

where $d\mathbf{S}$ is along the outward normal to Σ_ν . By (A11) and (A12), the volume integral in (A16) is < 0 , so finally

$$I^{1/2}(y) < \Omega' e^{-\beta|y-y_0|}, \tag{A17}$$

where Ω' is algebraic and y_0 is the nearest point of Σ_ν to the point y .

We wish to apply this theorem to the bounding of the χ_k of Sec. 2D inside the surfaces $\Sigma_P, P \neq 1$. Draw a straight line in configuration space from a point of Σ_1 to a point of Σ_P , and let these points be so chosen as to minimize the distance between them. Let y be the coordinate in the direction of this line, x_1, \dots, x_{n-1} the coordinates in all orthogonal directions. For most values of y , the hyperplane $y = \text{constant}$ will not pass near any point corresponding to a negative-ion configuration, and (A12) will be valid with [cf. (36)]

$$\beta^2 = (2m/\hbar^2)\eta\epsilon_I, \tag{A18}$$

where ϵ_I is the least of the atomic ionization energies and $\eta \approx 1$ is a factor by which ϵ_I must be reduced if the electron being removed is removed only to a distance L from its atom. For y values for which the hyperplane $y = \text{constant}$ passes close to a negative-ion configuration, ϵ_I in (18) should be replaced by ϵ_I

minus an electron affinity. However, there will be only finite ranges of y for which this occurs, and since the right of (A17) must contain $I^{1/2}(y_0)$ as a factor, we can apply (A17) consecutively to the large ranges of y values for which (A18) holds as written and the small ranges for which it must be modified. The result will be that (A17) holds everywhere outside Σ_1 , the only effect of the negative-ion configurations being to increase the coefficient Ω' .

Unfortunately, the bounding of I , defined by (A8), is not enough for our needs, since in our use of (35) and (40) we have to multiply values of χ_k inside Σ_P by a potential-energy perturbation which may become locally infinite. We expect, of course, that the maximum of χ_k on the x variables will obey a relation of the form (A17). This will be the case unless this maximum becomes more and more sharply peaked in x as y increases. This would mean that the x -momentum distribution would have to spread to ever larger momentum values. In mathematical terms, if $f(p,y)$ is the Fourier transform of χ_k on the x variables,

$$\int f(p,y) d^{3n-1}p / \left[\int |f(p,y)|^2 d^{3n-1}p \right]^{1/2}$$

would have to increase without limit. This seems physically unlikely.

Dynamics of Band Electrons in Electric and Magnetic Fields

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INTRODUCTION

THE following lines are a tribute to my teacher, Eugene Wigner, who introduced me to the subject of solid state physics.

The present communication reaches rather directly across a quarter century into the time when I was the Benjamin among his solid-state physics students at Princeton University. He first suggested to me that there ought to be a way to reconcile the local and the band concept for electrons, and that such a reconciliation would probably be useful in

understanding the spectra of insulators. The result of this suggestion was a paper on the electronic excitation levels in insulators.¹

When I did that work I felt that it had rather wide implications. Unfortunately, the trend of the times, and perhaps also my own negligence in clarifying the ideas sketched in the article (I had been taught in Switzerland that the cardinal sin of a physicist is to restate the obvious, a tenet to which I now no longer subscribe) left the duality of energy band and lattice cell in a haze from which it was not to emerge for some time.

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¹ Gregory H. Wannier, Phys. Rev. 52, 153 (1937).

When solid-state physics was taken up again after the war, the study of localized states in solids brought the issue back to the attention of physicists. Slater² showed the applicability of the original method to the problem of impurity states. The computational possibilities of the original article were thereupon quickly realized.^{3,4} The idea that the method reconciled the band and cell concepts as a matter of principle was not so easily accepted. This was so much the case that an "equivalent" method gained wide acceptance^{5,6} in which this reconciliation is an approximate feature valid in the neighborhood of the band edge only.

The course of experimental discovery, particularly the results for the de Haas-van Alphen effect, magnetoresistance, and cyclotron resonance in metals^{7,8} have made a restricted view of the "effective mass approximation" rather implausible. If one approaches this question from the point of view of theory, then the central problem is the status of interband matrix elements. There are two alternative views possible concerning them. Either they are considered as coupling the bands. The band picture is then approximate only and the laws of motion resulting from this picture are in competition with interband transitions. Or one may look upon the interband matrix elements as nonessential. One then sees them as modifiers of a poorly approximated band wave function. The effective mass picture is then considered exact in some sense. When I re-examined the question in this light in 1955, it seemed to me reasonable to hope that the band picture and the effective mass formalism might be exact in the presence of homogeneous fields. The reason for this hope was that bands arise from the periodicity of the crystal, and that this periodicity is not destroyed by such fields. Interband transitions would then be properly associated with field inhomogeneities which are, of course, a form of disorder just as thermal agitation or impurities.

Theory has confirmed this view in a general way, but the idea must not be interpreted too widely. Thus, it will be seen below that the greater part of

the theory is only proved asymptotically to all powers of the field. However, the theory as a whole cannot be dismissed as asymptotic, because a very crucial part of it can be proved exactly; exact proofs for other parts may very well follow in the future. Another direction in which one must be careful not to use too wide an interpretation is in the effect of time-dependent homogenous fields. It appears that such fields can produce true interband coupling and thus lead beyond the effective Hamiltonian formalism for single bands or band groups.

1. HAMILTONIAN BAND MECHANICS

In this section the basic ideas of band dynamics will be developed in the simplest possible way, namely, by the study of the field-free crystal. Clear concepts can be evolved this way, but interband coupling appears then as an obscure sort of competitive process. That this competition is, in fact, not severe is an extraneous piece of information to make the development meaningful.

