If $f(x)$ is a cell solution in the 0th cell, $c_1 f(x-a)$ will be a cell solution in the <u>1st</u> cell, $c_2 f(x-2a)$ a cell solution in the <u>2nd</u> cell, and so on. All these cell solutions will have the same slope - to - magnitude ratio at the ends of their respective cells. Therefore, if $c_1, c_2, \ldots$ are so chosen that the cell solutions have the same magnitudes

at their common cell boundaries, they will have there also the same slopes: they will fit together smoothly to form a continuous solution through the whole range of x. Since each solution changes by a factor λ in passing from the left end of the cell to the right end, the magnitudes can be made continuous by choosing $c_n = \lambda^n$. for all n, positive or negative (cf. Fig. 3). Thus one obtains from the given cell solution a solution of the wave equation for all x:

$$\psi(E;x) = \lambda^n f(E;\, x - na) \quad , \quad na < x < (n+1)a \, , \quad n = 0, \pm 1, \pm 2, \cdots \tag{3.4}$$

This solution has the same form in every cell; it changes from cell to cell only by a (possibly complex) multiplying constant λ.

It remains to investigate the existence of self-matching cell solutions. If the cell potential is symmetrical, a σ solution must (like any other solution in the $0^{\underline{th}}$ cell) be expressible as a linear combination of the special solutions g and u:

$$f(E;x) = \alpha(E)\, g(E;x) + \beta(E)\, u(E;x) \, . \tag{3.5}$$

The constants α and β must, by Eq. (3.1), be such that

$$\frac{\alpha g'(0) + \beta u'(0)}{\alpha g(0) + \beta u(0)} = \frac{\alpha g'(a) + \beta u'(a)}{\alpha g(a) + \beta u(a)} \, , \tag{3.6}$$

or

$$\left(\frac{\alpha}{\beta}\right)^2 = \frac{u_0 u_0'}{g_0 g_0'} \, . \tag{3.7}$$

If the energy under consideration is one for which the quantity on the right is neither zero nor infinite, there will be two values of α/β which satisfy this condition; for such energies there will be two independent σ cell solutions. These solutions will be distinguished, for all E, in the following way.

We define $\gamma(E) = g_0'/g_0$, $\mu(E) = u_0'/u_0$

$$\rho(E) = \frac{g_0'/g_0}{u_0'/u_0} = \frac{\gamma(E)}{\mu(E)} \, . \tag{3.8}$$

Then Eq. (3.7) becomes

$$\frac{\beta}{\alpha} = \mp \frac{g_0}{u_0} \rho^{1/2} \, . \tag{3.9}$$

The upper sign in this equation will apply to the σ solution $f_+(E;x)$, the lower sign to $f_-(E;x)$. The corresponding values of σ and λ follow from Eq. (3.1), written as

$$\sigma = \frac{g_0' + (\beta/a)\, u_0'}{g_0 + (\beta/x)\, u_0} \, . \tag{3.10}$$

and Eq. (3.3), written as

$$\lambda = \frac{g_0 - (\beta/\alpha)u_0}{g_0 + (\beta/\alpha)u_0} \quad . \tag{3.11}$$

Thus one obtains, by use of Eq. (3.2),

$$f_\pm(E;x) = \frac{1}{1 \mp \rho^{1/2}} \left\{ \frac{g(E;x)}{g_0} \mp \rho^{1/2} \frac{u(E;x)}{u_0} \right\} , \tag{3.12}$$

$$\sigma_\pm = \mp \mu \rho^{1/2} , \tag{3.13}$$

$$\lambda_\pm = \frac{1 \pm \rho^{1/2}}{1 \mp \rho^{1/2}} \tag{3.14}$$

It will be noted that as regards form (but not magnitude) f_+ and f_- are mirror images about the center of the cell. Also

$$\lambda_+ \lambda_- = 1 , \tag{3.15}$$

$$\sigma_- = -\sigma_+ . \tag{3.16}$$

Nature of the Crystal Solutions

From each σ cell solution one can construct a solution for all x, as already described:

$$f_+ \longrightarrow \psi_+ \quad , \quad f_- \longrightarrow \psi_- .$$

The character of these solutions, and in particular their boundedness or non-boundedness, depends on the value of ρ, which may be anything from $-\infty$ to $+\infty$, depending on the value of E. We shall here consider the characteristics of the ψ's as they depend on ρ, reserving for the next section the discussion of the occurrence of the various values of ρ.

