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ELECTRONIC STATES IN PERTURBED PERIODIC SYSTEMS

BY

H. M. JAMES

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By

Hubert M. James

Physics Division

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§6. Effective Momentum in a Periodic Potential.

The momentum of a particle in a periodic potential is not a constant, either in classical or wave mechanics. The quantity

$$p = -i\frac{\hbar}{a}\ln\lambda_+ , \tag{6.1}$$

which plays the role of momentum in this theory, is therefore properly to be called the effective momentum; the adjective will, however, be omitted where no confusion will result.

The logarithm in Eq. (6.1) is multiple-valued, with values differing by $2\pi i n$, where n is any integer, positive or negative. Change in $\ln\lambda_+$ by $2\pi i n$ will change p, as defined above, by $2\pi n\frac{\hbar}{a} = \frac{nh}{a}$. Equations (5.8) to (5.12) remain valid, however, no matter how this choice of p is made.

There are two ways in which one can make a systematic choice of the alternative values of p.

A. Restricting attention to permitted bands,

$$\lambda_+ = e^{i\theta} , \tag{6.2}$$

one can take

$$\ln\lambda_+ = i\theta , \qquad -\pi < \theta \leq \pi , \tag{6.3}$$

for every value of E. Then

$$-\frac{h}{2a} < p_r = \frac{\hbar}{a}\theta \leq \frac{h}{2a} . \tag{6.4}$$

The quantity thus defined will be called the reduced momentum. The dependence of p_r on E is sketched in Fig. 7, p. 19. The positive values shown in this sketch should be imagined to be supplemented by equal negative values for each E. Then for each value of E in the permitted bands there are two values of p_r, to each of which corresponds a solution of the wave equation of the form

$$\psi = e^{\frac{i}{\hbar} p_r x} P_r(p_r; x). \tag{6.5}$$

The relation of p_r to E takes on a familiar form when E is plotted against p_r, as shown in Fig. 8. For each value of p_r there is then a value of E in each permitted band. The vertical tangents of Fig. 7 here appear as horizontal tangents of $E(p_r)$ for $p_r = 0, \pm h/2a$.

B. It is possible to choose the value of the logarithm so that $|p|$ increases monotonely with E, as does the classical momentum. The resulting relation is shown in Fig. 9. This can be derived from the curve of Fig. 8 by displacing segments in p_r by appropriate multiples of h/a. For example, the left half of the second curve from the bottom is to be moved by h/a to the right, the right half by an equal amount to the left. In this way one associates with every E two uniquely defined values of p, negatives of each other. The momentum quantity thus defined is closely related to the classical total momentum, and will therefore be referred to as the total (effective) momentum, p_t. The energy is then a discontinuous function of the continuous variable p_t.

An important characteristic of the $E(p_t)$ curve can be understood by follow-

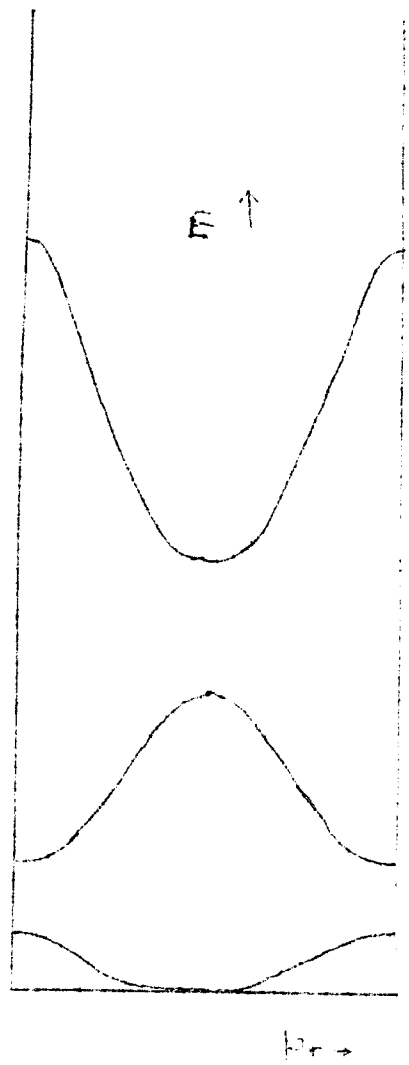

Figure 8. $F(kr)$

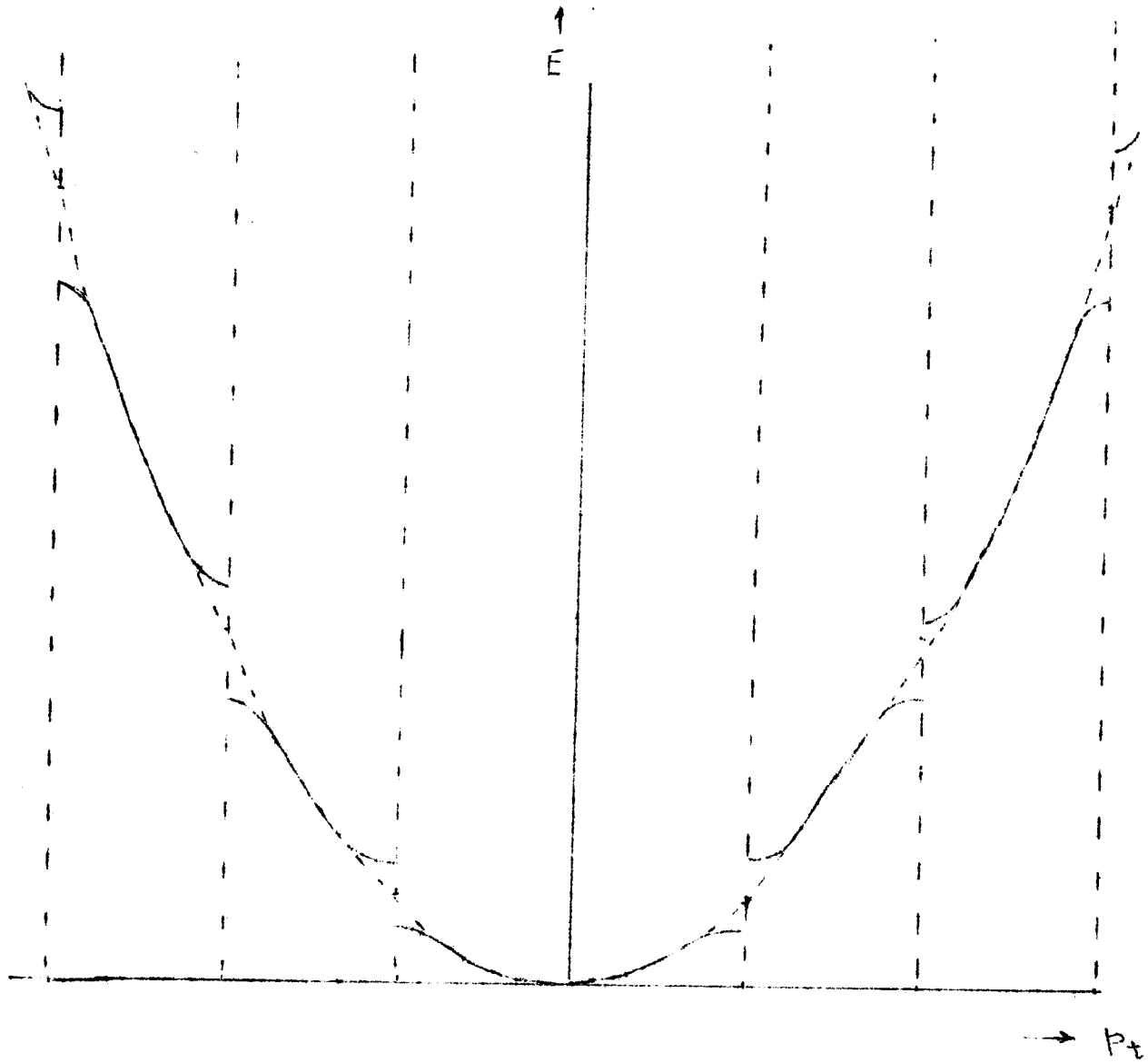

Figure 9. $E(p_t)$

ing the changes in form of this curve as the magnitude of the variations in the periodic potential is gradually increased from zero. When the potential energy is constant, $V = o$, one has

