Electronic States in Perturbed Periodic Systems*

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The occurrence in perturbed periodic systems, such as impure crystals, of localized states with discrete energies is discussed from both qualitative and quantitative points of view. Semiclassical considerations, modified in the usual way by wave concepts, make it clear that impurities will give rise to impurity states above or below corresponding permitted bands of energy, according as the ionic charge of the impurity is less than or greater than that of the ion it replaces. Localized states at crystal interfaces and free surfaces can be discussed in the same way. Consideration of the behavior of wave packets leads to formulation of the effective-mass wave equation of Peckar. Complete solutions of the perturbed-periodic wave equation are then constructed by joining together solutions valid for a single period of the unperturbed potential. When the perturbation is slowly varying (though not

necessarily small in its total effect) this approach leads to an analytic solution of the problem involving errors of the order of the ratio of the change in the perturbation potential across a single cell to the total kinetic energy of the particle. The effective-mass equation appears in connection with an approximate form of this solution, but the relation of its solution $\varphi(x)$ to the correct wave function $\psi(x)$ is more complex than has previously been realized. To construct $\psi(x)$ in any small region one should resolve $\varphi(x)$ locally into the sum of two exponentials $C \exp\{\pm(i/\hbar)p_d x\}$, multiply each by the appropriate periodic function, and add the results. A quadradically integrable $\varphi(x)$ corresponds to a quadratically integrable $\psi(x)$ with the same energy; thus stationary-state energies determined by solving the effective-mass wave equation are found to be surprisingly reliable.

I. INTRODUCTION

$\mathbf{E}$LECTRONIC states of crystals can be treated only approximately in wave mechanics, by a forced separation of variables. In many cases, however, one can with good approximation treat each electron as moving in a static potential field $W(x, y, z)$ due to the other electrons, and to all other charges in the system. If the crystal is ideally perfect and infinite, W is periodic throughout all space. The behavior of an electron with energy E is then described by a solution ψ of the wave equation

$$-(\hbar^2/2m)\nabla^2\psi+W(x, y, z)\psi=E\psi.$$

This equation, and its one-dimensional analog,

$$-(\hbar^2/2m)[d^2\psi(x)/dx^2]+W(x)\psi(x)=E\psi(x), \quad (1.1)$$

have been extensively studied.[1]

Recent work on the solid state has directed increasing interest to the behavior 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 cannot 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,[2] on the basis of study of a special one-dimensional model. The latest and most instructive work of this type is that of Shockley,[3] who discussed the solutions of the one-dimensional wave equation for a potential that is perfectly periodic in a finite range of x, representing the crystal, and rapidly approaches a constant value outside (Fig. 1(b)). In such a case one might write the wave equation as

$$\begin{cases} -\hbar^2/2m(d^2\psi/dx^2)+W(x)\psi=E\psi, & 0<x<L, \\ -\hbar^2/2m(d^2\psi/dx^2)+V(x)\psi=E\psi, & x<0, \ x>L, \end{cases} \quad (1.2)$$

where $W(x)$ 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,[4] 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.

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 that 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

$$-\hbar^2/2m(d^2\psi/dx^2)+[W(x)+V(x)]\psi=E\psi, \quad (1.3)$$

where $W(x)$ is again the periodic potential. A similar modification of a periodic potential may arise from

[1] References to the earlier literature are given in the preceding paper (H. M. James, Phys. Rev. 76, 1602 (1949)), which establishes the notation and many of the basic methods and results to be used in the present one. Familiarity of the reader with this paper will be assumed, and it will hereafter be referred to as (I).

[2] I. Tamm, Physik Zeits. Sowjetunion 1, 733 (1932).
[3] W. Shockley, Phys. Rev. 56, 317 (1939).
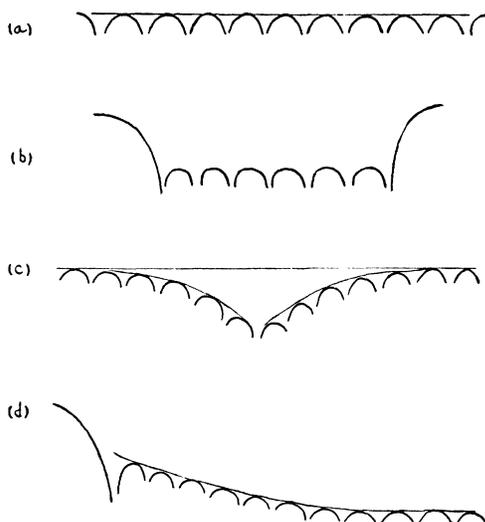[4] E. T. Goodwin, Proc. Camb. Phil. Soc. 35, 205 (1939).

FIG. 1. Modified periodic potentials.

charges outside a crystal, or on its surface. Figure 1(c) represents the total potential energy of an electron in the presence of a foreign ion with excess positive charge. Figure 1(d) represents the potential energy of an electron near the surface of a crystal that 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.

The present paper falls into two parts. The first is concerned with qualitative considerations that make clear the existence and nature of localized surface and impurity states in imperfect crystals. The second presents a quantitative attack on the solution of Eq. (1.3), for the special case of slowly varying (but not necessarily small) perturbations $V(x)$. The method here employed is based on the construction of solutions of the wave equation valid for all x by joining together solutions valid for a single period of the unperturbed periodic potential.[5] The same basic idea is suitable also for the treatment of random and abrupt changes in the potential, such as arise in very impure crystals and disordered alloys; such problems will be treated in a paper now in preparation.

II. QUALITATIVE CONSIDERATIONS

A. Semiclassical Discussion

A semiclassical discussion of the behavior of particles in perturbed periodic potentials can be based on the consideration of wave packets.

In a perfectly periodic potential there exist, for every energy E except the band-edge energies, two independ-

[5] In the case of perfectly periodic potentials this method has been used by R. deL. Kronig and W. G. Penney, Proc. Roy. Soc. 130, 499 (1931), for the special case of square-well potentials. It is discussed at length, for more general types of potential, in reference 1. It has been employed by Shockley (reference 3) in the discussion of Eq. (1.2).

ent stationary-state solutions of the general wave equation, of the form

$$\psi_\pm(E; x) \exp[-(i/h)Et)]$$
$$= P_\pm(E; x) \exp[i/h(\pm px - Et)]. \quad (2.1)$$

Here $P_\pm(E; x)$ are functions periodic with the period a of the potential, and p is a parameter, the effective momentum, which depends on E. As defined in (I), Fig. 4, p is real and positive in permitted bands of E, and complex in forbidden bands. When attention is to be restricted to permitted bands, one can treat $\pm p$ as a real parameter p ranging from $-\infty$ to $+\infty$, and can write the above solutions as

$$\psi(p; x) \exp[-(i/h)Et]$$
$$= P(p; x) \exp[i/h(px - Et)], \quad (2.2)$$

there being one such solution for every value of p. The most general physically acceptable wave function is then expressible as

$$\Psi(x, t) = \int_{-\infty}^{+\infty} a(p)P(p; x) \exp[i/h(px - Et)]dp, \quad (2.3)$$

E being a single-valued function of p. If $a(p)$ is very small except in a limited range about a mean value p_0, Ψ may be a wave packet describing a particle with well defined (but not exactly defined) position and effective momentum. In the small range about p_0 in which the integrand is appreciable, one may represent $px - Et$ by the first two terms of a Taylor's expansion in powers of $(p - p_0)$, to obtain

$$\Psi(x, t) = \exp[i/h(p_0x - E_0t)]\int_{-\infty}^{+\infty} dpa(p)P(p; x)$$

$$\times \exp\{i/h(p - p_0)[x - (dE/dp)_{p_0}t]\}. \quad (2.4)$$

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. If t is increased by $\Delta t = na/(dE/dp)_{p_0}$ 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: after the interval Δt the form of the wave packet is unchanged except for an increase Δx in all coordinates. The wave packet thus moves as a unit with velocity

$$v = (dE/dp)_{p=p_0}, \quad (2.5)$$

undergoing (in this approximation) only changes in form periodic with period a/v.

Equation (2.5) for v is valid both for free particles and for particles in crystals; in crystals, however, p is a quite different function of E, and v depends on E in a quite different way. If the periodic variation in the potential is small, p will approximate closely to the classical momentum for constant potential, and one can write

$$E = p^2/2m, \quad (2.6)$$

except for energies near the band edges. Where this is

valid the velocity $v = p/m$ of the wave packet is that of a classical particle with the same energy, momentum, and mass. Near any band edge one has, however, in any case,

$$E - E_e = (p - p_e)^2 / 2m^*, \qquad (2.7)$$

m^* being the effective mass of the particle at the band edge. The velocity of the wave packet,

$$v = (p - p_e)/m^*, \qquad (2.8)$$

is then that of a "classical" particle with kinetic energy $E - E_e$, momentum $p - p_e$, mass m^*. Near the bottom of a permitted band $E - E_e$ and m^* are positive, but near the top $E - E_0$ and m^* are negative.