For our purposes a crystal is an infinite⁹ medium having translational periodicity. It has three fundamental periods \mathbf{a} , \mathbf{b} , and \mathbf{c} . All points related to each other by a *lattice vector* $\boldsymbol{\rho}$ such that

$$\boldsymbol{\rho} = l\mathbf{a} + m\mathbf{b} + n\mathbf{c} \quad (1a)$$

$$l, m, n \text{ integer} \quad (1b)$$

have identical properties as a medium for electron motion.

The crucial variable in the discussion of band theory is the wave vector \mathbf{k} . For an understanding of this variable it is desirable to introduce a class of operators, called the *lattice translation operators*. They are defined as

$$T(\boldsymbol{\rho}) = \exp [(i\mathbf{p} \cdot \boldsymbol{\rho})/\hbar] \quad (2)$$

where \mathbf{p} is the momentum and $\boldsymbol{\rho}$ is given by (1). They obey the commutation relation

$$T(\boldsymbol{\rho})f(\mathbf{p}, \mathbf{x}) = f(\mathbf{p}, \mathbf{x} + \boldsymbol{\rho})T(\boldsymbol{\rho}). \quad (3)$$

Since the assumed one-electron Hamiltonian \mathcal{H}_0 has the property

$$\mathcal{H}_0(\mathbf{p}, \mathbf{x} + \boldsymbol{\rho}) = \mathcal{H}_0(\mathbf{p}, \mathbf{x}), \quad (4)$$

we have the result that the operators $T(\boldsymbol{\rho})$ are constants of the motion. Since, in addition, they also commute with each other, they are simultaneously

⁹ The formalism is developed for a finite Born-von Karman volume in G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), pp. 172-201. The presentation is simpler but has certain logical flaws which are removed by assuming the crystal infinite.

² J. C. Slater, *Phys. Rev.* **76**, 1592 (1949).

³ C. Kittel and A. H. Mitchell, *Phys. Rev.* **96**, 1488 (1954).

⁴ J. C. Slater, *Encyclopedia of Physics XIX* (Springer-Verlag, Berlin, 1956), pp. 70-78.

⁵ J. M. Luttinger and W. Kohn, *Phys. Rev.* **97**, 869 (1955).

⁶ W. Kohn, *Solid State Physics* (Academic Press Inc., New York, 1957), Vol. 5, pp. 271-281.

⁷ I. M. Lifshitz and V. G. Peshanskii *J. Exptl. Theoret. Phys. (U.S.S.R.)* **35**, 1251 (1958) [translation: *Soviet Phys.—JETP* **8**, 875 (1959)]; *ibid.* **38**, 188 (1960) [translation: *ibid.* **11**, 137, 1960].

⁸ The Fermi Surface, *Proceedings of an International Conference, Cooperstown, New York, 1960* (John Wiley & Sons, Inc., New York, 1960).

diagonalizable. The numerical values are reducible to the eigenvalues of the three generating elements $T(\mathbf{a})$, $T(\mathbf{b})$, and $T(\mathbf{c})$. These eigenvalues are on the unit circle because the operators are unitary. Let the three eigenvalues be $e^{2\pi i\lambda}$, $e^{2\pi i\mu}$, and $e^{2\pi i\nu}$. It is then clear that λ , μ , and ν are determined only up to an additive integer. In physics it is the custom to represent the eigenvalues of (2) in terms of a wave vector \mathbf{k} , that is, to write

$$T(\boldsymbol{\rho})\psi_{\mathbf{k}} = \exp(i\mathbf{k}\cdot\boldsymbol{\rho})\psi_{\mathbf{k}}. \tag{5}$$

It follows then from the preceding analysis that \mathbf{k} equals

$$\mathbf{k} = 2\pi\{\lambda\mathbf{a}^* + \mu\mathbf{b}^* + \nu\mathbf{c}^*\}, \tag{6a}$$

where \mathbf{a}^* , \mathbf{b}^* , and \mathbf{c}^* are the basis vectors of the lattice which is reciprocal to the lattice (1), or explicitly,

$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}, \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}. \tag{6b}$$

Since all distinct values of λ , μ , and ν arise within an interval of length unity, we see that all significant values of \mathbf{k} are reached if \mathbf{k} varies within one primitive cell of the reciprocal lattice expanded by 2π (first Brillouin zone). Outside this cell we reach \mathbf{k} values which are equivalent. In particular, all \mathbf{k} vectors lying on an (expanded) reciprocal lattice with respect to each other are equivalent. Consequently, any physically meaningful function of \mathbf{k} must be periodic in reciprocal space. This means, in general, that it can be written as Fourier series of the form

$$f(\mathbf{k}) = \sum_{\boldsymbol{\rho}} \varphi(\boldsymbol{\rho}) \exp(i\mathbf{k}\cdot\boldsymbol{\rho}), \tag{7}$$

where $\boldsymbol{\rho}$ is given by (1).

Bloch functions are the eigenfunctions of a Hamiltonian having the symmetry property (4), which are simultaneously eigenfunctions of the lattice translation operators (2). The idea of *Bloch bands* is still largely intuitive even today. It has been proved in one dimension for Schrödinger equations with periodic potentials^{10,11} that if one proceeds in the direction of increasing energy one can label successive bands of energies in such a way that each band contains the entire spectrum of eigenvalues of \mathbf{k} without energy overlap between successive bands. Bands can thus be labeled by successive integers which we call the *band index* q . It is certain that the idea of a band index cannot be used in the same simple way in

three dimensions. One must, at least, allow the property of degeneracy. By degeneracy we mean, in solid state physics, a set of wave functions degenerate in \mathbf{k} as well as in energy. Such degeneracy can occur on points, lines, or even occasionally surfaces of \mathbf{k} space.¹² Concurrently, one usually has to allow for overlapping of the bands in energy. It appears that with these restrictions the concept of a band index is valid for actual solids. However, even if this is the case, the Hamiltonian formalism cannot be significantly implemented without taking the degeneracy into account. This means the introduction of many component wave functions and matrix operators even in the classical limit. We shall not discuss this subject further, but refer the reader to the literature.¹³ Many aspects of this feature are actually not yet thoroughly explored.