Case 1. $\boxed{\rho > 0}$: Then $\sqrt{\rho}$ is real, α/β is real, and the ψ's are real.

If $0 < \rho < 1$, then λ_+ is real and greater than 1. Then ψ_+ increases in magnitude from cell to cell with increasing n; it oscillates with an amplitude which increases without limit as $x \to \infty$. As $x \to -\infty$, $\psi_+ \to 0$. On the other hand, λ_- is real but less than 1. Thus ψ_- oscillates with amplitude which increases exponentially as $x \to -\infty$, but $\psi_- \to 0$ as $x \to +\infty$. The general solution of the wave equation,

$$\psi = C_+ \psi_+ + C_- \psi_- ,$$

is necessarily unbounded either as $x \to +\infty$ or as $x \to -\infty$. In either case it is physically unacceptable.

If $\rho > 1$, λ_+ is real, and < -1. There is a change in sign in the function from cell to cell, but it remains true that ψ_+ shows an exponential increase in magnitude from cell to cell as $x \to \infty$. Similarly ψ_- increases exponentially in magnitude as $x \to -\infty$. Again there is no physically acceptable solution of the wave equation.

Case 2. $\boxed{\rho < 0}$

In this case $\sqrt{\rho}$ is imaginary; β/α is imaginary, and the functions f_+ and f_- are complex. Since $1+\sqrt{\rho}$ and $1-\sqrt{\rho}$ are complex conjugates, with the same modulus, it follows that their ratio λ_+ has modulus 1:

$$\lambda_+ = e^{i\theta} \quad , \quad \lambda_- = e^{-i\theta} \quad .$$

The solutions ψ_+ and ψ_- constructed from f_+ and f_- therefore change in phase from cell to cell, but they do not increase in magnitude; both remain bounded as $x \to \pm\infty$. The general solution of the wave equation,

$$\psi = C_+\psi_+ + C_-\psi_- ,$$

is bounded and therefore physically acceptable for all values of C_+ and C_-.

Case 3. $\boxed{\rho = 0}$

If $\rho = 0$ there is only one possible value of α/β, only one self-matching solution, with $\lambda = 1$. This repeats itself exactly from cell to cell; it is periodic with period a, remains bounded, and is physically acceptable.

There are, of course, other solutions without the property of changing by a constant factor from cell to cell. One of them can be constructed as follows. As $\rho \to 0$, ψ_+ and ψ_- approach a common periodic form. $\psi_+ - \psi_-$ is always a solution of the equation, and it can be shown to approach zero as $\sqrt{\rho}$. Therefore

$$\psi_\ell = \lim_{\rho \to 0} \frac{1}{\sqrt{\rho}} \left\{ \psi_+ - \psi_- \right\}$$

is a solution of the wave equation for $\rho = 0$; it is not bounded, and not physically acceptable.

The general solution of the wave equation, when $\rho = 0$, is

$$\psi = C_+\psi_+ + C_\ell \psi_\ell .$$

It is physically acceptable only if $C_\ell = 0$. Thus there is only one independent and physically acceptable solution of the wave equation for $\rho = 0$.

Case 4. $\boxed{\rho = \pm\infty}$

Here again there is only one value of α/β, and one self-matching solution, with $\lambda = -1$. This merely changes sign from cell to cell. It is periodic with period $2a$, bounded, and physically acceptable.

A second solution of the wave equation is

$$\lim_{\rho \to \pm\infty} \sqrt{|\rho|}\,\{\psi_+ - \psi_-\}.$$

It is not physically acceptable. For $\rho = \pm\infty$ there is only one independent and physically acceptable solution, ψ_+.

To summarize:

All solutions are bounded and physically acceptable for $\rho < 0$. No solutions are bounded and physically acceptable for $\rho > 0$. Only one solution (to a multiplying constant) is bounded and physically acceptable for $\rho = 0, \pm\infty$.

§4. Dependence of ρ on E.

To complete the proof of the band structure of the permitted energies in periodic potentials, it is only necessary to prove that ρ is positive for some ranges of E, negative for others. The following discussion is slightly more detailed than is required for this purpose, in order to bring out features of importance in other connections.