$$E = \frac{p^2}{2m}, \tag{6.6}$$

in wave mechanics as in classical mechanics. This parabola is indicated in Fig. 9. When the periodic potential is introduced, forbidden bands appear; breaks appear in the relation of E to p. The relation between E and p is most strongly modified near these breaks, and always in such a way that the tangents are horizontal at the breaks. The inner part of each segment will be little changed in form, if the variation in the potential is not too great. This is particularly true for very high E, when the variation in V has negligible effect on the form of the wave function. Equation (6.6) then applies except very close to the band edges, where there is a very abrupt curvature to give the horizontal tangent at $p_t = \frac{nh}{2a}$, $n = \pm 1, \pm 2, \ldots$ Roughly, one will expect Eq. (6.6) to apply to the total momentum p_t except for a range of E near the band edge which is comparable to the width of the forbidden band.

The form of the relation near the band edges follows from Eqs. (5.3) and (5.4). For p_t near the momentum p_e of any given band edge one can write

$$E - E_e = \frac{(p_t - p_e)^2}{2m^*}. \tag{6.7}$$

Here m^* is a constant of proportionality characteristic of the band edge under consideration; it will in general vary from edge to edge. Since Eq. (6.7) has the form of the classical relation between the kinetic energy $E - E_e$, momentum $p_t - p_e$, and mass m^* of a particle, m^* is called the effective mass of the

particle. It will appear later that it plays the role of the mass of the electron in other connections. The applicability of this concept, like that of Eq. (6.7), is restricted to the neighborhood of a band edge.

It will be noted that if E is in a permitted band and just above the band edge, then $E-E_e$ and hence m* will be positive. If, however, E is just below the top of a permitted band, $E-E_e$ will be negative and m* must be negative. Thus the effective mass of an electron near the bottom of a band is positive, but near the top of a band it is negative. The physical significance of this statement will appear in the next section.

As already noted, the curvature of $E(p_t)$ near the band edges becomes very great as E increases; that is, $\frac{1}{m^*}$ becomes very large, and m* correspondingly small. In general one can expect m* to decrease as one goes to higher and higher bands.

§7. Motion of a Wave Packet in a Periodic Potential.

The wave functions discussed thus far are stationary-state functions, describing electrons which have exactly defined energies, but may be anywhere in the crystal. To describe an electron with well-defined position, such that its motion through the crystal can be followed, one must use a <u>wave packet</u>, a wave function with a limited extent in space. Such wave functions must be solutions of the general wave equation, but can not be solutions of the stationary-state wave equation. Every such function can be expressed as a linear combination of the stationary-state solutions of the general wave equation, which have the form

$$\psi_i(x)\, e^{-\frac{i}{\hbar}Et} = P(p;x)\, e^{\frac{i}{\hbar}(px-Et)} \tag{7.1}$$

The general wave packet in one dimension has thus the form

$$\Psi(x,t) = \int_{-\infty}^{+\infty} dp \; a(p) \; P(p;x) \; e^{\frac{i}{\hbar}(px - Et)} \tag{7.2}$$

(Here and henceforward in this section p represents the total momentum of the preceding section.) It is possible to choose $a(p)$ to be zero except in a small range about a mean momentum p_0, and yet have $\Psi(x,t)$ with limited range in space, for not too great t. Such a wave packet describes a particle with well-defined (but not <u>exactly</u> defined) position and momentum. There is, of course, a limitation on the exactness with which these quantities can be simultaneously defined, arising from the uncertainty principle.

Let $a(p)$ be zero except in a small range about p_0. In this small range of p it will be a good approximation to represent px-Et by the first two terms of a Taylor expansion in powers of $(p-p_0)$:

$$px - Et = (p_0 x - E_0 t) + (p - p_0)\left[x - \left(\frac{dE}{dp}\right)_{p=p_0} t \right] . \tag{7.3}$$

Then Eq. (7.2) becomes

$$\Psi(x,t) = e^{\frac{i}{\hbar}(p_0 x - E_0 t)} \int_{-\infty}^{+\infty} dp \; a(p) \; P(p;x) \; e^{\frac{i}{\hbar}(p-p_0)\left[x - \left(\frac{dE}{dp}\right)_{p_0} t\right]} . \tag{7.4}$$

This has the form of a progressive wave with energy E_0, momentum p_0, modulated by a function of x and t given by the integral. Now if t is increased by $\Delta t = na \Big/ \left(\frac{dE}{dp}\right)_{p_0}$ and x by $\Delta x = na$, then both $P(p;x)$ and the exponential are unchanged, and the integral has the same value as before. This means that in the interval Δt the form of the wave packet is unchanged except for an increase Δx in all coordinates. The form of the wave packet is not completely constant; it undergoes changes as the packet moves in

the variable potential field, but it returns to the original form (to the approximation here considered) whenever it advances by an integral number of periods of the potential. The wave packet thus moves as a unit with velocity

$$v = \frac{\Delta x}{\Delta t} = \left(\frac{dE}{dp}\right)_{p = p_0} . \tag{7.5}$$

This formula for the velocity is valid both for free particles and for wave packets in crystals. For the crystal, however, E is a quite different function of p (see Fig. 9): the v for the packet depends on its energy in a quite different way. If the energy is well in the middle of a band, where Eq. (6.6) is valid, then

$$v = p/m \; ; \tag{7.6}$$

the velocity of the packet is the same as that of a free particle with the same mass and energy. If, however, E approaches the edge of a band, so that Eq. (6.7) is valid, one has

$$v = \frac{p_t - p_e}{m^*} \; ; \tag{7.7}$$

the velocity of the packet is that of a particle of mass m*, momentum $p_t - p_e$, and [cf. Eq. (6.7)] kinetic energy $E - E_c$. More generally, v can be determined as the slope, for the given E, of an $E(p_t)$ curve such as is shown in Fig. 9. The velocity of a wave packet always goes to zero as its energy approaches that of a band edge.