In the following, we shall introduce nondegeneracy of the band under consideration as an additional postulate which is rarely true, but which allows us to bring out qualitatively and quantitatively certain features of Bloch bands. If a band is nondegenerate, and its band index q is a good quantum number, both the energy eigenvalue and the Bloch function may be expanded in Fourier series of the type (7). We thus write for the energy $W_q(\mathbf{k})$

$$W_q(\mathbf{k}) = \sum_{\boldsymbol{\rho}} w_q(\boldsymbol{\rho}) \exp(i\mathbf{k}\cdot\boldsymbol{\rho}) \tag{8}$$

and for the wave functions $b_q(\mathbf{x};\mathbf{k})$

$$b_q(\mathbf{x};\mathbf{k}) = \sum_{\boldsymbol{\rho}} \exp(i\mathbf{k}\cdot\boldsymbol{\rho}) a_q(\mathbf{x};\boldsymbol{\rho}). \tag{9}$$

The functions $a_q(\mathbf{x};\boldsymbol{\rho})$ have the property that they depend only on the difference of the two arguments. This is seen in the following way. We may modify the above equation to write

$$b_q(\mathbf{x} - \boldsymbol{\rho}';\mathbf{k}) = \sum_{\boldsymbol{\rho}} \exp(i\mathbf{k}\cdot\boldsymbol{\rho}) a_q(\mathbf{x} - \boldsymbol{\rho}';\boldsymbol{\rho}).$$

An alternative way of writing this follows from the definition of \mathbf{k} :

$$b_q(\mathbf{x} - \boldsymbol{\rho}';\mathbf{k}) = \sum_{\boldsymbol{\rho}} \exp[i\mathbf{k}\cdot(\boldsymbol{\rho} - \boldsymbol{\rho}')] a_q(\mathbf{x};\boldsymbol{\rho}),$$

or with a shift in the summation index:

$$b_q(\mathbf{x} - \boldsymbol{\rho}';\mathbf{k}) = \sum_{\boldsymbol{\rho}} \exp(i\mathbf{k}\cdot\boldsymbol{\rho}) a_q(\mathbf{x};\boldsymbol{\rho} + \boldsymbol{\rho}').$$

Identifying the coefficients in the two series and setting $\boldsymbol{\rho}$ equal to zero we finally get

$$a_q(\mathbf{x} - \boldsymbol{\rho}';\mathbf{0}) = a_q(\mathbf{x};\boldsymbol{\rho}').$$

¹⁰ H. A. Kramers, *Physica* 2, 483 (1935).

¹¹ E. C. Titchmarsh, *Eigenfunction Expansions* (Oxford University Press, New York, 1958), Chap. 21.

¹² C. Herring, *Phys. Rev.* 52, 361 (1937).

¹³ J. M. Luttinger, *Phys. Rev.* 102, 1030 (1956). See also the references 3, 5, and 6.

We shall drop the superfluous argument $\mathbf{0}$ and write (9) in the form

$$b_q(\mathbf{x};\mathbf{k}) = \sum_{\rho} \exp(i\mathbf{k}\cdot\boldsymbol{\rho}) a_q(\mathbf{x} - \boldsymbol{\rho}). \quad (10)$$

The functions $a_q(\mathbf{x} - \boldsymbol{\rho})$ are known as the *Wannier functions* associated with the band of index q . A single one of them, say, $a_q(\mathbf{x})$ contains within itself the entire information about any one band. Computation of a Wannier function appears to be troublesome; consequently, they are primarily devices for reasoning. They are also plagued by a certain indeterminacy since the left-hand side can be multiplied with an arbitrary periodic function of \mathbf{k} . Gibson¹⁴ has shown that there is a "best" choice of the a_q 's giving the least mean square deviation to the coordinate \mathbf{x} in $a_q(\mathbf{x})$. The function $a_q(\mathbf{x})$, so determined, converges exponentially at large distances, unless the band is degenerate with other bands.¹⁵

Since the a_q 's are Fourier coefficients of the b_q 's they are given by

$$a_q(\mathbf{x} - \boldsymbol{\rho}) = \frac{\omega}{8\pi^3} \int_{\omega^{**}} \exp(-i\mathbf{k}\cdot\boldsymbol{\rho}) b_q(\mathbf{x};\mathbf{k}) d\mathbf{k}. \quad (11)$$

Here ω is the volume of the primitive cell of the crystal. ω^{**} is a primitive cell ω^* of reciprocal space whose linear dimensions are enlarged by 2π . One can show with the help of (6b) that ω and ω^* are reciprocals of each other.