The significance of a negative effective mass becomes particularly clear when one considers a particle moving in a periodic potential, but subject to an additional constant force F. This problem was treated, very early in the development of wave mechanics, by Bloch,[6] who showed that the mean momentum of a wave packet changes with time in the classical way,

$$dp_0/dt = F, \qquad (2.9)$$

except near the band edges. It has been shown by Jones and Zener,[7] Zener,[8] and Houston[9] that as the momentum and energy of the packet reach those of a band edge it is split by a partial Bragg reflection; the particle which it represents may have its momentum changed abruptly (reversed in sign in the one-dimensional case) or it may continue to increase, with a corresponding jump in energy to the next permitted band. The probability of reflection is very great, unless the forbidden band is narrow. Attention is called particularly to the work of Zener, who has computed the probability of transmission using ideas closely related to those of the present paper.

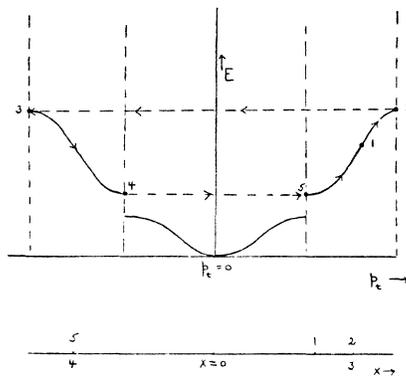The motion of such a packet subject to a constant force to the right is illustrated in Fig. 2. Let its initial

FIG. 2. Motion of a particle in a periodic potential, subject to an additional constant force to the right.

[6] F. Bloch, Zeits. f. Physik **52**, 555 (1928).
[7] H. Jones and C. Zener, Proc. Roy. Soc. **144**, 101 (1934).
[8] C. Zener, Proc. Roy. Soc. **145**, 523 (1934).
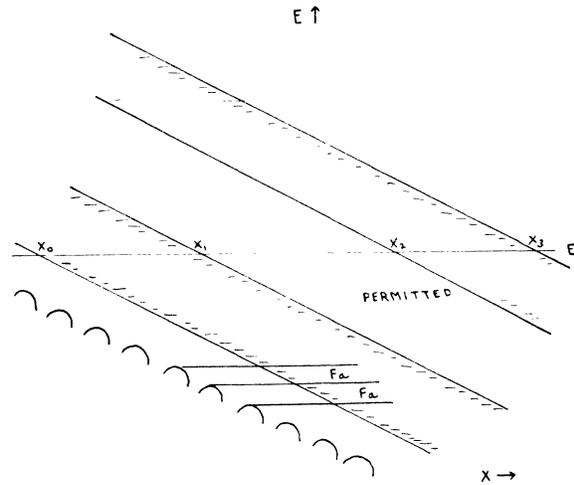[9] W. V. Houston, Phys. Rev. **57**, 184 (1940).

FIG. 3. Potential and band edges in a periodic potential perturbed by an additional constant force to the right.

energy be near the top of the second permitted band, and its momentum p_0 positive. Its position on the E, p diagram and in space are indicated in Fig. 2. by the numeral 1. As p_0 increases at a constant rate the energy of the packet will increase, but $|p_0 - p_e|$ and v will *decrease*. Thus a force to the right produces an acceleration to the left: the ratio of these quantities, the effective mass, is negative. As the energy of the electron reaches the top of the permitted band the packet comes to a stop (points 2 in Fig. 2) and reverses its direction of motion. This reversal of p brings the momentum to point 3. As the packet moves to the left it loses energy; its velocity increases until, in the middle of the band, it may approach 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 at the bottom of the band (point 4). It now undergoes a change in its direction of motion, through Bragg reflection of its momentum to point 5, and its energy increases as it moves to the right until its original position and energy are regained. Since the total change of momentum in the cycle is h/a, the period of the oscillation will be

$$\tau = h/Fa. \qquad (2.10)$$

It may be noted that for a cell diameter of 4A and an applied field of 1000 volts/cm the period of oscillation of an electron in a crystal would be about 10^{-10} sec., in the microwave region. However, since the distance traversed in such oscillations would be of the order of 10^{-3} cm, much greater than the mean free path in most real crystals, it may be difficult to observe them in nature.

Instead of treating this motion as one of variable energy in a periodic potential field, one can treat it as a motion with constant total energy in a periodic poten-

tial field perturbed by the addition of the potential

$$V(x) = -Fx, \qquad (2.11)$$

from which the constant force F is derived.

Assume now that the perturbing potential $V(x)$ changes slowly as compared with the periodic potential $W(x)$ of the crystal, though its total effect need not be small. (If the particle is an electron in a crystal, and the constant force is due to a field of 1000 volts/cm, $V(x)$ will change by some 10^{-5} ev in a cell diameter, whereas the variations in the crystal field will be of the order of 1 ev or more.) One can then suppose that the nature of the band structure, determined by the form of the cell potential (or, more properly, by the potential in a limited sequence of cells) will be the same as in the unperturbed case, but that the bands will everywhere be shifted up or down by the amount of the perturbation energy $V(x)$ in that region. This is a suitable basis for qualitative thinking about such problems (see reference 8). As an illustration of this situation, Fig. 3 greatly exaggerates the dimensions of the cell and the change in potential across a cell. A particle with energy E will be in a permitted band between x_1 and x_2, in forbidden bands between x_0 and x_1, or x_2 and x_3. The oscillation of the wave packet described above is an oscillation between x_1 and x_2, with speed at any point corresponding to its position in the band at that point. Reflection occurs with high probability when the packet is about to enter a forbidden band, but there is a small probability of transmission to the next permitted band (splitting of the packet).

The generalization to slowly varying but non-linear perturbations $V(x)$ is immediate. Figure 4(a) shows a periodic potential modified by a perturbation $V(x)$ downward, say the change in potential energy of an electron in a crystal due to a local excess of positive
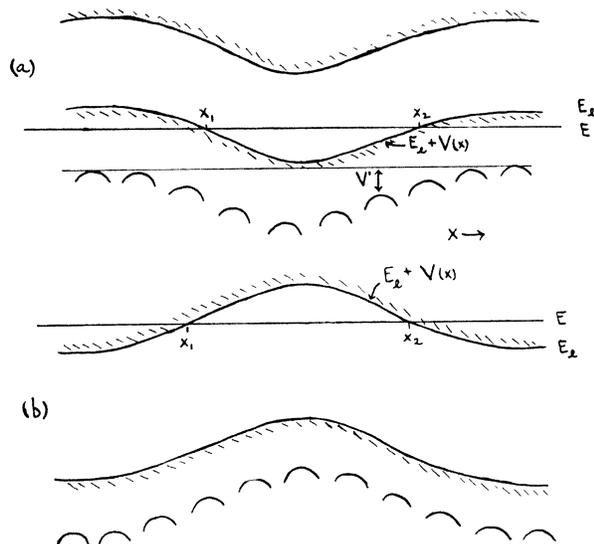
charge. A band edge of energy E_e in the *unperturbed* crystal will then lie at energy $E_e + V(x)$. If a wave packet has an energy everywhere so near the band edge that Eq. (2.7) applies, one will expect it to move at any x like a particle of mass m^*, kinetic energy $E - E_e - V(x)$, and potential 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.

Similar stable oscillations of a packet can occur when the particle is subject to a local *repulsive* force, if its energy lies as shown in Fig. 4(b). Its oscillation will be 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 cannot pass outside the range $x_1 \le x \le x_2$, 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.

B. Discussion in Terms of Waves

In essence, the preceding section applies to the discussion of perturbed periodic systems a particle picture derived from the 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 limited, however, for it leaves out of account characteristic wave phenomena that appear in imperfectly periodic systems: quantization of energy, the penetration of barriers, and reflections due to potential changes. For purposes of qualitative argument, these deficiencies can be corrected by use of the following wave ideas:

1. Let $\psi_+(E; x)$ and $\psi_-(E, x)$, as defined by Eq. (2.1) and discussed at length in reference 1, be wave functions for the unperturbed periodic potential. If $V(x)$ is slowly varying, then, in any small region there $V(x) \cong V_0$ and the potential is effectively periodic, the wave equation has good approximate solutions of the form $\psi_+(E - V_0; x)$ and $\psi_-(E - V_0; x)$. 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

$$\psi = A\psi_+(E - V(x); x) + B\psi_-(E - V(x); x), \quad (2.12)$$

where A and B are constants.