Equation (7.7) illustrates again how the constant of proportionality in Eq. (6.7), m*, plays the role of an effective mass for the particle. The effective momentum of the particle, $p_t - p_e$, is easily seen to be either p_T,

where this approaches zero at the band edge, or $p_0 \pm \frac{h}{2a}$, when this approaches zero. It is evident from Fig. 9 that if a packet has positive mean momentum its velocity will be positive. The positive v in Eq. (7.7) will be associated with positive values of effective momentum and effective mass near the bottom of each band, but with negative values of both these quantities near the top of the band. For intermediate E this equation does not apply! For negative p_0, v is negative, and the effective mass and momentum have different signs.

The significance of a negative effective mass may be illustrated by considering an electron moving in a periodic potential, and subject to an additional constant force to the right. Let its energy be near the top of a band and its momentum p_0 positive. Its position on the energy diagram and in space are indicated in Fig. 10 by the numeral (1). As the packet proceeds in the direction of the force its kinetic energy will increase, but $|p - p_0|$ and v will <u>decrease</u>. Thus a force to the right produces an acceleration to the left: the ratio of force to acceleration, the effective mass, is negative. It is not sufficient to think of the effective charge of the electron as positive, rather than the effective mass as negative: although the motion of the electron is that of a positive mass with positive change, it transports a negative charge. A material conducting by a few electrons near the top of an otherwise empty band would have a negative resistance.

In relation to this last remark, it may be useful to consider conduction by a material in which all the electronic states but one in a band are filled. A completely filled band would give a uniform change distribution and no transport of change even under an external field. The uniform change distribution can be considered as a sum of distributions from electrons in non-localized stationary states, or as the sum of distributions associated with electronic wave packets. If an electron is removed from the band in a localized way -- that is, if we remove the electron described by one of these wave packets --

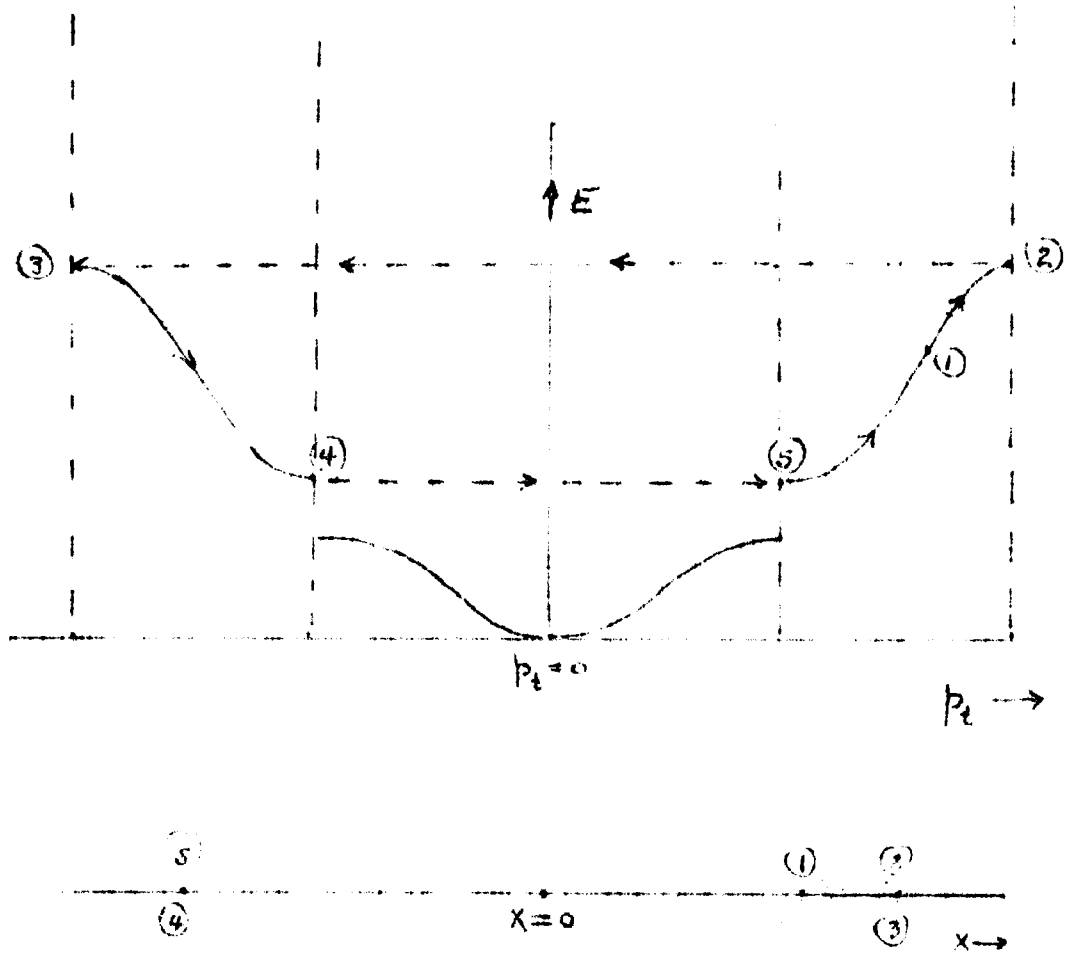

Fig. 10. Motion of a Particle in a Periodic Potential, subject to an Additional Constant Force to the right.

there will be a deficit of negative charge which will move like the wave packet describing the missing electron. If this "hole" has an energy near the top of the band, the motion of this wave packet will, as we have seen, be that of a positive charge with positive mass. The charge transport by the moving hole is also that of a positive charge, since the local deficit of negative charge could be obtained by introducing a positive charge. In all respects, then, a hole in an otherwise full band will behave, in conduction, like an ordinary positive charge with positive mass $|m^*|$. In particular, a material conducting by such holes has a positive resistance; on the other hand, a material conducting by holes near the bottom of a band would have negative resistance. This oversimplified presentation leaves out of consideration some effects due to the interaction of the electrons that are taken into account in Heisenberg's theory of holes.

We now return to the consideration of the electron in a periodic field, and subject to an additional constant force to the right. As the energy of the electron reaches the top of the permitted band the packet comes to a stop (points 2 in Fig. 10) and reverses its direction of motion. This abrupt change in the sign of p, or reflection of the wave packet, is analogous to the Bragg reflection of X-rays by a crystal, for it occurs whenever the wave length of the packet,

$$\lambda = \frac{h}{p_t} \quad . \tag{7.8}$$

satifies the relation

$$n\lambda = 2a. \tag{7.9}$$

This reversal of p brings the momentum to the point (3) in Fig. 10. As the packet moves to the left it loses energy; its velocity increases until, in the middle of the band, it has the classical value for a free electron. As the energy

approaches the bottom of the band the velocity again decreases and the electron begins to move like a particle of positive effective mass m^* ; it comes to a stop (though it may have a large negative momentum p_t) at the bottom of the band (point 4 in Fig. 10). It now undergoes a change in its direction of motion, through Bragg reflection of its momentum to point (5), and its energy begins to increase as it moves to the right. It then repeats the whole cycle already described, oscillating back and forth indefinitely. The period of this oscillation can be estimated by neglecting the time required for the motion near the band edges, and applying the classical equation,

$$F = \frac{dp}{dt} , \tag{7.10}$$

valid for the rest of the motion.(12) Integrating both sides of this equation

(12) cf. W. V. Houston, Phys. Rev. 57, 184 (1940).

over half a cycle of the motion, of duration $\frac{\tau}{2}$, where τ is the period, we obtain

$$\int \frac{dp}{dt}\, dt = \frac{h}{2a} = \int F\, dt = F\,\frac{\tau}{2} , \tag{7.11}$$

or

$$\tau = h/Fa . \tag{7.12}$$

For a cell-length of $4\,\mathring{A}$ and an applied field of 1000 volts/cm the period of such an oscillation by an electron in a crystal would be about 10^{-10} sec., in the microwave region. Since the distance traversed in such oscillations would be of the order of 10^{-3} cm. [see later, Eq. (8.1)], much greater than the mean free path in most real crystals, it may be impossible to observe them in nature. The example will, however, be useful in the next section.