An energy E is in a forbidden band if the slope-to-magnitude ratios of g(x) and u (x) have the same sign at the cell edge, and in a permitted band if the signs are different. The behavior of these quantities, γ and μ, is easily deduced.

Since

$$\frac{d^2 g}{dx^2} = -\frac{2m}{\hbar^2}\{E - W(x)\}\,g \quad \text{, etc.,} \qquad (4.1)$$

the curves g(x) and u(x) will be concave to the x-axis when $E > W(x)$, and convex when $E < W$. Figure 4 indicates the general form of the solutions for a cell potential with minimum in the center, for a sequence of energies; only the part of the solutions for $0 < x < a/2$ is shown. For $E < W_{min}$ both curves are everywhere convex to the axis; γ and μ are certainly negative. As E is raised the following quantities vanish in the indicated order: $g_0', g_0, u_0', u_0, g_0', g_0, u_0', u_0, \ldots$.

The curves of $\gamma(E)$ and $\mu(E)$ have alternate zeros and infinities, resembling the tangent function in form. When E becomes so large that the variation in W is negligible one has approximately

$$\gamma(E) \approx C\sqrt{E}\,\tan(K\sqrt{E}),$$

$$\mu(E) \approx -C\sqrt{E}\,\cot(K\sqrt{E}). \tag{4.2}$$

In Fig. 5 are sketched the forms of $\mu(E)$ and $\gamma(E)$; Fig. 6 shows the corresponding form of $\rho(E)$, and the alternating forbidden and permitted bands of energy.

The exact succession of zeros of g_0, g_0', u_0, u_0' shown in Fig. 5 does not hold for all forms of cell potential. It can be shown that for other types of potential one may have reversals in the orders of zeros of g_0 and u_0', or of u_0 and g_0'. That is, one can only say that zeros will always occur in the following order: g_0', (g_0, u_0'), (u_0, g_0'), (g_0, u_0'), ...
The form of Fig. 6 is, however, unchanged by such reversals; it applies also when cell potentials are unsymmetrical.

If the associated zeros of g_0 and u_0', or g_0' and u_0, happen to coincide <u>exactly</u>, the corresponding forbidden band disappears without a trace. The constant potential is a very special kind of periodic potential for which all forbidden bands disappear.

§5. Characteristics of the Solutions.

In the permitted regions the solutions undergo only a phase change from cell to cell. This change is given by

$$\lambda_+ = e^{i\theta} = \frac{1+\sqrt{\rho}}{1-\sqrt{\rho}} = \frac{1+i\sqrt{|\rho|}}{1-i\sqrt{|\rho|}}, \tag{5.1}$$

whence it follows easily that

$$\tan\frac{\theta}{2} = \sqrt{|\rho|}. \tag{5.2}$$

The variation of θ with E is sketched in Fig. 7. Near the band edges where $\rho \to 0$ one has