Normalization of Bloch and Wannier functions is somewhat a matter of taste, except for the physical fact that the former are not, and the latter are normalizable over all space. If the Bloch functions are normalized to unity within a primitive cell then the Wannier functions defined by (10) and (11) are normalized to unity over all space. To prove this we start out with the completeness relation for the Fourier series (10) which reads

$$\int_{\omega^{**}} |b_q(\mathbf{x};\mathbf{k})|^2 d\mathbf{k} = (8\pi^3/\omega) \sum_{\rho} |a_q(\mathbf{x} - \boldsymbol{\rho})|^2. \quad (12)$$

Now calculating the normalization integral of $a_q(\mathbf{x})$ we proceed in two steps. First, we split the integral into a sum over cells, then we integrate over one cell. This yields with (12)

$$\begin{aligned} \int_{\Omega} |a_q(\mathbf{x})|^2 d\mathbf{x} &= \int_{\omega} \sum_{\rho} |a_q(\mathbf{x} - \boldsymbol{\rho})|^2 d\mathbf{x} \\ &= \frac{\omega}{8\pi^3} \int_{\omega} d\mathbf{x} \int_{\omega^{**}} |b_q(\mathbf{x};\mathbf{k})|^2 d\mathbf{k}. \end{aligned}$$

As both integrals are over a finite range, there is no

difficulty about exchanging the order of integration. If we impose the suggested normalization on b , namely,

$$\int_{\omega} |b_q(\mathbf{x};\mathbf{k})|^2 d\mathbf{x} = 1, \quad (13)$$

then we finally get

$$\int_{\Omega} |a_q(\mathbf{x})|^2 d\mathbf{x} = (\omega/8\pi^3) \int_{\omega^{**}} d\mathbf{k} = 1. \quad (14)$$

If the phase of $b_q(\mathbf{x};\mathbf{k})$ is chosen appropriately, the probability density of $a_q(\mathbf{x})$ can be concentrated near the origin. The probability density of $a_q(\mathbf{x} - \boldsymbol{\rho})$ is then concentrated near the lattice point $\boldsymbol{\rho}$. The Wannier functions thus offer a limited definition of localization compatible with the existence of a band index q . These notions are expressed in operator language by the definition of the *lattice vector operator* \mathbf{r} which is defined through

$$\mathbf{r} a_q(\mathbf{x} - \boldsymbol{\rho}) = \boldsymbol{\rho} a_q(\mathbf{x} - \boldsymbol{\rho}). \quad (15)$$

From (10) it follows then that the result of operating with \mathbf{r} on $b_q(\mathbf{x};\mathbf{k})$ is

$$\mathbf{r} b_q(\mathbf{x};\mathbf{k}) = -i \frac{\partial b_q(\mathbf{x};\mathbf{k})}{\partial \mathbf{k}}. \quad (16)$$

The proper operator relation connecting \mathbf{r} and \mathbf{k} results from this by treating an arbitrary wave function ψ as a superposition of such Bloch functions. In other words we write

$$\psi(\mathbf{x}) = \sum_q \int_{\omega^{**}} \alpha(q;\mathbf{k}) b_q(\mathbf{x};\mathbf{k}) d\mathbf{k}.$$

The result of the operator \mathbf{r} on ψ then takes the form

$$\mathbf{r} \psi = \sum_q \int_{\omega^{**}} \alpha(q;\mathbf{k}) \left(-i \frac{\partial b_q(\mathbf{x};\mathbf{k})}{\partial \mathbf{k}} \right) d\mathbf{k}.$$

From what was said previously, both α and b_q must be periodic in \mathbf{k} . We can therefore integrate by parts with integrated out part 0. This yields

$$\mathbf{r} \psi = \sum_q \int_{\omega^{**}} i \frac{\partial \alpha(q;\mathbf{k})}{\partial \mathbf{k}} b_q(\mathbf{x};\mathbf{k}) d\mathbf{k}$$

or

$$\mathbf{r} \alpha(q;\mathbf{k}) = i \frac{\partial \alpha(q;\mathbf{k})}{\partial \mathbf{k}}. \quad (17)$$

\mathbf{r} is thus a variable conjugate to $\hbar\mathbf{k}$ within the band q .

The usefulness of (17) for a quantum mechanics of solids is treated extensively elsewhere. What has been very seldom done¹⁶ and what is worth pointing

¹⁴ J. B. Gibson, Bull. Am. Phys. Soc. **3**, 146 (1958).

¹⁵ W. Kohn, Phys. Rev. **115**, 809 (1959).

¹⁶ The point being made here was made previously in reference 2. However, the inclusion of magnetic fields in the formalism is new.

out here is that we may use \mathbf{r} and $\hbar\mathbf{k}$ as conjugate variables for a quasi-classical form of mechanics. Such a passage to the limit is favored by the fact that the number of quantum states in a band is very large. Thus, even though the band as such must be accepted as a quantum phenomenon, events involving electrons from one band only can often be formulated in quasiclassical language.

Let us start with the simplest case, an electron moving under no forces except those arising from the crystalline medium. We have

$$\mathcal{H} = W_q(\mathbf{k}) . \tag{18}$$

Hamilton's equations for (18) read

$$\hbar \frac{d\mathbf{r}}{dt} = \partial W_q / \partial \mathbf{k} \tag{19}$$

$$\hbar \frac{d\mathbf{k}}{dt} = 0 . \tag{20}$$

These are well-known relationships.