3. In any region, however long, where the perturbing potential is constant, Eq. (2.12) will give an exact solution.

4. Where $V(x)$ is slowly varying one will have slow variations in the form of ψ_+ and ψ_-, and the appropriate values of A and B for exact representation of a given ψ

FIG. 4. Stable oscillations of a wave packet in a perturbed periodic potential.

will also change slowly with x:

$$\psi = A(x)\psi_+(E-V(x); x) + B(x)\psi_-(E-V(x); x). \quad (2.13)$$

It must, however, be remarked that the problem of extending solutions of the form of Eq. (2.13) 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. 4(a), assuming that $V(x)=0$ outside a finite range of x. If ψ is to be bounded as $x\to\infty$, and thus be physically acceptable, it is essential that $B(x)=0$ 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 $A(x)=0$ in the region of large negative x. This condition also can be satisfied by only one independent solution for a given E. In general these conditions will be inconsistent, but for special values of E one can expect to find a ψ that satisfies both conditions simultaneously. Thus one concludes that for discrete energies in the forbidden band there may exist wave functions that are physically acceptable. These are exponentially attenuated 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. 4(b) there will be discrete permitted energies above the permitted band of the unperturbed crystal.

The system of Fig. 3 exhibits the analog of ordinary weak quantization. For certain narrow bands of energy there will exist stationary-state solutions of the wave equation for which $B(x)$ vanishes near x_3 and $A(x)$ 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 them will be

$$\nu = n(Fa/h), \quad (2.14)$$

as one must expect also from Eq. (2.10).

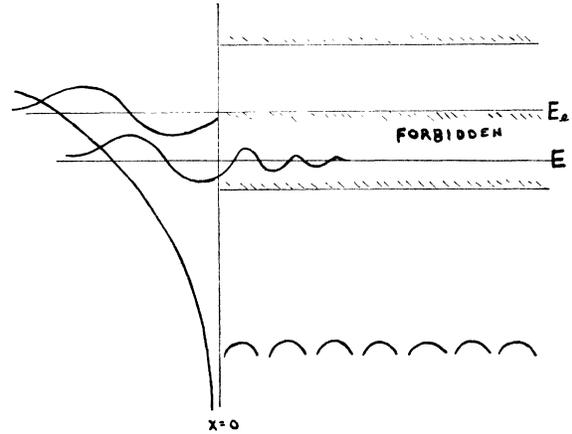Figure 5 represents the potential near the surface of a crystal, with the potential periodic inside the crystal

FIG. 5. Quantization of the energy of "end states" of a terminated periodic potential.

$(x>0)$ 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 (see reference 1) physically acceptable, periodic solution, say with zero slope at the edge of the first cell, $x=0$. (Symmetric cell potentials are assumed; then the well-behaved solution has at the cell boundary either zero slope or zero magnitude.) These two functions cannot 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 cannot move away from the crystal because of the image force, and it cannot 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 regions where E is forbidden or less than the potential energy. Figure 6(a) illustrates the termination of a periodic potential by an abrupt potential jump. For energy E the entire region $x<0$ is a non-classical 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_+.

It is shown in (I), Eq. (2.39), that σ_+ will be positive in some forbidden regions, where u_0'/u_0 is positive, and negative where u_0'/u_0 is negative; 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, these localized states may arise in any band for which σ_+ 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 infinite crystals. Shockley's conclusions (reference 3) concerning the location of surface states in forbidden bands apply to states of this type, but not to those considered in the second preceding paragraph.

Figure 6(b) illustrates another situation of this sort, as where crystals of two different types meet. There can then exist quadratically integrable ψ's for discrete energies E in the forbidden band for both crystals—provided the forbidden band to the right is one of positive u_0'/u_0 and the band to the left is one of negative u_0'/u_0, 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 ideal crystal interfaces, with
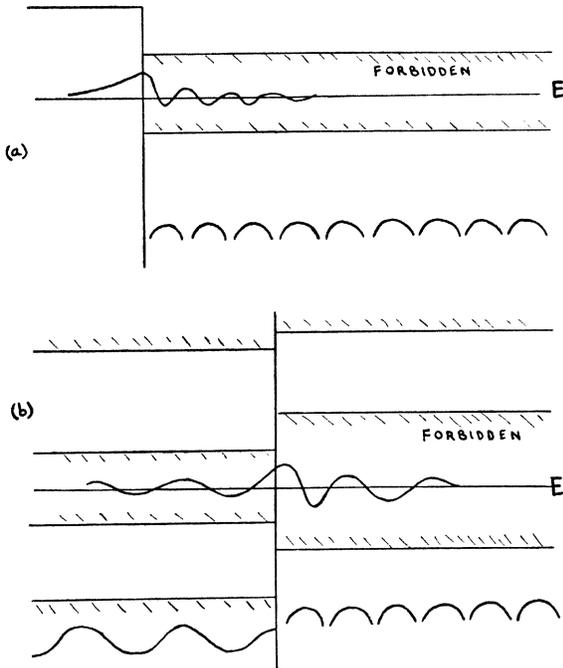

Fig. 6. Occurrence of localized states in forbidden bands.

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

III. THE REDUCED-MASS WAVE EQUATION

We now turn to the problem of treating in detail the wave equation for a perturbed periodic potential. In preparation for a more systematic attack, an intuitive approach to the problem will first be described, with attention restricted to cases in which the energy E of the particle is everywhere near the energy $E_e + V(x)$ of a band edge of the perturbed system, as in Fig. 4.

Let p_t denote the effective total momentum of the particle, as defined in (I), Fig. 4; let p_{te} be the value of p_t at the band edge, and let

$$p_d = p_t - p_{te}. \qquad (3.1)$$

The local value of p_d will then satisfy the relation (see Eq. (2.7))

$$E - E_e - V(x) = p_d^2/2m^*. \qquad (3.2)$$

In the semiclassical approximation, the motion of the particle 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. 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 that satisfies the general wave equation for a particle of mass m^* and potential energy $E_e + V(x)$:

$$-(\hbar^2/2m^*)(\partial^2\Phi/\partial x^2) + \{E_e + V(x)\}\Phi$$
$$= -(\hbar/i)(\partial\Phi/\partial t). \qquad (3.3)$$

We shall be particularly interested in the solutions with definite energy E. These have space factors $\phi(x)$ which satisfy a corresponding stationary-state equation:

$$-(\hbar^2/2m^*)(d^2\phi/dx^2) + \{E_e + V(x)\}\phi = E\phi. \qquad (3.4)$$

These equations will be called the "effective-mass equations."

The relation between the solutions Φ and ϕ of the effective-mass equations and the solutions Ψ and ψ of the ordinary wave equations for the same system is particularly clear when $V = 0$. Equation (3.4) then has the solutions

$$\phi_\pm = \exp\{\pm(i/\hbar)[2m^*(E-E_e)]^{\frac{1}{2}}x\}$$
$$= \exp[\pm(i/\hbar)p_d x], \qquad (3.5)$$

and Eq. (1.3) the corresponding solutions [see (I), Section IV]

$$\psi_\pm = \exp[\pm(i/\hbar)p_d x]P_{d\pm}(E; x). \qquad (3.6)$$

Here the ϕ's appear in the ψ's as factors modulating periodic functions. Further, Eq. (3.3) has been so constructed that it will have wave packet solutions

behaving like the wave packet solutions of

$$-(\hbar^2/2m)(\partial^2\Psi/\partial x^2)+\{W(x)+V(x)\}\Psi$$
$$=-(\hbar/i)(\partial\Psi/\partial t) \quad (3.7)$$

wherever the ideas of the semiclassical discussion are valid. The similarity of Ψ and Φ extends, however, only to the envelopes or modulating functions of the wave packets; the local wave-length of the packet Φ will be h/p_d, whereas that of Ψ will be h/p_t. In general, then, the most that one can expect is that the solutions of the reduced-mass equation shall play the role of modulating factors in the true wave functions. They will then give an incomplete, but perhaps very useful, representation of the electronic state. In particular, if

$$\psi(x)=\phi(x)P(x), \quad (3.8)$$

where $P(x)$ is not necessarily periodic but has the same integral in the square over every cell, then $\phi^*\phi(x)$ will give the relative probability of finding the particle in the several cells.

The relation between ψ and ϕ is, in general, more complex than that of Eq. (3.8). One can, however, make some progress by guessing as to the form of this relation, and testing the validity of the resulting ψ as a solution of the correct wave equation. This has, in effect, been the procedure of Tibbs[10] and of Peckar.[11] Their guesses will be described briefly.