§ 8. Semi-classical Discussion of Motion of Particles in a Perturbed Periodic Potential.

The ideas developed to this point can be made the basis of a semi-classical discussion of the motion of particles in a perturbed periodic potential. For this purpose it is necessary to assume that the perturbing potential changes very slowly with x, though its net effect need not be small. Under this limitation, the form of the potential in any single cell, or even in regions containing many cells, will be inappreciably affected by the perturbation; its important effect will be a displacement of the general level of the potential energy which varies from region to region. As an example we may take the case, considered in the preceding section, of a particle moving in a periodic potential and subject to an additional constant force F to the right. Instead of treating the potential as periodic and following the transfer of kinetic energy to the particle by the external force, we can consider the motion as one of constant total energy where the potential energy consists of two parts; the periodic potential and the linear potential from which the constant force F is derived. (See Fig. 11). If the particle is an electron, the periodic potential that of a crystal, and the constant force due to a field of 1000 volts/cm, then the stated restriction will be abundantly satisfied. The periodic potential will change through many ev. in a cell diameter, of the order of Angstroms in dimensions; on the other hand, the potential energy change due to the field, in this distance, will be of the order of 10^{-5} ev, quite negligible in comparison. One can not neglect, however, the fact that the potential is different in different parts of the crystal, since the total change in potential through the crystal may be large compared with the width of a permitted band. As an illustration of the situation, Fig. 11 greatly exaggerates the dimensions of the cell and the change in potential across a cell.

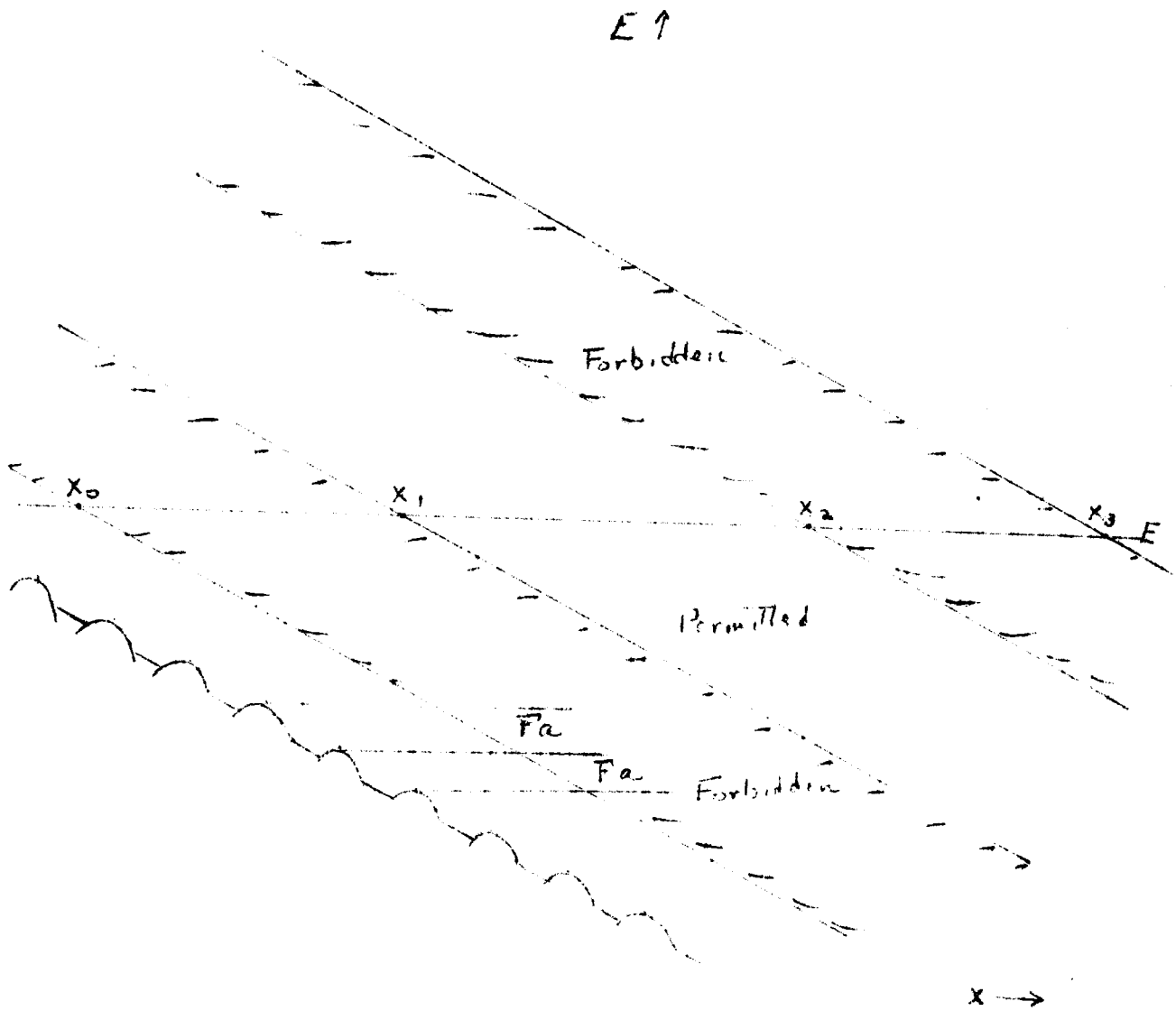

Fig. 11. Band Structure for a Periodic Potential Perturbed by a Linear Potential.

Under the restriction just described, one can suppose that the band structure of the crystal, determined by the form of the cell potential, is everywhere the same as in the unperturbed crystal; the bands are, however, shifted up or down by just the amount of the perturbation energy in that region. This is the basic assumption of qualitative thinking about such problems.

Figure 11 shows the band structure for the problem in question. A particle with energy E can be in the permitted band only for $x_1 \leq x \leq x_2$. The oscillation of a wave packet described in the preceding section is an oscillation between these limits, through a distance

$$\Delta x = B/F \quad , \tag{8.1}$$

where B is the width of the band in question. The velocity of the packet at any x corresponds to its position in the band at that x, as already described.

This type of argument is particularly easy to apply when the energy E of the particle is everywhere so close to the energy of a band edge that one can employ the idea of an effective mass. Figure 12(a) shows a periodic potential modified by a perturbation $V(x)$ downward (say the potential energy of an electron in a crystal, as modified by a local excess of positive charge). A band edge of energy E_e in the unperturbed crystal will then lie at energy $E_e + V(x)$. Generalizing the results of Section 7, one will expect that a wave packet will at any x move like a particle of mass m*, kinetic energy $E - E_e - V(x)$, and potential energy $E_e + V(x)$. For the energy illustrated it would then oscillate between the turning points x_1 and x_2 where the energy of the particle equals the energy of the band edge.