If we add a potential $V(\mathbf{x})$ to this Hamiltonian we may hope that we can replace the argument \mathbf{x} by the lattice vector \mathbf{r} .¹⁷ We are then led to consider a Hamiltonian of the form

$$\mathcal{H} = W_q(\mathbf{k}) + eV(\mathbf{r}) . \tag{21}$$

The expression (21) is the one which explains impurity and exciton states and their similarity to the Rydberg series.^{1,6} In the quasi-classical approximation we get from it the equations of motion

$$\hbar \frac{d\mathbf{r}}{dt} = \partial W_q / \partial \mathbf{k} \tag{22}$$

$$\hbar \frac{d\mathbf{k}}{dt} = -e \partial V / \partial \mathbf{r} . \tag{23}$$

If a magnetic field is present we make the substitution

$$\mathbf{K} = \mathbf{k} - (e/\hbar c)\mathbf{A}(\mathbf{r}) , \tag{24}$$

and write the Hamiltonian in the form

$$\mathcal{H} = W_q(\mathbf{K}) . \tag{25}$$

The correctness of this step is proved below for the case of a homogeneous magnetic field. In the quasi-classical approximation we derive from (24) and (25) the equations of motion

$$\hbar \frac{d\mathbf{r}}{dt} = \frac{\partial W_q}{\partial \mathbf{K}} \tag{26}$$

$$\hbar \frac{d\mathbf{k}}{dt} = \frac{e}{\hbar c} \frac{\partial W_q}{\partial K_i} \frac{\partial A_i}{\partial \mathbf{r}} . \tag{27}$$

Equation (27) is inconvenient and is better modified

¹⁷ Simple qualitative estimates such as the one in reference 9, p. 180, as to when this step is valid give a criterion which is too stringent. For it will be shown that the step can be justified rigorously for a homogeneous electric field.

to yield the time derivative of the quantity (24). We get with (26)

$$\hbar \frac{d\mathbf{K}}{dt} = \frac{e}{\hbar c} \frac{\partial W_q}{\partial K_i} \left(\frac{\partial A_i}{\partial \mathbf{r}} - \frac{\partial \mathbf{A}}{\partial r_i} \right) ,$$

or more simply

$$\frac{d\mathbf{K}}{dt} = \frac{e}{\hbar^2 c} \frac{\partial W_q}{\partial \mathbf{K}} \times \mathbf{H} . \tag{28}$$

Equation (28) is the magnetic part of the Lorentz force law which is thus seen to apply to the variable \mathbf{K} . The results (21) and (25) can be combined to yield a Hamiltonian when both electric and magnetic fields are present. The Hamiltonian then reads

$$\mathcal{H} = W_q[\mathbf{k} - (e/\hbar c)\mathbf{A}(\mathbf{r},t)] + eV(\mathbf{r},t) . \tag{29}$$

The result is that the Lorentz force law applies in its entirety to the variable \mathbf{K} . The Hamiltonian (29) can again be justified rigorously for the case that the fields are homogeneous and independent of time.

There is a second way of doing Hamiltonian mechanics which is implicit in the Eqs. (25) and (29). We can shift our attention to motion in \mathbf{K} -space and treat (26) as an auxiliary equation telling us what is going on in ordinary space. If the fields are homogeneous the Lorentz force equation contains, in fact, no reference to \mathbf{x} -space at all. As an example, we may analyze (28), assuming a constant magnetic field in the z direction. We find

$$\frac{dK_x}{dt} = \frac{eH}{\hbar^2 c} \frac{\partial W_q(\mathbf{K})}{\partial K_y} \tag{30a}$$

$$\frac{dK_y}{dt} = -\frac{eH}{\hbar^2 c} \frac{\partial W_q(\mathbf{K})}{\partial K_x} \tag{30b}$$

$$dK_z/dt = 0 . \tag{31}$$

Rather surprisingly, the Eqs. (30) are in themselves a Hamiltonian system of equations in which $W_q(\mathbf{K})$ plays the role of a Hamiltonian, and $(\hbar^2 c/eH)^{1/2} K_x$ and $(\hbar^2 c/eH)^{1/2} K_y$ play the role of conjugate variables; according to (31), K_z acts as a fixed parameter of no dynamical status. The trajectories lie in the K_x - K_y plane. They have an energy integral, that is, it follows from (30) that

$$\frac{dW_q(\mathbf{K})}{dt} = \frac{\partial W_q(\mathbf{K})}{\partial K_x} \frac{dK_x}{dt} + \frac{\partial W_q(\mathbf{K})}{\partial K_y} \frac{dK_y}{dt} = 0 . \tag{32}$$

The trajectories in \mathbf{K} -space are therefore the intersections of planes $K_z = \text{const}$ with surfaces of constant energy W_q . These curves are either open, in which case they are periodic in reciprocal space, or they are closed. In either case, the motion in \mathbf{K} -space

is periodic in time. Specializing for the latter case, we may calculate the period T for traversing a closed curve by the formula

$$\begin{aligned} T &= \oint \frac{dK_x}{\dot{K}_x} = \frac{\hbar^2 c}{eH} \oint \frac{dK_x}{(\partial W / \partial K_y)_{K_x, K_z}} \\ &= \frac{\hbar^2 c}{eH} \oint \left(\frac{\partial K_y}{\partial W} \right)_{K_x, K_z} dK_x \\ &= \frac{\hbar^2 c}{eH} \frac{\partial}{\partial W} \left(\oint K_y dK_x \right)_{K_x}. \end{aligned}$$

The integral is the area A enclosed in the K_x - K_y plane by the chosen trajectory. Hence, we can write for the period T

$$T = (\hbar^2 c / eH) (\partial A / \partial W)_{K_x}. \quad (33)$$

The Hamiltonian structure of the Eqs. (30) with respect to K_x and K_y is no accident. The result holds also in the quantum situation. It follows from (24) that \mathbf{K} obeys the commutation rule

$$\mathbf{K} \times \mathbf{K} = ie\mathbf{H} / \hbar c. \quad (34)$$

We find therefore again that $(\hbar^2 c / eH)^{1/2} K_x$ and $(\hbar^2 c / eH)^{1/2} K_y$ are conjugate variables. Furthermore, since the Hamiltonian (25) depends only on \mathbf{K} , we deal with a problem in \mathbf{K} -space only, also in the quantum limit. The two formulations are equivalent within the limitations of the Bohr-Sommerfeld correspondence principle; the energy spacing of the quantum levels equals \hbar/T , with T given by (33). This reduces to the cyclotron resonance formula in the appropriate special case.