It has been assumed that the energy E is everywhere close to the energy of the band edge. One might then try as a solution

$$\psi_T(x)=\phi(x)P(E_e;x), \quad (3.9)$$

where $P(E_e;x)$ is the uniquely defined periodic solution of the unperturbed wave equation having the energy of the band edge:

$$-\frac{\hbar^2}{2m}\frac{d^2P(E_e;x)}{dx^2}+W(x)P(E_e;x)=E_eP(E_e;x). \quad (3.10)$$

If one ignores the difference between the real and effective masses of the particle, writing

$$-(\hbar^2/2m)(d^2\phi/dx^2)+\{E_e+V(x)\}\phi=E\phi, \quad (3.11)$$

then Eq. (3.9) defines the approximate solution used by Tibbs. If this were an exact solution of Eq. (1.3) one would have (substituting Eq. (3.9) into Eq. (1.3) and rearranging terms),

$$\phi(x)\left[-\frac{\hbar^2}{2m}\frac{d^2P(E_e;x)}{dx^2}+(W(x)-E_e)P(E_e;x)\right]$$
$$+P(E_e;x)\left[-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2}+(E_e+V(x)-E)\phi\right]$$
$$=\frac{\hbar^2}{m}\frac{d\phi}{dx}\frac{dP(E_e;x)}{dx}. \quad (3.12)$$

[10] S. R. Tibbs, Trans. Faraday Soc. 35, 1471 (1939).
[11] S. Peckar, J. Phys. U.S.S.R. 10, 431 (1946). The author is indebted to Dr. K. Lark-Horovitz for calling his attention to this paper.

By Eqs. (3.10) and (3.11) the terms on the left vanish identically; Ψ_T would be an exact solution of the wave equation if the quantity on the right also vanished.

One can estimate the magnitude of this term as follows: If the periodic potential were constant, Eq. (3.10) would have solutions

$$P(E_e;x)=C\exp\{\pm[i/\hbar]p_{te}x\}. \quad (3.13)$$

If V is locally constant, solutions of Eq. (3.11) may assume the form

$$\phi(x)=C\exp\{\pm[i/\hbar]p_dx\}. \quad (3.14)$$

Thus, to orders of magnitude only, one has

$$\frac{dP(E_e;x)}{dx}\approx\frac{p_{te}}{\hbar}P(E_e;x), \quad (3.15)$$

$$d\phi/dx\approx(p_d/\hbar)\phi. \quad (3.16)$$

The error term in Eq. (3.12) is thus of the order of $(p_{te}p_d/m)\psi$. The kinetic and potential energy terms in Eq. (1.3) are, however, of the order of $(p_{te}^2/2m)\psi$. Thus the relative error in ψ_T (or, more precisely, in $d^2\psi_T/dx^2$) is of the order of $2p_d/p_{te}$.

A more sophisticated guess as to the relation of ϕ to ψ has been made by Peckar. With the unperturbed periodic potential each modulating function $\exp(i(p_d/\hbar)x)$ is associated with a different periodic function $P(p_d;x)$. If a solution of Eq. (3.4) is expressible as a sum of such functions,

$$\phi(x)=\sum_{pd}c(p_d)\exp[i(p_d/\hbar)x] \quad (3.17)$$

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

$$\psi_P(x)=\sum_{pd}c(p_d)\exp[(i/\hbar)p_dx]P_d(p_d;x). \quad (3.18)$$

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

$$\psi_M(x)=\phi(x)P(E_e;x), \quad (3.19)$$

identical with Tibbs' except for the use of the reduced mass in the calculation of $\phi(x)$. This is the only solution that Peckar examines in detail. He shows that the errors in this solution are of relative order p_{dm}^3/p_{te}^3, where p_{dm} is the largest value of p_d appearing in an important way in the Fourier expansion of $\phi(x)$, Eq. (3.17). Thus the use of the reduced mass in computing $\phi(x)$ will greatly improve the accuracy of the solution $\psi_T(x)$, at least in cases where p_{dm} is not too large. It will appear later that Eq. (3.18) defines a still more accurate solution. Unfortunately, the mathematical and practical difficulties in the use of such expansions are excessive.

IV. CONSTRUCTION OF COMPLETE SOLUTION BY JOINING CELL SOLUTIONS

We now apply to the treatment of the perturbed periodic wave equation the method, developed in (I), of constructing a complete solution of the wave equation by joining cell solutions. This leads to an analytic solution closely allied to that of Eq. (3.18), but of more convenient form, and to other solutions that are still more accurate and more generally applicable.

A. Definitions

We shall assume that the potential consists of two parts, a periodic potential $W(x)$, which for simplicity we shall take to be symmetric about the center of each cell, and a slowly varying potential $V(x)$, which can on occasion be treated as constant within any single cell.

Since the total potential varies from cell to cell, the special cell solutions of the wave equation, as discussed in (I), will differ from cell to cell. For the nth cell, $na \leq x \leq (n+1)a$, we define the y solutions of the wave equation $y_{1n}(E; x)$ and $y_{2n}(E; x)$, such that

$$\left.\begin{array}{ll} y_{1n}(E; na)=1, & y_{1n}'(E; na)=0, \\ y_{2n}(E; na)=0; & y_{2n}'(E; na)=1. \end{array}\right\} \quad (4.1)$$

We define also the self-matching solutions

$$f_{n\pm}(E; x)=y_{1n}(E; x)\pm\sigma_{n+}y_{2n}(E; x) \quad (4.2)$$

such that

$$\frac{f_{n\pm}'(E; na)}{f_{n\pm}(E; na)}=\frac{f_{n\pm}'(E, (n+1)a)}{f_{n\pm}(E, (n+1)a)}. \quad (4.3)$$

Since the perturbing potential within each cell can be treated as constant, we can define the solutions $g_n(E; x)$ and $u_n(E; x)$, symmetric and antisymmetric, respectively, about the center of the nth cell. For each cell we define the quantities $c_{ij}^{(n)}$, g_{0n}, g_{0n}', u_{0n}, u_{0n}', ρ_n, $r_{n\pm}$, σ_{n+}, p_n, and p_{dn}, all of which depend on the energy and satisfy, for each n, the relations given in (I). In particular, we note that

$$\rho_n=\frac{g_{0n}'u_{0n}}{g_{0n}u_{0n}'}, \quad (4.4)$$

$$\sigma_n=\sigma_{n+}=\left(\frac{g_{0n}'u_{0n}'}{g_{0n}u_{0n}}\right)^{\frac{1}{2}}, \quad (4.5)$$

$$r_{n\pm}=\frac{1\mp\rho_n^{\frac{1}{2}}}{1\pm\rho_n^{\frac{1}{2}}}=\exp[\pm(i/h)p_na]. \quad (4.6)$$

The subscript $+$ is here dropped in the case of σ, as having no further value, since $\sigma_{n-}=-\sigma_{n+}$ will not appear; p or p_n will denote the reduced momentum of (I), Fig. 3. Finally, we define the functions $P_{n\pm}(E; x)$, periodic with period a, which have in the nth cell the form

$$P_{n\pm}(E; x)=\exp[\mp(i/h)p_n(x-na)]f_{n\pm}(x),$$
$$[na \leq x \leq (n+1)a]. \quad (4.7)$$

In the above notation all quantities appear to depend on two parameters, E and n; in fact, however, they depend on a single parameter. If the perturbing potential in the nth cell is treated as constant, equal to V_n, then the special functions defined above are solutions of

$$-h^2/2m(d^2\psi/dx^2)+W(x)\psi=(E-V_n)\psi. \quad (4.8)$$

Since $W(x)$ is the same in every cell, the forms of the cell solutions, and the values of the constants derived from them, depend only on $E-V_n$. Let the solutions of the unperturbed problem in the zeroth cell be $y_1(E;x)\cdots$, the periodic functions $P_\pm(E; x)$, the associated constants $\rho(E)$, $p(E)$, and so on. Then all the quantities defined in the preceding paragraph are given by relations of the form

$$y_{1n}(E;x)=y_1(E-V_n;x-na), \quad [na \leq x \leq (n+1)a], \quad (4.9)$$

$$P_{n\pm}(E; x)=P_\pm(E-V_n; x), \quad (4.10)$$

(by the periodicity of $P_\pm$), and

$$p_n=p(E-V_n). \quad (4.11)$$

In a detailed calculation all quantities could thus be determined with reasonable ease, even by numerical integration, for any special form of $W(x)$.