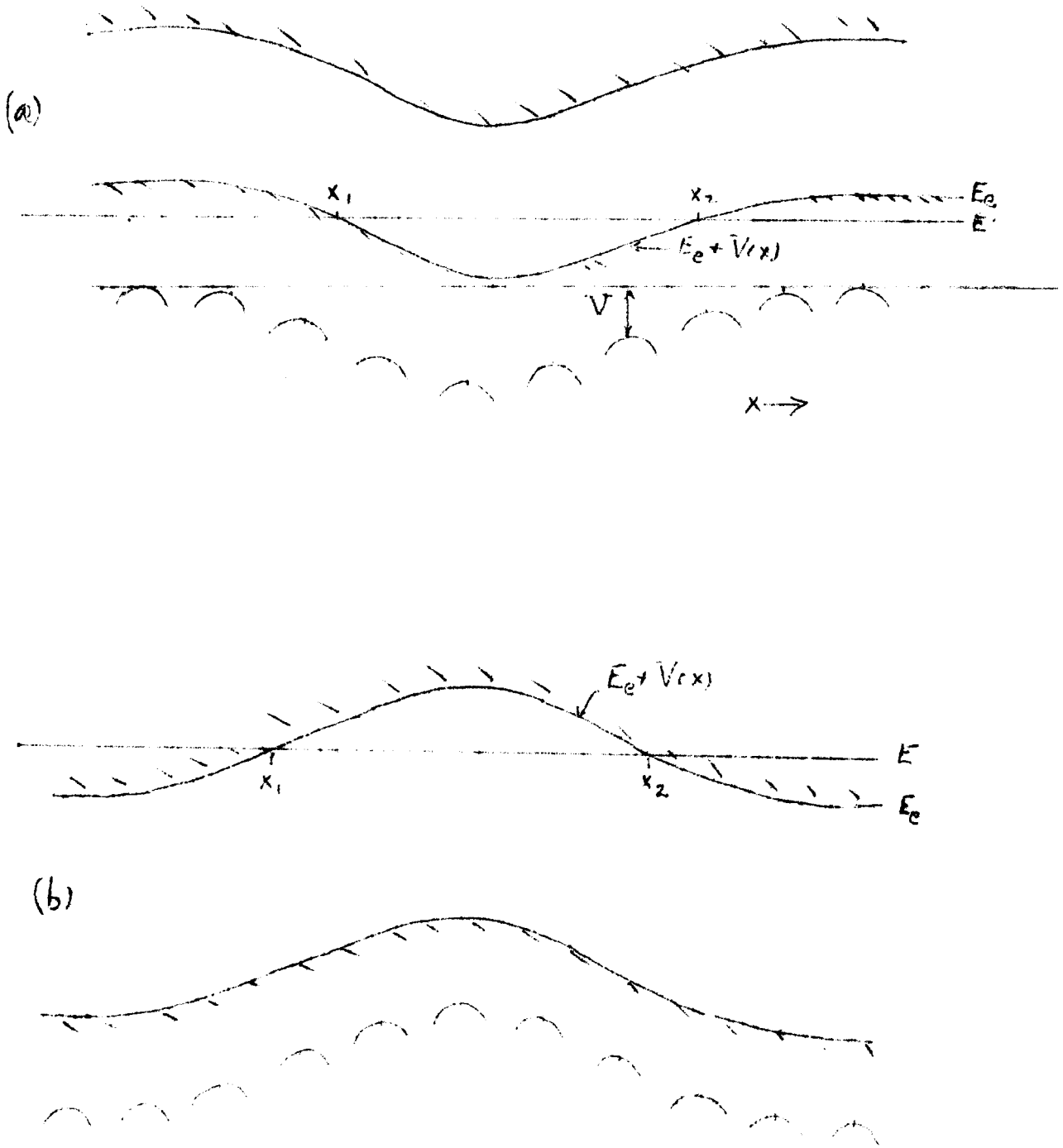

Fig. 12. Stable Oscillations of a Wave Packet in a Perturbed Periodic Potential.

Similar stable oscillations can occur when the particle is subject to a local repulsive force, if its energy lies as shown in Fig. 12(b). Its oscillation is that of a particle of negative mass m^* in a region of negative kinetic energy $E - E_e - V(x)$, or, in more familiar terms, that of a particle of positive mass $|m^*|$, positive kinetic energy $E_e + V(x) - E$. It can not pass outside the range $x_1 \leq x \leq x_2$, for there its energy would lie in a forbidden band.

It will be noted that the energy of these stable oscillations lies outside the permitted band for the unperturbed crystal -- below if the potential is perturbed downward, above if it is perturbed upward.

§9. Qualitative Wave Discussion of the Motion of Particles in a Perturbed Periodic Potential.

The semi-classical discussion of the preceding section is essentially an application of a particle picture derived from a wave-mechanical treatment of perfectly periodic systems. It is useful for some purposes, and is commonly applied in discussions of rectification at crystal surfaces. The validity of the method is strongly limited, however, for it leaves out of account characteristic wave phenomena which appear in imperfectly periodic systems:

(a) quantization of energy,
(b) penetration of barriers,
(c) reflection of potential changes.

For purposes of qualitative argument, these deficiencies can largely be corrected by more complete use of wave ideas developed in preceding sections.

The essential points to be borne in mind are the following:

1. If $V(x)$ is slowly varying, then in any small region where the potential is effectively periodic the wave equation has good approximate solutions of the form of $\psi_+(p;x)$ and $\psi_-(p;x)$ [Eq. (5.9)]. In a permitted region these are periodic functions modulated by progressive waves;

in a forbidden region they are periodic functions exponentially attenuated to the right and to the left, respectively.

2. In a limited region one can express any solution approximately as

$$\psi = A\psi_+(p;x) + B\psi_-(p;x) \tag{9.1}$$

where A and B are constants.

3. In any region, however long, where the perturbing potential is constant, p will be constant, $\psi_\pm$ will have constant forms, and Eq. (9.1) will give an exact solution.

4. Where $V(x)$ and p are slowly varying one will have slow variations in the form of ψ_+ and ψ_-, and the appropriate values of A and B for representation of a given ψ will also change slowly with x. It may be remarked that the problems of extending solutions of the form of Eq. (9.1) from a permitted to a forbidden region is completely parallel to the problem of connecting W. B. K. solutions for non-periodic problems across a classical turning point.

Let us now return to the problem of Fig. 12(a), assuming that $V(x) \equiv 0$ outside of a finite range of x. If ψ is to be bounded as $x \to \infty$, and thus be physically acceptable, it is essential that $A = 0$ in the region of large positive x. For any given E this can be satisfied by only one independent solution of the wave equation. If ψ is to be bounded as $x \to -\infty$ it is also essential that $B = 0$ in the region of large negative x. This condition also can be satisfied by only one independent solution for a given E. In general one must expect these conditions to be inconsistent, but for special values of E one can expect to find a ψ which satisfies both of these conditions simultaneously. Thus one concludes that for discrete energies in the forbidden band there may exist wave functions which are physically acceptable. These are exponentially at-

tenuated away from the perturbation in the lattice, and represent particles remaining indefinitely in the neighborhood of the perturbation. One may say that the particle is trapped in a region where its energy is permitted, because it is perfectly reflected by the surrounding unperturbed part of the crystal where its energy is in the forbidden band.