2. HOMOGENEOUS FIELDS; GENERAL THEORY

Having studied in the previous section the physical implications of band mechanics, we shall be concerned in the following with its justification. The theory of the field-free crystal is an extremely narrow base for a general theory of motion under forces, and the experiment itself indicates a much greater range for it than one would expect from such a starting point. We shall see now that the formalism can be rigorously justified for homogeneous fields, as stated in the introduction. Such an extension broadens the base in the sense that interband transitions are now linked to inhomogeneities or sudden switches of the field in time. This is as it should be on the basis of physical intuition.

In the derivation of a result it is not necessary to indicate the physical reasoning which led to it. This

attitude was taken in the original publications.^{18,19} However, it seems useful here to indicate the physical motivation since there might well be other problems benefitting from that aspect. The physical motivation again involves the localized functions associated with a band. Originally the purpose of these functions was to permit the handling of localized problems. Now it comes out that they are also instrumental in solving the problem of homogeneous fields. The reason is, of course, that it is relatively easier to predict the effect of a field on a localized function. If the postulate of no band coupling is introduced in addition the structure of the equations comes out to be entirely determined. We shall now proceed to carry out this sort of derivation.

As a first step we must observe the effect of a periodic Hamiltonian on its Wannier functions. Suppose we have

$$\mathcal{H}_0(\mathbf{p}, \mathbf{x}) = (1/2m)\mathbf{p}^2 + V(\mathbf{x}) \quad (35)$$

with $V(\mathbf{x})$ periodic. $\mathcal{H}_0(\mathbf{p}, \mathbf{x})$ then obeys relation (4) and has Bloch functions as eigenfunctions.

$$\mathcal{H}_0(\mathbf{p}, \mathbf{x}) b_a(\mathbf{x}; \mathbf{k}) = W_a(\mathbf{k}) b_a(\mathbf{x}; \mathbf{k}). \quad (36)$$

Since (36) is based on symmetry only the exact form (35) of the Hamiltonian is not essential here. In view of the growing importance of many-particle and quasi-particle formulations, it is important to keep the more general case in mind.

We now substitute into (36) the Fourier expansions (8) and (10) and collect terms. We get

$$\mathcal{H}_0 a_a(\mathbf{x} - \boldsymbol{\rho}) = \sum_{\boldsymbol{\rho}'} w_a(\boldsymbol{\rho} - \boldsymbol{\rho}') a_a(\mathbf{x} - \boldsymbol{\rho}'). \quad (37)$$

We see that in the Wannier representation \mathcal{H}_0 is represented by a matrix without interband coupling terms which is cyclic with respect to the lattice vector $\boldsymbol{\rho}$.

Let us take up the electric field as the next step in difficulty. We now add to the Hamiltonian \mathcal{H}_0 a term $-e\mathbf{E} \cdot \mathbf{x}$ and set

$$\mathcal{H} = \mathcal{H}_0(\mathbf{p}, \mathbf{x}) - e\mathbf{E} \cdot \mathbf{x}. \quad (38)$$

The new term destroys necessarily the cyclic property (37). The reason for it is that we have now a potential which varies from point to point. As a consequence, the result of operating with \mathcal{H} on a $a_a(\mathbf{x} - \boldsymbol{\rho})$ must differ from the result of operating on $a_a(\mathbf{x})$ by the amount $-e\mathbf{E} \cdot \boldsymbol{\rho}$. Thus, we may write

$$\mathcal{H} a_a(\mathbf{x} - \boldsymbol{\rho}) = -e\mathbf{E} \cdot \boldsymbol{\rho} a_a(\mathbf{x} - \boldsymbol{\rho}) + \text{cyclic terms}. \quad (39)$$

¹⁸ Gregory H. Wannier, Phys. Rev. 117, 432 (1960).

¹⁹ G. H. Wannier and D. R. Fredkin, Phys. Rev. 125, 1910 (1962).

The above statement is true for any localized set of functions. Now if we add to this the postulate that there are no interband terms in the cyclic part, we are led to the completely specified equation

$$\{3\mathcal{C} + e\mathbf{E} \cdot \boldsymbol{\rho}\} a_q(\mathbf{x} - \boldsymbol{\rho}) = \sum_{\rho'} w_q(\boldsymbol{\rho} - \boldsymbol{\rho}') a_q(\mathbf{x} - \boldsymbol{\rho}') \quad \text{or with (38)}$$

$$\begin{aligned} & \{3\mathcal{C}_0(\mathbf{p}, \mathbf{x}) - e\mathbf{E} \cdot (\mathbf{x} - \boldsymbol{\rho})\} a_q(\mathbf{x} - \boldsymbol{\rho}) \\ & = \sum_{\rho'} w_q(\boldsymbol{\rho} - \boldsymbol{\rho}') a_q(\mathbf{x} - \boldsymbol{\rho}') . \end{aligned} \quad (40)$$

The Bloch form of Eq. (40) results through multiplication with $\exp i\mathbf{k} \cdot \boldsymbol{\rho}$ and the summation over $\boldsymbol{\rho}$. We find with (8) and (10)

$$\{3\mathcal{C}_0(\mathbf{p}, \mathbf{x}) - e\mathbf{E}(\mathbf{x} + i \partial/\partial \mathbf{k})\} b_q(\mathbf{x}; \mathbf{k}) = W_q(\mathbf{k}) b_q(\mathbf{x}; \mathbf{k}) \quad (41)$$

The sense in which (41) is a correct equation will not be discussed here in detail. We shall only observe that the operator in curly brackets is a periodic operator because $\mathbf{x} + i \partial/\partial \mathbf{k}$ is a periodic operator. A good justification for (41) is provided by proceeding in powers of E in determining b_q and W_q . Such a justification "to all power of E " is found elsewhere.¹⁸ A rigorous proof of (41) will be found below in Sec. 3.