It is now a simple matter to define the numbers and functions considered above as continuously variable with x. We shall write

$$p(x)=p(E-V(x)), \quad \sigma(x)=\sigma(E-V(x)), \quad (4.12)$$

thus defining continuous functions which take on at the center of the nth cell the values p_n and σ_n, respectively. Treatment of p and σ as functions of $E-V(x)$ corresponds to the assumption, made in the preceding qualitative discussion, that the perturbation everywhere displaces the band edges by an amount $V(x)$. Similarly,

$$P_\pm(x)=P_\pm(E-V(x); x) \quad (4.13)$$

will be functions which change form slowly from cell to cell, taking on the value $+1$ at the left edge of each cell, and within that cell approximating very closely to the periodic functions $P_{n\pm}(E; x)$ defined for that cell. As in (I), Eq. (4.10), we also define the functions

$$\left.\begin{array}{ll} P_{d\pm}(x)=P_\pm(x), & \text{where } 0 \leq p \leq h/4a, \\ P_{d\pm}(x)=\exp(\pm i\pi x/a)P_\pm(x), & \\ & \text{where } h/4a < p \leq h/2a. \end{array}\right\} \quad (4.14)$$

At every band edge P_{d+} and P_{d-} approach a common form, the form of the periodic solution at that band edge, which is periodic with period a or $2a$, according as p is there 0 or $h/2a$.

Since p changes slowly, one can write

$$r_{n\pm}=\exp\left\{\pm[i/h]\int_{na}^{(n+1)a}p\,dx\right\}. \quad (4.15)$$

One can also write

$$r_{n\pm}{}^2 = \exp\left\{\pm[2i/h]\int_{na}^{(n+1)a} p_d dx\right\}, \quad (4.16)$$

since a change of the integrand by $-h/2a$ does not affect the value of this quantity.

B. The Connection Formulas

An arbitrary wave function ψ can be expressed within the nth cell as a linear combination of any pair of independent cell solutions. A particularly useful expression of this type is

$$\psi = A_n y_{1n}(x) + B_n y_{2n}(x), \quad \begin{cases} na \le x \le (n+1)a, \\ n = 0, \pm 1, \pm 2 \cdots, \end{cases} \quad (4.17)$$

because the coefficients A_n and B_n give direct and useful measures of the magnitude of the wave function. By the definition of the y cell solutions they are, respectively, the magnitude and slope of ψ at the left edge of the nth cell. Together, they give a fairly precise measure of the local amplitude of ψ: if ψ can be treated as locally sinusoidal with wave-length $\lambda = h/p_t$ [p_t being the total effective momentum of Fig. 4, (I)], then one has

$$y_1(x) = \cos(2\pi x/\lambda), \quad y_2(x) = (\lambda/2\pi) \sin(2\pi x/\lambda), \quad (4.18)$$

and

$$\psi_{\max}{}^2 = A_n{}^2 + (\lambda/2\pi)^2 B_n{}^2. \quad (4.19)$$

These virtues are not shared by the coefficients appearing in other such expressions for ψ. For instance, the coefficients α_n and β_n in the alternative expressions

$$\begin{aligned}\psi &= \alpha_n f_{n+}(x) + \beta_n f_{n-}(x), \\ \psi &= \alpha_n \exp[(i/h)p_n(x-na)]P_{n+}(x) \\ &\quad + \beta_n \exp[-(i/h)p_n(x-na)]P_{n-}(x);\end{aligned} \quad (4.20)$$

are not always satisfactory measures of the magnitude of ψ because the functions $f_{n\pm}$, $P_{n\pm}$ may change strongly in amplitude, tending to become infinite at band edges where σ becomes infinite.

Continuity of ψ and its first derivation at $x = (n+1)a$ requires

$$\begin{aligned}A_{n+1} &= c_{11}{}^{(n)}A_n + c_{12}{}^{(n)}B_n, \\ B_{n+1} &= c_{21}{}^{(n)}A_n + c_{22}{}^{(n)}B_n.\end{aligned} \quad (4.21)$$

By Eq. (2.17) of (I), these relations can be expressed as

$$\begin{aligned}A_{n+1} &= \{u_{0n}'g_{0n} + g_{0n}'u_{0n}\}A_n - \{2u_{0n}g_{0n}\}B_n, \\ B_{n+1} &= -\{2u_{0n}'g_{0n}'\}A_n + \{u_{0n}'g_{0n} + g_{0n}'u_{0n}\}B_n;\end{aligned} \quad (4.22)$$

on further use of Eqs. (2.14), (2.36), and (2.39) of (I), they become

$$A_{n+1} = \frac{1}{2}(r_{n+} + r_{n-})A_n + \frac{1}{2\sigma_n}(r_{n+} - r_{n-})B_n,$$

$$B_{n+1} = \frac{\sigma_n}{2}(r_{n+} - r_{n-})A_n + \frac{1}{2}(r_{n+} + r_{n-})B_n. \quad (4.23)$$

It is evident from Eqs. (4.21) and (4.22) that the coefficients in these relations all remain finite, even at band edges where σ_n may vanish or become infinite.

Although these connection formulas are of simple structure, they do not define a particularly simple behavior of the coefficients A_n and B_n; even when $V(x)$ is constant, and one can write $\sigma_n = \sigma$, $r_{n\pm} = r_\pm$, one has as the solution of Eq. (4.23)

$$A_n = \frac{1}{2}(r_+{}^n + r_-{}^n)A_0 + \frac{1}{2\sigma}(r_+{}^n - r_-{}^n)B_0,$$

$$B_n = \frac{\sigma}{2}(r_+{}^n - r_-{}^n)A_0 + \frac{1}{2}(r_+{}^n + r_-{}^n)B_0. \quad \}$$

$$(n = 0, \pm 1 \cdots). \quad (4.24)$$

In studying the variation of A_n, B_n, and ψ with n and x it is therefore convenient to shift attention for the moment to parameters that are constant when $V(x)$ is constant and change only slowly as $V(x)$ changes slowly.

In (I) the functions $f_\pm(x)$ have been so defined that when V is constant the coefficients α_n and β_n of Eq. (4.20) change from cell to cell by factors r_+ and r_-, respectively. Thus, if one writes

$$\psi(x) = C_n{}^+\left\{\prod_{\tau=0}^{n-1} r_{\tau+}\right\}f_{n+}(x) + C_n{}^-\left\{\prod_{\tau=0}^{n-1} r_{\tau-}\right\}f_{n-}(x), \quad (4.25)$$

$$(na \le x \le (n+1)a),$$

one can be sure that the coefficients $C_n{}^\pm$ will be constant throughout any region where $V(x)$ is constant.[12] One might also expect that they will vary slowly wherever $V(x)$ varies slowly. This is not the case, however, in the neighborhood of band edges where σ, f_{n+}, and f_{n-} become infinite.

This difficulty can be avoided in the following way. Let such a band edge occur in the zeroth cell: $\sigma_0 = \infty$. Since, by Eq. (4.2),

$$\frac{1}{2}\{f_{n+}(x) + f_{n-}(x)\} = y_{1n}(x),$$

$$\frac{1}{2\sigma_n}\{f_{n+}(x) - f_{n-}(x)\} = y_{2n}(x), \quad \}$$

$$(4.26)$$

the functions

$$F_{n+}(x) = \frac{1}{2}\left[\left\{\prod_{\tau=0}^{n-1} r_{\tau+}\right\}f_{n+}(x) + \left\{\prod_{\tau=0}^{n-1} r_{\tau-}\right\}f_{n-}(x)\right], \quad (4.27a)$$

$$na < x < (n+1)a,$$

---

[12] This notation does not express well the situation for $n \le 0$, but the generalization is obvious.

$$F_{n-}(x) = \frac{1}{2\sigma_n}\left[\left\{\prod_{\tau=0}^{n-1} r_{\tau+}\right\}f_{n+}(x)\right.$$

$$\left. -\left\{\prod_{\tau=0}^{n-1} r_{\tau-}\right\}f_{n-}(x)\right], \quad (4.27b)$$

do not tend to become infinite as $n\to0$ and the band edge is approached. If, then, one writes Eq. (4.25) as

$$\psi(x) = D_n{}^+ F_{n+}(x) + D_n{}^- F_{n-}(x),$$
$$na < x < (n+1)a, \quad (4.28)$$

where

$$D_n{}^+ = C_{n+} + C_{n-}, \quad D_n{}^- = \sigma_n(C_{n+} - C_{n-}), \quad (4.29)$$

one can expect $D_n{}^+$ and $D_n{}^-$ to vary slowly when $V(x)$ varies slowly, even at the band edge. Comparison of Eqs. (4.17) and (4.28), with use of Eqs. (4.26) and (4.27), shows that

$$A_n = \frac{1}{2}\left\{\prod_{\tau=0}^{n-1} r_{\tau+} + \prod_{\tau=0}^{n-1} r_{\tau-}\right\}D_n{}^+$$

$$+ \frac{1}{2\sigma_n}\left\{\prod_{\tau=0}^{n-1} r_{\tau+} - \prod_{\tau=0}^{n-1} r_{\tau-}\right\}D_n{}^-,$$

$$\left.\begin{array}{l}\end{array}\right\} \quad (4.30)$$

$$B_n = \frac{\sigma_n}{2}\left\{\prod_{\tau=0}^{n-1} r_{\tau+} - \prod_{\tau=0}^{n-1} r_{\tau-}\right\}D_n{}^+$$

$$+ \frac{1}{2}\left\{\prod_{\tau=0}^{n-1} r_{\tau-} + \prod_{\tau=0}^{n-1} r_{\tau-}\right\}D_n{}^-,$$

where $D_n{}^+$ and $D_n{}^-$ can be expected to vary slowly so long as $V(x)$ varies slowly. This result is an obvious generalization of Eq. (4.24) to the case of variable potential, except in that it is essential to treat as the zeroth cell any cell wherein $\sigma = \infty$.