$$\rho \approx -|E-E_e|,$$
$$\theta \approx \sqrt{|E-E_e|}. \tag{5.3}$$

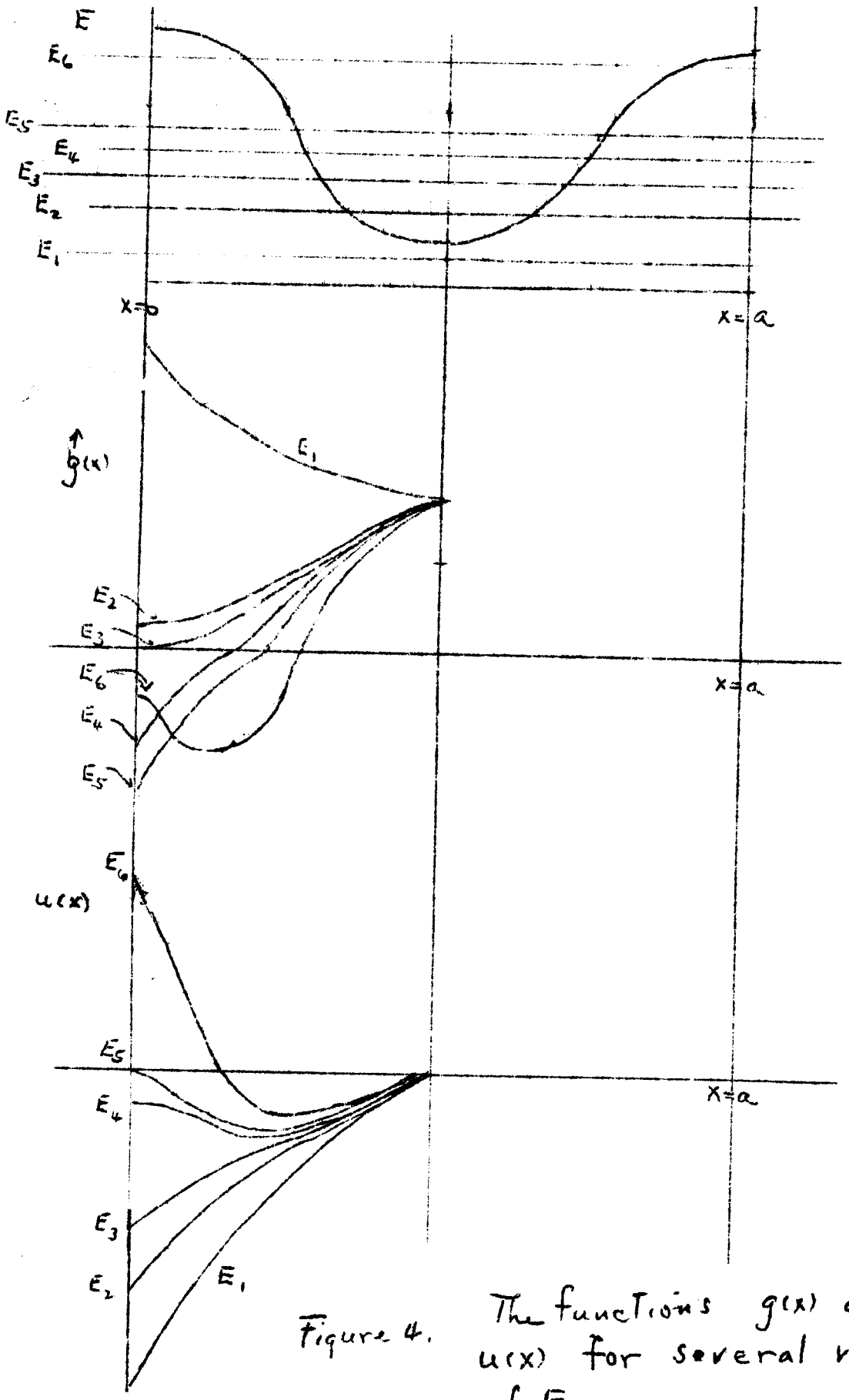

Figure 4. The functions g(x) and u(x) for several values of E.