Equations (40) and (41) already constitute a partial solution of the Hamiltonian problem. Since operation with \mathcal{C} on a function of band index q leads only to functions of the same index, any solution will necessarily be a linear combination of functions of equal index only. In the present case the problem is even simpler, if we are willing to accept time-dependent solutions. A set of such solutions can be worked out with the help of the lattice translation operators (2). It is true that these operators are no longer commuting with the Hamiltonian, but they are still simultaneously diagonalizable and have a very simple time dependence. From (3) and (38) we get

$$i\hbar dT(\boldsymbol{\rho})/dt = -e\mathbf{E} \cdot \boldsymbol{\rho} T(\boldsymbol{\rho}) . \quad (42)$$

This means that the time derivative of $T(\boldsymbol{\rho})$ is diagonal if $T(\boldsymbol{\rho})$ is diagonal, and \mathbf{k} can be treated as a number varying in time. We get with (5)

$$d\mathbf{k}/dt = e\mathbf{E}/\hbar , \quad (43)$$

and hence

$$\mathbf{k} = \mathbf{k}_0 + e\mathbf{E}t/\hbar . \quad (44)$$

It follows from this that it is possible to write down solutions of the Schrödinger equation which diagonalize the lattice translation operators rather than the Hamiltonian. Houston first wrote down such solutions which were approximate in his case.²⁰ The

²⁰ W. V. Houston, Phys. Rev. 57, 184 (1940).

same type of solution now becomes exact. It reads

$$\begin{aligned} \psi(\mathbf{x}, t) = & b_q \left(\mathbf{x}; \mathbf{k}_0 + \frac{e\mathbf{E}t}{\hbar} \right) \\ & \exp \left[-\frac{i}{eE} \int_{k_{0x}}^{k_{0x} + eEt/\hbar} W_q(\mathbf{k}) dk_x \right] , \end{aligned} \quad (45)$$

where b_q and W_q are solutions of (41) and x is the direction of the \mathbf{E} field. The statement is verified by direct substitution of (41) and (45) into the equation of motion

$$i\hbar \partial\psi/\partial t = \{3\mathcal{C}_0(\mathbf{p}, \mathbf{x}) - e\mathbf{E} \cdot \mathbf{x}\} \psi .$$

The solution (45) may be Fourier analyzed to yield the constant energy solutions associated with one band. If \mathbf{E} is in a direction of the reciprocal lattice having period \mathbf{a}^* , then a Fourier series for (45) will contain the frequencies

$$\omega_{qn} = \frac{1}{\hbar a^*} \int_{k_{0x}}^{k_{0x} + 2\pi a^*} W_q(\mathbf{k}) dk_x + neE/\hbar a^* .$$

This yields the energy spectrum

$$\mathcal{E}_{qn} = \frac{1}{2\pi a^*} \int_{k_{0x}}^{k_{0x} + 2\pi a^*} W_q(\mathbf{k}) dk_x + neE/a^* . \quad (46)$$

Equation (46) is easily interpreted. The first term is a mean value of the energy in the band, and the second yields a uniformly spaced system of levels. The spacing is the energy difference between states which are shifted in space from one lattice plane to the next (since $1/a^*$ is the distance of separation of the lattice planes perpendicular to E). This Stark ladder system has a characteristic instability, in the sense that the slightest change in the direction of E completely alters the level system. The Houston solutions do not have this instability and seem therefore a more reliable basis for the study of associated effects, such as interband tunneling. They also have the \mathbf{k} conservation explicitly built in which is an advantage.

We may close the electric case with the remark that the derivation yields also the effective Hamiltonian (21). If we substitute the definition (16) into (41) we get

$$3\mathcal{C}_0(\mathbf{p}, \mathbf{x}) - e\mathbf{E} \cdot \mathbf{x} \approx W_q(\mathbf{k}) - e\mathbf{E} \cdot \mathbf{r} . \quad (47)$$

The relation holds in the sense of an equivalence within the band of index q . It permits the Hamiltonian treatment of motion within a band outlined in Sec. 1. This treatment is also free of the instability just discussed; the instability arises only upon quantization.

The problem of motion in a magnetic field poses

qualitatively the same problem, but its solution is more difficult. One of the possible forms of the Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0(\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{x}, \mathbf{x}), \quad (48)$$

where $\mathcal{H}_0(\mathbf{p}, \mathbf{x})$ satisfies (4) and may or may not have the form (35). In writing down (48) we have chosen the symmetric gauge and a fixed origin. The choice of gauge has no real importance here. The effects of a change of gauge are well known and we could reason with any other gauge if we wanted. The choice of an origin is the difficult problem. It singles out a particular cell and shows that the result of operating with (48) on localized functions can never be cyclic. In Eq. (39) we could handle this simply by adding a term. This would not work here because the non-periodic part of \mathcal{H} is at least quadratic in \mathbf{x} and involves \mathbf{p} as well as \mathbf{x} . The solution to this dilemma was found by Peierls²¹ while studying the effect of magnetic fields on tight binding wave functions. He showed that it is possible to find a phase factor for tight binding functions which permits shifting of the origin in the vector potential. His argument is applicable to any set of localized functions. It is expressed in the formula

$$\begin{aligned} & \{ \mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{x} \} \exp [-\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \mathbf{x} \times \boldsymbol{\rho}] \\ & \times a_q(\mathbf{x} - \boldsymbol{\rho}) = \exp [-\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \mathbf{x} \times \boldsymbol{\rho}] \\ & \times \{ \mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{x} - \boldsymbol{\rho}) \} a_q(\mathbf{x} - \boldsymbol{\rho}). \end{aligned} \quad (49)$$