Substitution of Eqs. (4.30) into Eqs. (4.23) yields the connection formulas for the D's. By Eq. (4.16), one has

$$\prod_{\tau=0}^{n} r_{\tau\pm}{}^2 = \exp\left\{\pm\frac{2i}{\hbar}\int_0^{(n+1)a} p_d dx\right\}. \quad (4.31)$$

The connection formulas can then be written as

$$D_{n+1}{}^+ - D_n{}^+ = \frac{\sigma_{n+1} - \sigma_n}{2\sigma_{n+1}}\left[\cos\left\{\frac{2}{\hbar}\int_0^{(n+1)a} p_d dx\right\} - 1\right]D_n{}^+$$

$$+ \frac{i}{2}\frac{(\sigma_{n+1} - \sigma_n)}{\sigma_{n+1}\sigma_n}\sin\left\{\frac{2}{\hbar}\int_0^{(n+1)a} p_d dx\right\}D_n{}^-, \quad (4.32)$$

$$D_{n+1}{}^- - D_n{}^- = -\frac{i}{2}(\sigma_{n+1} - \sigma_n)\sin\left\{\frac{2}{\hbar}\int_0^{(n+1)a} p_d dx\right\}D_n{}^+$$

$$- \frac{\sigma_{n+1} - \sigma_n}{2\sigma_n}\left[\cos\left\{\frac{2}{\hbar}\int_0^{(n+1)a} p_d dx\right\} - 1\right]D_n{}^-. \quad (4.33)$$

It is evident that the coefficients on the right are small, and the variation of the D's is relatively slow, except

possibly near the band edge, $n=0$, where σ may vanish or become infinite. It is easily verified that they remain small even at the band edge.

C. Replacement of the Connection Formulas by Differential Equations

We shall now replace the difference equations that define the numbers $D_n{}^\pm$ by differential equations defining continuous functions $D_+(x)$ and $D_-(x)$ such that

$$D_n{}^\pm = D_\pm([n+\tfrac{1}{2}]a) \quad (4.34)$$

with good approximation, for not-too-long ranges of integration. Since $D^+(x)$ and $D^-(x)$ vary slowly, we can write

$$D_{n+1}{}^\pm - D_n{}^\pm \cong a\frac{dD_\pm}{dx}\Bigg|_{x=(n+1)a}. \quad (4.35)$$

We write also

$$\frac{\sigma_{n+1} - \sigma_n}{\sigma_{n+1}} \cong a\frac{d}{dx}(\ln\sigma)\Bigg|_{x=(n+1)a}; \quad (4.36)$$

factors multiplying this expression vanish at the band edges, where the approximation may not be good. Finally we treat the upper limit in the integrals of Eqs. (4.32) and (4.33) as continuously variable.[13] We thus obtain the differential equations

$$\frac{dD_+}{dx} = \frac{1}{2}\frac{d}{dx}(\ln\sigma)\left[\cos\left\{\frac{2}{\hbar}\int_0^x p_d dx\right\} - 1\right]D_+$$

$$- \frac{i}{2}\frac{d}{dx}\left(\frac{1}{\sigma}\right)\sin\left\{\frac{2}{\hbar}\int_0^x p_d dx\right\}D_-,$$

$$\left.\begin{array}{l}\end{array}\right\} \quad (4.37)$$

$$\frac{dD_-}{dx} = -\frac{1}{2}\frac{d\sigma}{dx}\sin\left\{\frac{2}{\hbar}\int_0^x p_d dx\right\}D_+$$

$$- \frac{1}{2}\frac{d}{dx}(\ln\sigma)\left[\cos\left\{\frac{2}{\hbar}\int_0^x p_d dx\right\} - 1\right]D_-.$$

This cumbersome relation can immediately be replaced by a much simpler one.

We define functions $A(x)$ and $B(x)$ by the relations

$$A(x) = D_+(x)\cos\left\{\frac{1}{\hbar}\int_0^x p_d dx\right\}$$

$$+ \frac{i}{\sigma(x)}D_-(x)\sin\left\{\frac{1}{\hbar}\int_0^x p_d dx\right\},$$

$$\left.\begin{array}{l}\end{array}\right\} \quad (4.38)$$

$$B(x) = i\sigma(x)D_+(x)\sin\left\{\frac{1}{\hbar}\int_0^x p_d dx\right\}$$

$$+ D_-(x)\cos\left\{\frac{1}{\hbar}\int_0^x p_d dx\right\}.$$

---

[13] In the interior of a pass band the integrals change rapidly with n, and this step can be justified only because these terms are negligible.

These relations are the continuous analogs of Eqs. (4.30). If n is even,

$$\exp\left\{\pm\frac{i}{h}\int_0^{na} p_d dx\right\} = \exp\left\{\pm\frac{i}{h}\int_0^{na} p dx\right\} = \prod_{\tau=1}^{n-1} r_{\tau\pm}; \quad (4.39)$$

if n is odd, the exponentials are identical if $p_d = p$, but differ in sign if $p_d = p - (h/2a)$. Thus one has in any case

$$\left.\begin{array}{l} A_n = A(na), \\ B_n = B(na), \end{array}\right\} (n \text{ even}). \quad (4.40)$$

(The small change of $D_\pm(x)$ in the distance $a/2$ has been ignored.) If n is odd, changes in sign may be required in Eqs. (4.40), but this is a matter of little interest, since the magnitude of ψ is sufficiently indicated by the values for even n.

When Eq. (4.38) is substituted into Eq. (4.37), extensive cancelation of terms occurs, and one obtains simple equations for $A(x)$ and $B(x)$:

$$\frac{dA}{dx} = -\frac{i}{h}\frac{p_d(x)}{\sigma(x)}B, \quad (4.41a)$$

$$\frac{dB}{dx} = \frac{i}{h}p_d(x)\sigma(x)A. \quad (4.41b)$$

The coefficients $p_d(x)/\sigma(x)$ and $p_d(x)\sigma(x)$ are everywhere finite; their values at the various types of band edge are given in (I), Eqs. (5.26) and (5.27).

From Eqs. (4.29), (4.38) it follows that if

$$\left.\begin{array}{l} C_+(x) = \frac{1}{2}\left\{D_+(x) + \dfrac{D_-(x)}{\sigma(x)}\right\} \\[2mm] = \frac{1}{2}\left\{A(x) + \dfrac{B(x)}{\sigma(x)}\right\}\exp\left\{-\dfrac{i}{h}\int_0^x p_d dx\right\}, \\[4mm] C_-(x) = \frac{1}{2}\left\{D_+(x) - \dfrac{D_-(x)}{\sigma(x)}\right\} \\[2mm] = \frac{1}{2}\left\{A(x) - \dfrac{B(x)}{\sigma(x)}\right\}\exp\left\{+\dfrac{i}{h}\int_0^x p_d dx\right\}, \end{array}\right\} \quad (4.42)$$

then

$$C_{n\pm} = C_\pm([n+\tfrac{1}{2}]a). \quad (4.43)$$

D. Continuous Representations of ψ

Using the functions just defined, one can now replace the cell-by-cell representation of ψ by a continuous one. By Eqs. (4.7), (4.14), and (4.15), one can write

$$\left\{\prod_{\tau=0}^{n-1} r_{\tau\pm}\right\}f_{n\pm}(x) = \exp\left\{\pm\frac{i}{h}\int_0^x p dx\right\}P_{n+}(x)$$

$$[na < x < (n+1)a] \quad (4.44)$$

$$= \exp\left\{\pm\frac{i}{h}\int_0^x p_d dx\right\}P_{dn+}(x).$$

These cell functions are approximated within every cell by the continuous functions (see Eqs. (4.10), (4.13))

$$\psi_\pm(x) = \exp\left\{\pm\frac{i}{h}\int_0^x p dx\right\}P_\pm(E - V(x); x)$$

$$= \exp\left\{\pm\frac{i}{h}\int_0^x p_d dx\right\}P_{d\pm}(E - V(x); x). \quad (4.45)$$