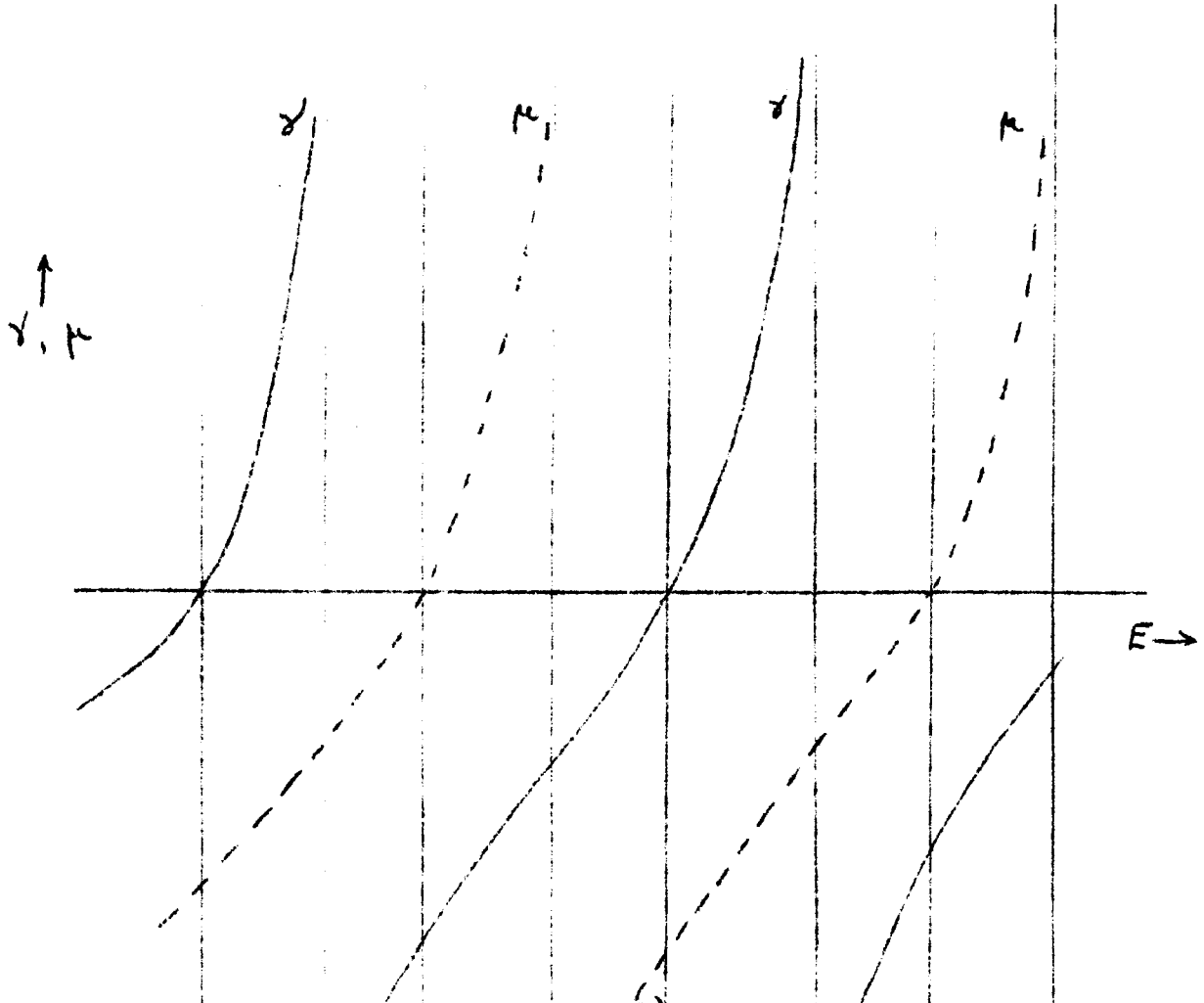

Figure 5. $\gamma(E)$; $\mu(E)$

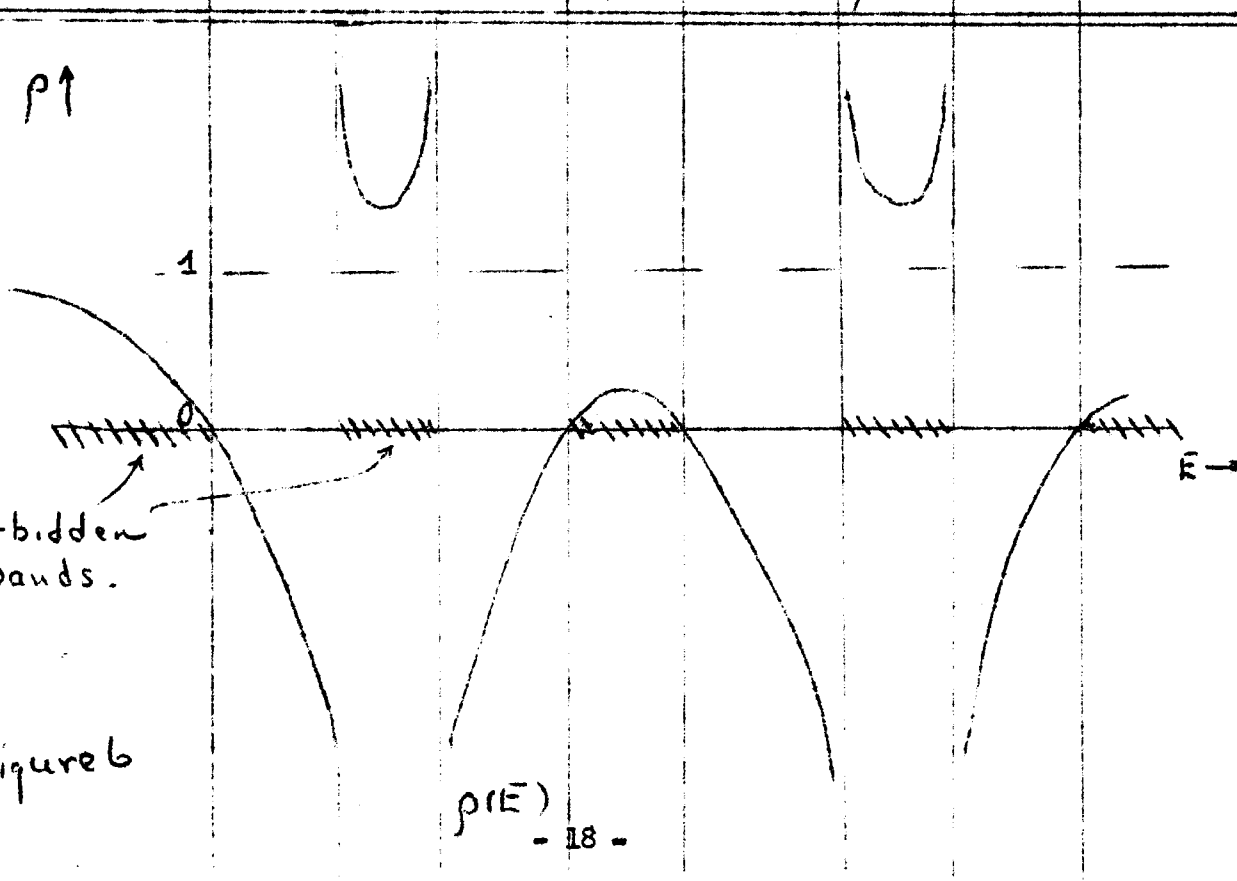

Figure 6 $\rho(E)$

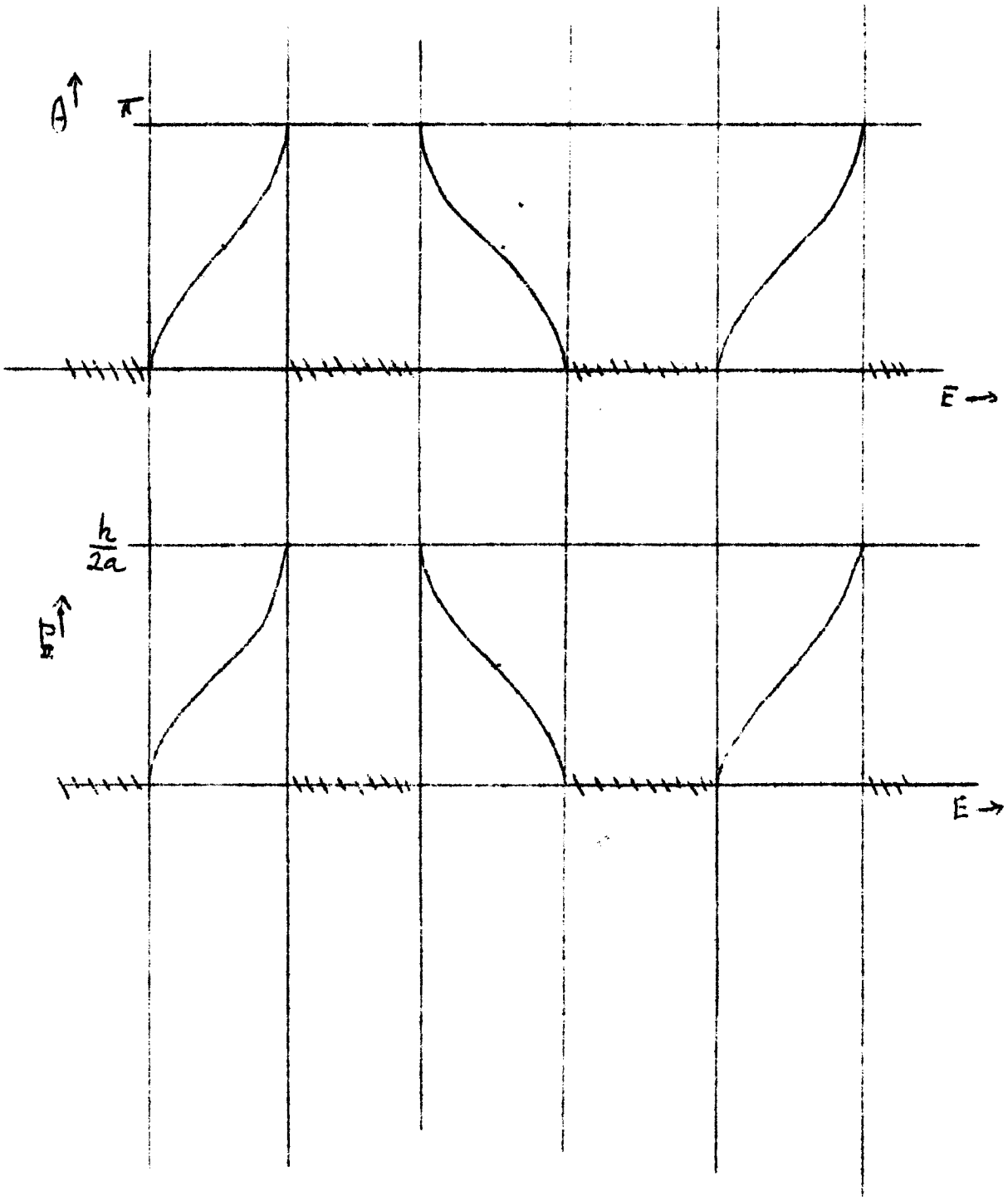

Figure 7. $\theta(E)$ and $p_x(E)$

Near the band edges where $\rho = -\infty$ one has

$$\begin{aligned} \mu &\approx \pm(E - E_e) \\ \rho &\approx -\frac{1}{|E - E_e|}, \\ \pi - \theta &\approx \sqrt{|E - E_e|}. \end{aligned} \tag{5.4}$$

In each band the phase change from cell to cell ranges from 0 to π. If we take two cells as the unit, the phase change from unit to unit is twice as great; it changes from 0 to 2π in each band. But a phase change of 2π leaves the function unchanged. Thus the function undergoes a slow change in phase from unit to unit at the edge of any band; in the middle of the band, however, the phase is changing rapidly.

In a forbidden region it is not the phase of the solution but its magnitude that changes from cell to cell. The change is exponential, but very slow at the edge of a band. It changes magnitude at maximum rate near the middle of a band.