By the same argument one sees that in the situation of Fig. 12(b) there will be discrete permitted energies above the permitted band of the unperturbed crystal. Their existence can be understood in exactly the same way.

The system of Fig. 11 exhibits the analogue of ordinary weak quantization. For certain narrow bands of energy there will exist solutions of the wave equation for which A vanishes near x_1 and B vanishes near x_0. Such solutions will be oscillatory in the central permitted region, strongly attenuated in the forbidden region on either side, and very small in the permitted regions beyond. Particles known to be in the central permitted region will have one of these weakly quantized energies with very high probability. In the course of time, however, they may penetrate the barriers formed by the forbidden bands and appear in nearby permitted regions.

The spacing of the weakly quantized states is easily determined. It is obvious that if $\psi(x)$ is a solution of the wave equation of this system for energy E, then $\psi(x-na)$ is a solution for energy $E-nFa$, where n is any integer. The spacing of the weakly quantized states is thus $\Delta E = Fa$ and the frequencies emitted in transitions between the states will be

$$\nu = n \cdot \frac{Fa}{h} . \tag{9.3}$$

It is not surprising that these frequencies are multiples of the frequency of oscillation of the particle, as deduced in a previous section [Eq. (7.12)].

Figure 13 represents the potential near the surface of a crystal, with the potential periodic inside the crystal ($x > 0$) and having the form of an image force potential outside. Part of the band structure for the periodic potential is sketched. Consider first the solutions for the band-edge energy E_e. A solution well-behaved for negative x will have exponential character in the non-classical region to the left, will oscillate in the classical region near the crystal, and will reach $x = 0$ with definite slope-to-magnitude ratio. On the other hand, for $x > 0$ there will exist only one physically-acceptable, periodic solution, say with zero slope at the edge of the first cell, $x = 0$. (At other band edges it may be the <u>magnitude</u> of the well-behaved solution that vanishes at the cell edge.) These two functions can not in general be fitted together to form a continuous physically-acceptable solution. As E is lowered, however, the acceptable solution for negative x will reach $x = 0$ with smaller slope-to-magnitude ratio, whereas the well-behaved solution for $x > 0$ will have a greater and greater value for this ratio. For some E these values will become equal, and there will exist a continuous quadratically-integrable solution of the wave equation, exponentially attenuated as $x \to \pm\infty$. This represents a discrete energy state in which an electron is trapped near the surface of the crystal; it can not move away from the crystal because of the image force, and it can not go far into the crystal, being perfectly reflected because its energy is in the forbidden band of the crystal. Such surface states can occur only for energies in the forbidden bands of crystals; they may be above or below nearby permitted bands.

It would be incorrect to infer that localized electronic states of energy E can arise only when E is a permitted energy in a region surrounded by other

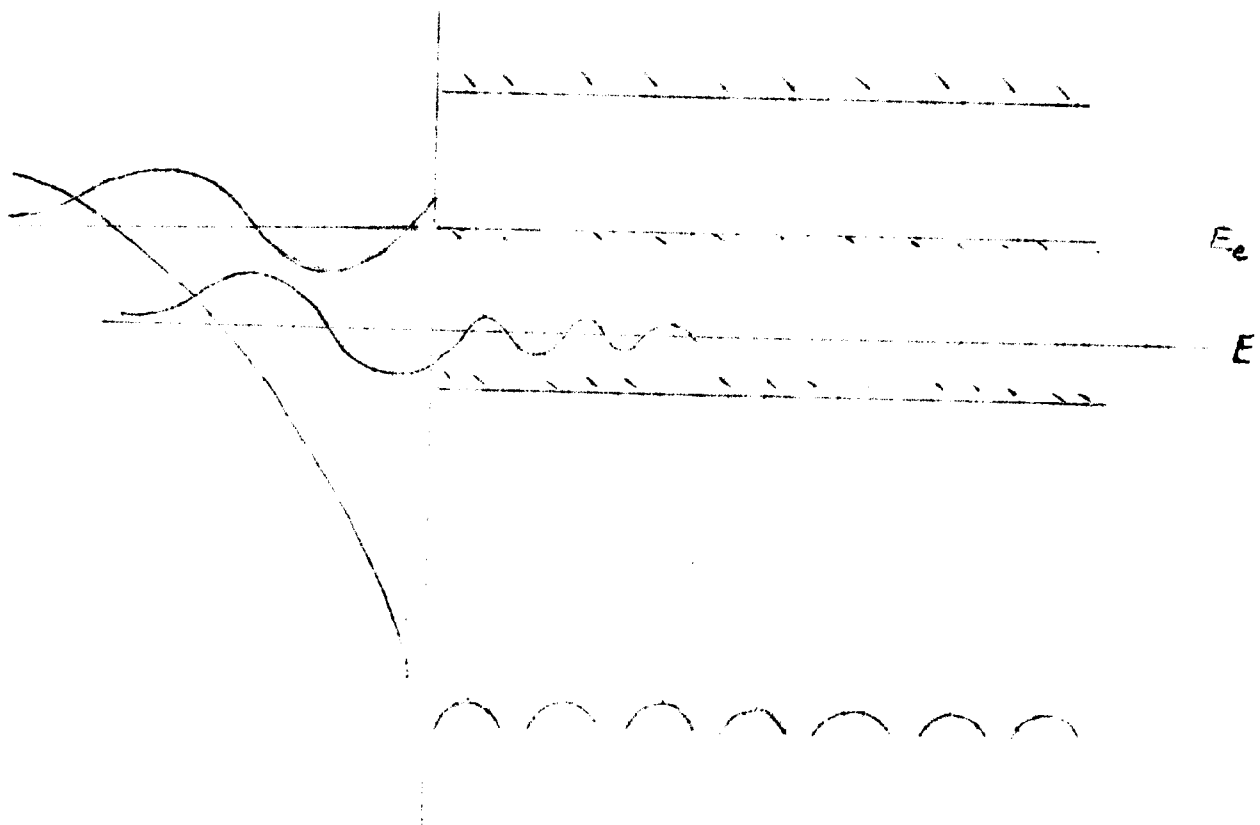

Fig. 13. Quantization of Energy of "End States" of a Terminated Periodic Potential.

regions where E is forbidden or less than the potential energy. Figure 14(a) illustrates the termination of a crystal by a potential jump. For energy E the entire region $x<0$ is a nonclassical one, and for $x>0$ E is a forbidden energy. Nevertheless, if E is properly chosen there may exist a ψ large near $x=0$ but exponentially attenuated as $x \to \pm\infty$. This will occur only if the forbidden band in question has the right character. A solution well-behaved for $x<0$ necessarily has a positive slope-to-magnitude ratio at $x=0$, and can therefore be fitted to a well-behaved solution for $x>0$ only if this well-behaved solution, ψ_-, has a positive value of σ_-. Now [cf. Eq. (3.13)]

$$\sigma_- = \mu \rho^{1/2} \tag{9.4}$$

will be positive in some forbidden regions, where μ is positive, and negative in others; all forbidden bands of a crystal may have one character, or all the other, or the two types of forbidden band may alternate. At any rate, the localized states mentioned above may arise in any band for which μ is positive. The electron is then trapped, but not in a region where it is to be expected by either classical ideas or by those derived from consideration of perfect crystals.