Similarly, the functions $F_{n\pm}(x)$ are approximated closely in every cell by

$$\begin{array}{l} F_+(x) = [\psi_+(x) + \psi_-(x)]/2, \\ F_-(x) = [\psi_+(x) - \psi_-(x)]/2\sigma(x). \end{array} \quad (4.46)$$

Since D_n^+ and D_n^- are closely approximated in every cell by $D_+(x)$ and $D_-(x)$, one can replace the cell-by-cell representation of ψ in Eq. (4.28) by a closely equivalent continuous representation:

$$\psi(x) = D_+(x)F_+(x) + D_-(x)F_-(x). \quad (4.47)$$

By use of Eqs. (4.42), (4.44), and (4.46) this can also be written as

$$\psi(x) = C_+(x)\psi_+(x) + C_-(x)\psi_-(x), \quad (4.48)$$

or

$$\psi(x) = A(x)\left[\frac{P_{d+}(E - V(x); x) + P_{d-}(E - V(x); x)}{2}\right]$$

$$+ B(x)\left[\frac{P_{d+}(E - V(x); x) - P_{d-}(E - V(x); x)}{2\sigma(x)}\right]. \quad (4.49)$$

Of these representations the last is the most convenient. It has been shown that the functions $A(x)$ and $B(x)$ by themselves give a good indication of the amplitude of ψ. Unlike ψ_+ and ψ_-, the quantities in brackets are everywhere finite; the forms which they assume when $E - V(x) = E_e$ are given in (I), Section V.

E. Generalization of the Effective-Mass Equation

We shall now derive and interpret the effective-mass equation, as it appears in the treatment of problems such as are illustrated in Fig. 4.

We assume that the energy E to be considered lies everywhere closer (in p) to one band edge than to any other, thus avoiding the possibility that p_d will be discontinuous at any point. The quantities $p_d(x)/\sigma(x)$ and $p_d(x)\sigma(x)$ which appear in Eq. (4.41) will then be continuous everywhere, and, as follows immediately from (I), Eq. (5.20), both will have zero derivative at the band edge. One of these quantities will also vanish at the band edge [see (I), Eqs. (5.26), (5.27)]. We shall assume that this quantity is $p_d(x)\sigma(x)$ (i.e., that g_e' or $u_e' = 0$); when $p_d(x)/\sigma(x)$ vanishes the roles of $A(x)$ and $B(x)$ are simply interchanged.

By Eq. (4.41a),

$$\frac{d^2A}{dx^2} = \frac{i}{\hbar}\frac{p_d(x)}{\sigma(x)}\frac{dB}{dx} + \frac{i}{\hbar}B\frac{d}{dx}\left(\frac{p(x)}{\sigma(x)}\right). \quad (4.50)$$

The last term will vanish at the band edge and be small everywhere, if $V(x)$ varies slowly. We therefore neglect it. Using (4.42b), we obtain

$$(d^2A/dx^2) + (p_d^2(x)/\hbar^2)A = 0. \quad (4.51)$$

If E is everywhere so close to $E_e + V(x)$ that Eq. (3.2) is valid, Eq. (4.51) becomes identical with the effective mass equation, Eq. (3.4), and one can write

$$A(x) = \phi(x) \quad (4.52)$$

and, by Eq. (4.41a),

$$B(x) = \frac{\hbar}{i}\frac{\sigma(x)}{p_d(x)}\frac{d\phi}{dx}. \quad (4.53)$$

Then, by Eq. (4.49), one has

$$\psi(x) = \phi(x)Q(x) + (d\phi/dx)R(x) \quad (4.54)$$

where

$$Q(x) = [P_{d+}(E - V(x); x) + P_{d-}(E - V(x); x)]/2, \quad (4.55)$$

$$R(x) = \frac{\hbar}{ip_d}\frac{P_{d+}(E - V(x); x) - P_{d-}(E - V(x); x)}{2}. \quad (4.56)$$

We have thus shown the applicability of the effective-mass equation to problems in which there is a well defined effective mass, but have arrived at a new and more precise interpretation of its solution $\phi(x)$.

At the same time, Eq. (4.51) defines a solution of the perturbed periodic problem that is not limited by the assumption that the energy E is everywhere so close to the band edge that Eq. (3.2) applies. For any periodic, unperturbed potential one can in principle determine the function $p_d^2(E)$. In treating a given perturbed problem, for a particular energy E, one can determine

$$p_d^2(x) = p_d^2(E - V(x)), \quad (4.57)$$

and can define a function $V_{\text{eff}}(x)$ by the relation

$$E - E_e - V_{\text{eff}}(x) = p_d^2(x)/2m^*, \quad (4.58)$$

where m^* is the effective mass at the neighboring band edge. Equation (4.51) then becomes

$$-\frac{\hbar^2}{2m^*}\frac{d^2A(x)}{dx^2} + \{E_e + V_{\text{eff}}(x)\}A(x) = EA(x). \quad (4.59)$$

$A(x)$ is thus a solution of a one-dimensional wave equation involving an effective perturbation energy $V_{\text{eff}}(x)$ that is in general different from $V(x)$; in particular, it may depend on the E considered, as well as on $V(x)$. Since p_d^2 increases more rapidly than $E - E_e$ [(I),

Fig. 4], one sees easily that the effective potential $V_{\text{eff}}(x)$ tends to be larger than the real perturbing potential. In this more general case, Eq. (4.54) is replaced by

$$\psi(x) = A(x)Q(x) + (dA/dx)R(x). \quad (4.60)$$

In principle, ψ can be determined still more accurately by integrating Eqs. (4.41), without neglect of the last term in Eq. (4.50). These solutions will not be discussed here.

F. Significance of the New Solutions

The structure of the wave function given in Eq. (4.60), and of its less accurate counterpart Eq. (4.54), becomes clearest when it is written as

$$\psi(x) = \frac{1}{2}\left\{A(x) + \frac{\hbar}{ip_d}\frac{dA}{dx}\right\}P_{d+}(x)$$

$$+ \frac{1}{2}\left\{A(x) - \frac{\hbar}{ip_d}\frac{dA}{dx}\right\}P_{d-}(x). \quad (4.61)$$

(Note, however, that in this expression the two quantities on the right become infinite at the band edge.) In any very small region one can regard $p_d(x)$ as constant and can write $A(x)$, a solution of Eq. (4.51), as

$$A(x) = C_1 \exp\{[i/\hbar]p_d x\} + C_2 \exp\{-[i/\hbar]p_d x\}, \quad (4.62)$$

a linear combination of special exponential solutions; thus,

$$\tfrac{1}{2}\{A(x) + [\hbar/ip_d]dA/dx\} = C_1 \exp\{[i/\hbar]p_d x\} \quad (4.63a)$$

and

$$\tfrac{1}{2}\{A(x) - [\hbar/ip_d]dA/dx\} = C_2 \exp\{-[i/\hbar]p_d x\} \quad (4.63b)$$

are the locally determined exponential components of $A(x)$. In each small neighborhood $\psi(x)$ can then be formed from $\phi(x)$ or $A(x)$ by resolving that function locally into real or complex exponentials of the form $\exp\{\pm[i/\hbar]p_d x\}$, multiplying each exponential by the appropriate periodic function $P_{d+}(x)$ or $P_{d-}(x)$, and adding the results.

It will now be shown that the $\psi(x)$ of Eq. (4.54), constructed from $\phi(x)$, is essentially the solution $\psi_P(x)$ [Eq. (3.18)] proposed but not discussed by Peckar. This solution is not precisely defined unless one specifies the normalization of the functions $P_d(p_d; x)$. For simplicity, we shall here assume that the band edge is one at which the periodic functions defined in this paper remain finite; specifically, one where $g_e' = 0$. From Eq. (5.22) of (I) and Eqs. (4.55) and (4.56) of this paper, it follows that

$$P_d(p_d; x) = Q_e(x) + (ip_d/\hbar)R_e(x) + O(p_d^2), \quad (4.64)$$

$Q_e(x)$ and $R_e(x)$ being the forms assumed by $Q(x)$ and $R(x)$ at the band edge. Neglecting second-order terms

in p_d, one can then write

$$\psi_P(x) = \{\sum_{pd} c(p_d)\exp[(i/h)p_dx]\}Q_e(x)$$
$$+ \{\sum c(p_d)(ip_d/h)\exp[(i/h)p_dx]\}R_e(x). \quad (4.65)$$

The first of the sums on the right is just the initial expansion of $\phi(x)$, and the second is $d\phi/dx$ if (as assumed by Peckar) one can operate on the expansion term by term. Thus,

$$\psi_P(x) = \phi(x)Q_e(x) + (d\phi/dx)R_e(x), \quad (4.66)$$

which agrees with Eq. (4.54) to within terms in p_d^2.