We shall now define the quantity

$$p = -i \frac{\hbar}{a} \ln \lambda_+ , \tag{5.5}$$

a function of E. It will soon appear that if one takes the principal value of the many-valued logarithm, then p is the reduced momentum familiar in the theory of crystals. In a permitted band, where

$$\lambda_+ = e^{i\theta} \tag{5.6}$$

we have

$$p = \frac{\hbar}{a} \theta , \tag{5.7}$$

a real quantity, as the momentum must be. In a forbidden band, where λ_+ is real, p is imaginary, again as is characteristic of wave mechanical momentum in a non-classical region. In any case

$$\lambda_\pm = e^{\pm \frac{i}{\hbar} pa} . \tag{5.8}$$

Since

$$\psi_\pm(x) = \lambda_+^{\pm n} f_\pm(x - na) , \quad na \leq x \leq (n+1)a , \tag{5.9}$$

one has

$$\psi_\pm(x) = e^{\pm \frac{i}{\hbar} px} \left\{ \lambda_+^{\pm n} e^{\mp \frac{i}{\hbar} px} f_\pm(x - na) \right\}, \quad na \leq x \leq (n+1)a. \tag{5.10}$$

The quantity in brackets is continuous, since it is the product of continuous factors $\psi_\pm$ and $\exp\{\mp\frac{i}{\hbar}px\}$. Increase of x by a, together with the corresponding increase in n by 1, changes its first factor by $\lambda_+^{\pm 1}$, its second by $\exp\{\mp(i/\hbar)pa\} = \lambda_+^{\mp 1}$, and the last factor not at all; the product is unchanged. It follows that

$$P_\pm(x) = \lambda_+^{\pm n} e^{\mp\frac{i}{\hbar}px} f_\pm(x-na) \tag{5.11}$$

is periodic with period a.

Thus

$$\psi_\pm(x) = e^{\pm\frac{i}{\hbar}px} P_\pm(x) \tag{5.12}$$

where $P_\pm(x)$ are periodic with the period of the potential. In a permitted region $\psi_\pm$ have the form of a periodic function modulated by progressive waves with momenta $\pm p$; in a forbidden region they have the form of periodic functions modulated with real exponentials, increasing or decreasing to the right.