Figure 14(b) illustrates another situation of this type, where crystals of two different types meet. There can then exist quadratically integrable solutions for discrete energies E in the forbidden band for both crystals -- provided the forbidden band to the right is one of positive μ and the band to the left is one of negative μ, or conversely. In such cases it is possible to fit together smoothly at $x=0$ a solution for $x>0$ attenuated to the right and a solution for $x<0$ attenuated to the left. Thus one can have localized electronic states existing at crystal interfaces, with energies in the forbidden band for both types of crystal. The existence of such states is easily understood, however, since the potential deviates strongly from periodicity in the region

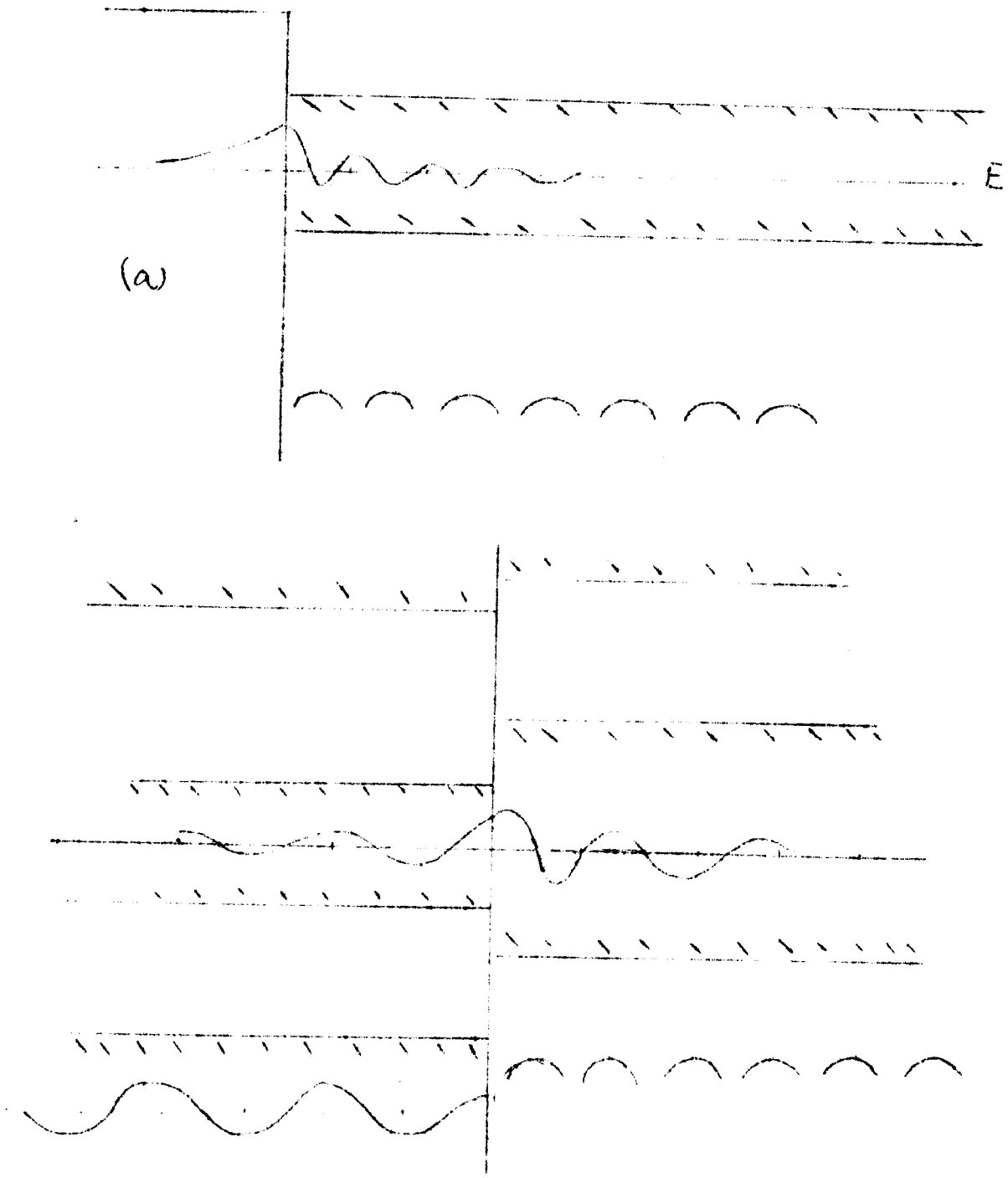

Fig. 14. Occurrence of Localized States in Forbidden Bands.

where the two types of potential meet; for an electron in this region the forbidden bands for the individual crystals have no absolute significance.

§10. The Reduced-Mass Wave Equation.

We now turn to the problem of treating in detail the wave equation for a perturbed periodic potential. An intuitive approach to the problem will first be described, in preparation to a more systematic attack to be given later. Attention will be restricted to cases in which the energy E of the particle is everywhere near the energy $E_e + V$ of the lower edge of a band in the perturbed system, as in Fig. 12(a). To simplify the notation we shall also assume that the band edge is one at which $p_r = p_t - p_e$. Then Eq. (6.7) will become

$$E - E_e - V(x) = \frac{p_r^2}{2m^*}, \tag{10.1}$$

and Eq. (7.7) will be

$$v = \frac{p_r}{m^*}. \tag{10.2}$$

In the semi-classical approximation, the motion of the particle in a perturbed periodic potential will be that of a classical particle with mass m^*, energy E, potential energy $E_e + V(x)$. We have seen that this approximation has the defects to be expected when particle ideas are applied but wave ideas are more appropriate: in particular, it does not yield the quantization of energy for stable states of motion. It is therefore natural to guess that a more satisfactory description of the behavior of the particle would be given by a wave function Φ which satisfies the general wave equation for a particle of mass m^* and potential energy $E_e + V(x)$:

$$-\frac{\hbar^2}{2m^*}\frac{\partial^2 \Phi}{\partial x^2} + \{E_e + V(x)\}\Phi = -\frac{\hbar}{i}\frac{\partial \Phi}{\partial t}. \tag{10.3}$$

This equation has as solutions wave packets which move, like the wave packets already considered, according to Eqs. (10.1) and (10.2). We shall be particularly interested in the solutions with definite energy E. These have space factors $\varphi(x)$ which satisfy a corresponding stationary-state equation

$$-\frac{\hbar^2}{2m^*}\frac{d^2\varphi}{dx^2} + \left\{E_e + V(x)\right\}\varphi = E\varphi . \tag{10.4}$$

This equation will be called the "reduced-mass equation".

Now the solution φ of the reduced-mass equation is certainly not the same as, or even an approximation to, the stationary-state wave function which describes the state of the particle in the usual wave-mechanical sense. This is a solution of a quite different wave equation which involves the true mass m and the true potential energy $V(x) + W(x)$ of the particle:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \left\{W(x) + V(x)\right\}\psi = E\psi . \tag{10.5}$$

In particular, φ has a local wavelength

$$\lambda_r = \frac{h}{\sqrt{2m^*(E - E_e - V(x))}} = \frac{h}{p_r} , \tag{10.6}$$

whereas ψ has the much smaller local wavelength

$$\lambda = \frac{h}{\sqrt{2m(E - W(x) - V(x))}} = \frac{h}{p} , \tag{10.7}$$

p here being the true classical momentum of the particle.