The less accurate approximation actually discussed by Peckar, ψ_M, in which $\phi(x)$ appears merely as an amplitude modulating a periodic function, is obtained by neglecting the last term in Eq. (4.66). From Eq. (5.22) of (I) it follows that

$$Q_e(x) = g_e(x)/g_e,$$
$$R_e(x) = [(a/2)-x]g_e(x)/g_e - (a/2)u_e(x)/u_e; \quad (0<x<a)$$

$R_e(x)$ differs in magnitude from $Q_e(x)$ by a factor of the order of a. The term neglected by Peckar is thus of order $a(d\phi/dx)/\phi = \Delta\phi/\phi$ compared to the term retained, $\Delta\phi$ being the change in ϕ across a cell. This ratio will be small if E is near a band edge, but it is not a direct measure of the local errors in ψ_M as a solution of the wave equation; the magnitude of these has been indicated previously.

G. Accuracy of the New Solutions

The accuracy of the solutions derived here can be tested by substituting them into the perturbed-periodic wave equation, and observing the magnitude of the non-vanishing terms. For this purpose it is convenient to make more explicit the dependence on x of the terms in Eq. (4.60):

$$\psi(x) = Q(E-V(x);x)A(x) + R(E-V(x);x)A'(x). \quad (4.67)$$

We shall distinguish the derivatives of $Q(E-V(x);x)$ with respect to x in the first and second arguments by $'Q$ and Q', respectively; a similar notation will be used with R. Then

$$[dQ(E-V(x);x)]/dx = 'Q+Q'. \quad (4.68)$$

Considered as functions of $E-V(x)$ or p_d, Q and R can be expanded in powers of $p_d^2a^2/4h^2$, with the multiplying functions of x having the same order of magnitude. Thus near a band edge $'Q$ is a small quantity of the order of

$$\frac{dV}{dx}\frac{d}{dE}\left(\frac{p_d^2a^2}{4h^2}\right)Q = \frac{m^*}{2}\frac{a^2}{h^2}\frac{dV}{dx}Q, \quad (4.69)$$

whereas Q' is much larger, of the order of $(p_t/h)Q$ [Eq. (3.15)]. R and its derivatives are smaller than Q and its corresponding derivatives by a factor of the

order of a, as has been shown in the case of $Q_e(x)$ and $R_e(x)$ at the end of the preceding section.

Now the functions

$$f_\pm(x) = \exp[\pm(i/h)p_dx]P_{d\pm}(E;x) \quad (4.70)$$

are exact solutions of

$$f'' = -(2m/h^2)(E-W(x)-V)f \quad (4.71)$$

for constant V and p_d. It follows easily that, under the same conditions,

$$P_{d\pm}''(E;x) \pm \frac{2ip_d}{h}P_{d\pm}'(E;x)$$

$$= -\frac{2m}{h^2}\left\{E-W(x)-V-\frac{p_d^2}{2m}\right\}P_{d\pm}(E;x) \quad (4.72)$$

and that

$$Q''(E-V;x) = 2\frac{p_d^2}{h^2}R'(E-V;x)$$

$$-\frac{2m}{h^2}\left\{E-W(x)-V-\frac{p_d^2}{2m}\right\}Q(E-V;x), \quad (4.73)$$

$$R''(E-V;x) = -2Q'(E-V;x)$$

$$-\frac{2m}{h^2}\left\{E-W(x)-V-\frac{p_d^2}{2m}\right\}R(E-V;x). \quad (4.74)$$

Equations (4.73) and (4.74) remain true, in the notation introduced above Eq. (4.68), even when one treats V as a parameter varying with x. When p_d varies with x one has

$$A'' = -\frac{p_d^2(x)}{h^2}A \quad (4.75)$$

and

$$A''' = -\frac{1}{h^2}\frac{dp_d^2}{dx}A - \frac{p_d^2(x)}{h^2}A'. \quad (4.76)$$

On substituting Eq. (4.67) into the perturbed-periodic wave equation, and using Eqs. (4.73) to (4.76), one finds, after extensive cancellation of terms,

$$\psi'' - \frac{2m}{h^2}\{W(x)+V(x)-E\}\psi$$

$$= -\frac{1}{h^2}\frac{dp_d^2}{dx}AR + 2A('Q')+2A'('Q)+A(''Q)$$

$$-\frac{2p_d^2}{h^2}A('R)+2A'('R')+A'(''R). \quad (4.77)$$

The local error in the solution is measured by the terms on the right. Of these, all but the first vanish if one neglects the slow variation of Q and R with varying V, in taking derivatives. As compared with the in-

dividual terms on the right, this term is of relative magnitude:

$$\frac{1}{\hbar^2}\frac{dp_d^2}{dx}AR \bigg/ \frac{2m}{\hbar^2}\{W(x)+V(x)-E\}AQ$$

$$\sim \frac{m^*}{m}\bigg(\frac{a(dV/dx)}{W+V-E}\bigg), \quad (4.78)$$

since

$$R/Q \sim a, \quad (4.79)$$

near a band edge, where the effective mass is defined. The first of the remaining terms is the largest of these, and can be shown to be of the same order of magnitude as the term just considered. It thus appears that Eq. (4.67) gives a solution for which the error terms in the wave equation are small, in about the ratio of the

change in perturbation energy across a single cell to the true value of the local kinetic energy. For a slowly varying perturbation the solution is locally very accurate indeed; the long-range effect of accumulated local errors cannot be discussed here.

Perhaps the most interesting qualitative result of this analysis is the confidence it gives in the use of the effective-mass wave equation for the calculation of stationary-state energies, when $V(x)$ varies slowly. To each quadratically integrable solution ϕ of this equation there corresponds a quadratically integrable ψ *with the same energy*, providing a good approximate solution of the perturbed-periodic equation. The error in the energy E as an approximation to a stationary-state energy corresponds to the small error in this ψ, and not to the roughness in the arguments usually employed in arriving at the effective-mass equation.

The Radiation Spectra of Barium140 and Lanthanum140

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The radiations of Ba140 and La140 have been measured with a small 180° spectrometer. For the case of Ba140 three gamma-rays are present, all of which are converted, with energies 0.16, 0.31, and 0.54 Mev. The beta-ray spectrum shows the presence of two groups with maximum energies of 0.48 (40 percent) and 1.022 (60 percent) Mev.

The radiations of La140 are complex. Six gamma-rays of energies 0.093?, 0.335, 0.49, 0.82, 1.60, and 2.5 Mev are present, the first three being internally converted. The beta-ray spectrum is resolved into three groups with end points at 1.32 (70 percent), 1.67 (20 percent), and 2.26 (10 percent) Mev. Decay schemes for these isotopes are suggested.

I. INTRODUCTION

THE radiations of 12.8-day Ba140 and its daughter, 40-hour La140, have been re-investigated with the aim of formulating the mode of decay of these elements. These isotopes have been studied by numerous workers[1-7] and their results tend toward consistency insofar as energy values are concerned. However, previous investigations have been fragmentary and no integrated survey has been reported.

The present work was carried out with a small 180° spectrometer and very thin window G-M tube detection. Equilibrium samples of Ba140 and La140 obtained

from Oak Ridge were used. Beta-ray sources were of the order of 0.1 mg/cm² in thickness. Photoelectron spectra were obtained with a lead radiator 30 mg/cm² thick. The procedure consisted of measuring the beta-ray and photoelectron spectra initially with equilibrium sources, and finally with chemically isolated sources of Ba140 and La140.

II. EQUILIBRIUM MEASUREMENTS

The composite radiations were first measured by using sources in which the constituents were in equilibrium. Since the gamma-radiation of La140 is complex and the half-life relatively short, equilibrium photoelectron measurements furnish more reliable values of the energies. Subsequent runs with separated sources were, of course, necessary to identify the gamma-rays with the correct isotope.

Figure 1 shows the equilibrium photoelectron spectrum. The K and L photoelectron peaks associated with five gamma-rays are superimposed on a pronounced Compton-electron distribution. The photoelectron lines may be resolved into gamma-rays of energies 0.335,

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