The relation between φ and ψ is easily determined when $V = 0$. Then Eq. (10.3) has solutions

$$\varphi = e^{\pm\frac{i}{\hbar}\sqrt{2m^*(E-E_e)}\,x} = e^{\frac{i}{\hbar}p_r x} , \tag{10.8}$$

and Eq. (10.4) has solutions

$$\psi(x) = e^{\frac{i}{\hbar} p_r x} P(p_r; x). \tag{10.9}$$

Thus φ's appear in ψ's as factors modulating functions periodic with period a.

One can reasonably anticipate a similar relation in other cases. The particle ideas on which the reduced-mass equation is based were developed as descriptions of the motions of wave packets, and refer to the behavior in time of modulating functions, without regard to the periodic functions which they multiply. Thus no more can be expected of the functions Φ and φ than that they should be the <u>modulating functions</u> in, respectively, the general case and the case of motion with definite energy E. If this is actually the case, Φ and φ will give very useful (though incomplete) representations of the electronic state. In particular, if

$$\psi(x) = \varphi(x) P(x), \tag{10.10}$$

and $P^* P$ is the same in every cell, then $\varphi^* \varphi$ will give the relative probability of finding the particle in the several cells.

More complex relationships between ψ and φ than that of Eq. (10.10) are easily imagined. It remains, then, to determine whether a wave equation set up on such naive grounds as Eq. (10.4) can really give correct stationary-state energies, and what is the relation between φ and ψ. One method of investigating this question is to make a guess as to a relation between φ and ψ, and then see to what approximation the ψ determined from a given φ satisfies the correct wave equation, Eq. (10.5). This procedure has, in effect, been used by Tibbs[13] and Peckar[14]. Their guesses will be described briefly.

(13) S. R. Tibbs, Proc. Farad. Soc. 35, 1471 (1939)
(14) S. Peckar, Russian Journal of Physics, 10, 431 (1946)

Since the energy E is always close to the band edge, one might guess that $\varphi(x)$ modulates the periodic function obtained by solving the unperturbed wave equation for the band-edge energy. This idea leads to a solution

$$\psi(x) = \varphi(x)\, P(0;x) , \tag{10.11}$$

with

$$-\frac{\hbar^2}{2m}\frac{d^2 P(0;x)}{dx^2} + W(x)\,P(0;x) = E_e\, P(0;x) . \tag{10.12}$$

One ignores the difference between the real and effective masses of the electron, writing

$$-\frac{\hbar^2}{2m}\frac{d^2\varphi(x)}{dx^2} + \left\{ E_e + V(x) \right\} \varphi(x) = E\,\varphi(x) , \tag{10.13}$$

then Eq. (10.11) defines the approximate solution used by Tibbs. (It is evident from Fig. 9 that identification of m with m^* is reasonable for the lowest band, but very dubious for higher ones.) If this were an exact solution of Eq. (10.5) one would have [substituting Eq. (10.11) into Eq. (10.5) and rearranging terms]

$$\varphi(x)\left[-\frac{\hbar^2}{2m}\frac{d^2 P(0;x)}{dx^2} + (W-E_e)\,P(0;x)\right] + P(0;x)\left[-\frac{\hbar^2}{2m}\frac{d^2\varphi}{dx^2} + (E_e + V - E)\,\varphi\right] = \frac{\hbar^2}{m}\frac{d\varphi}{dx}\frac{d P(0;x)}{dx} . \tag{10.14}$$

By Eqs. (10.12) and (10.13), the terms on the left vanish identically; ψ would be an exact solution of Eq. (10.5) if it were not for the presence of the term on the right. The magnitude of this term can be estimated as follows. Eq. (10.12) can be written as

$$\frac{d^2 P}{dx^2} = -\frac{p_e^2}{\hbar^2} P , \tag{10.15}$$

where p_e is the classical momentum when $E = E_e$; and Eq. (10.13) can be written as

$$\frac{d^2\varphi}{dx^2} = -\frac{p_r^2}{\hbar^2}\varphi , \tag{10.16}$$

again ignoring the difference between m and m*. First approximate solutions are of the form

$$P = C e^{\pm i \frac{p_e}{\hbar} x} , \tag{10.17}$$

$$\varphi = C e^{\pm i \frac{p_r}{\hbar} x} . \tag{10.18}$$

Thus, to orders of magnitude only, one has

$$\frac{d P(0,x)}{dx} \approx i \frac{p_e}{\hbar} P(0,x) , \tag{10.19}$$

$$\frac{d\varphi}{dx} \approx i \frac{p_r}{\hbar} \varphi . \tag{10.20}$$

The error term in Eq. (10.14) is thus of order $\frac{p_r p_e}{m}\psi$. The kinetic energy term in Eq. (10.5) is, however, of the order of $(p^2/2m)\psi$. Thus Tibbs' solution satisfies Eq. (10.5) with relative errors of the order of

$$\frac{2 p_e p_r}{p^2} \cong \frac{2 p_r}{p} . \tag{10.21}$$

A more sophisticated guess as to the relation of φ to ψ has been made by Peckar. In a perfectly periodic potential each modulating function $e^{i\frac{p_r}{\hbar}x}$ is associated with a different periodic function $P(p_r; x)$. If a solution of Eq. (10.4) is expressible as a sum of such functions,

$$\varphi(x) = \sum_{p_r} c(p_r)\, e^{i\frac{p_r}{\hbar}x} , \tag{10.22}$$

then one may suppose that in ψ each of these exponentials will appear with the same coefficient, but multiplied by its appropriate periodic function:

$$\psi_p(x) = \sum_{p_r} c(p_r)\, e^{\frac{i}{\hbar} p_r x}\, P(p_r; x). \tag{10.23}$$

This is the solution proposed by Peckar, reduced to the one-dimensional case. If one assumes that the sum contains only terms with p_r so small that one can replace $P(p_r; x)$ by $P(0; x)$, then this solution becomes

$$\psi(x) = \varphi(x)\, P(0; x), \tag{10.24}$$

identical with Tibbs' except for the use of the reduced mass in the calculation of $\varphi(x)$. This is the only solution that Peckar examines in detail. It can be shown that the errors in this solution are of relative order $(p_r)^3_{max} / p^3$, where $(p_r)_{max}$ is the largest value of p_r appearing in an important way in the Fourier expansion of $\varphi(x)$, Eq. (10.22). Thus the use of the reduced mass in computing $\varphi(x)$ will greatly improve the accuracy of the solution $\psi(x)$, at least in cases where $(p_r)_{max}$ is not too large. It will appear later that Eq. (10.23) defines a still more accurate solution, though the mathematical and practical difficulties in the use of such expansions are excessive.

The remainder of this report will deal with a systematic attack on the problem of solving Eq. (10.5). This leads to a solution closely allied to that of Eq. (10.23), but of more convenient form, and to other solutions which are still more accurate and more generally applicable.