This means that if we take a set of identical localized functions we get a very complicated result when operating on them with the same Hamiltonian, but if we give to each of the functions its Peierls phase factor results will, in fact, be cyclic in $\boldsymbol{\rho}$. We therefore choose our basis functions in the form

$$A_q(\mathbf{x}; \boldsymbol{\rho}) = \exp [-\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \mathbf{x} \times \boldsymbol{\rho}] a_q(\mathbf{x} - \boldsymbol{\rho}) \quad (50)$$

and get

$$\begin{aligned} & \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{x}, \mathbf{x}] A_q(\mathbf{x}; \boldsymbol{\rho}) \\ & = \exp [-\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \mathbf{x} \times \boldsymbol{\rho}] \\ & \times \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{x} - \boldsymbol{\rho}), \mathbf{x}] a_q(\mathbf{x} - \boldsymbol{\rho}). \end{aligned} \quad (51)$$

We could now postulate that the right-hand-side operator in (51), together with the wave function following, yields a cyclic matrix when expanded in functions $a_q(\mathbf{x} - \boldsymbol{\rho}')$. This assumption leads to a dead end, because there is an exponent in front dependent on x which prevents this from being a

proper matrix expansion. We are led to choose a better ansatz by the observation that

$$\mathbf{x} \times \boldsymbol{\rho} + \boldsymbol{\rho} \times \boldsymbol{\rho}' + \boldsymbol{\rho}' \times \mathbf{x}$$

is an expression depending only on the differences of the three vectors \mathbf{x} , $\boldsymbol{\rho}$, $\boldsymbol{\rho}'$ and that multiplication of $a_q(\mathbf{x} - \boldsymbol{\rho}')$ with

$$\exp [\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot (\mathbf{x} \times \boldsymbol{\rho} + \boldsymbol{\rho} \times \boldsymbol{\rho}' + \boldsymbol{\rho}' \times \mathbf{x})]$$

will simultaneously remove the incorrect exponent in (51) and bring in the correct one so that expansion is with respect to the wave functions (50). The exponent containing $\boldsymbol{\rho} \times \boldsymbol{\rho}'$ is the price we pay for this privilege. We therefore make the assumption that

$$\begin{aligned} & \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{x} - \boldsymbol{\rho}), \mathbf{x}] a_q(\mathbf{x} - \boldsymbol{\rho}) \\ & = \sum_{\boldsymbol{\rho}'} \exp [\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot (\mathbf{x} \times \boldsymbol{\rho} + \boldsymbol{\rho} \times \boldsymbol{\rho}' + \boldsymbol{\rho}' \times \mathbf{x})] \\ & \times w_q(\boldsymbol{\rho} - \boldsymbol{\rho}') a_q(\mathbf{x} - \boldsymbol{\rho}') \end{aligned} \quad (52)$$

is our basic set of uncoupled quasi-cyclic equations. We can then substitute this into (51), make use of (50), and come out with

$$\begin{aligned} & \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times \mathbf{x}, \mathbf{x}] A_q(\mathbf{x}; \boldsymbol{\rho}) \\ & = \sum_{\boldsymbol{\rho}'} \exp [\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot \boldsymbol{\rho} \times \boldsymbol{\rho}'] w_q(\boldsymbol{\rho} - \boldsymbol{\rho}') A_q(\mathbf{x}; \boldsymbol{\rho}'). \end{aligned} \quad (53)$$

Equations (52) and (53) contain the final answer in embryonic form. From (52) one can work back to a Bloch-type equation defining the band parameters. (53), on the other hand, is a matrix expansion of the operator \mathcal{H} when acting on a localized wave function $A_q(\mathbf{x}; \boldsymbol{\rho})$; the expansion is free of interband terms. It can be made to yield the traditional effective Hamiltonian. We shall take up these two tasks in sequence.

To get the Bloch-type equation inherent in (52) we multiply with $\exp[i\mathbf{k} \cdot \boldsymbol{\rho}]$ and sum over $\boldsymbol{\rho}$. We get

$$\begin{aligned} & \sum_{\boldsymbol{\rho}} \exp [i\mathbf{k} \cdot \boldsymbol{\rho}] \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{x} - \boldsymbol{\rho}), \mathbf{x}] \\ & \times a_q(\mathbf{x} - \boldsymbol{\rho}) = \sum_{\boldsymbol{\rho}, \boldsymbol{\rho}'} \exp [i\mathbf{k} \cdot \boldsymbol{\rho}] \\ & \times \exp [\frac{1}{2}i(e/\hbar c)\mathbf{H} \cdot (\mathbf{x} \times \boldsymbol{\rho} + \boldsymbol{\rho} \times \boldsymbol{\rho}' + \boldsymbol{\rho}' \times \mathbf{x})] \\ & \times w_q(\boldsymbol{\rho} - \boldsymbol{\rho}') a_q(\mathbf{x} - \boldsymbol{\rho}'). \end{aligned}$$

We now replace $\boldsymbol{\rho}$ on the right by $\boldsymbol{\rho} + \boldsymbol{\rho}'$ and adopt the definition (10) on both sides. We find

$$\begin{aligned} & \mathcal{H}_0[\mathbf{p} - \frac{1}{2}(e/c)\mathbf{H} \times (\mathbf{x} + i\partial/\partial\mathbf{k}), \mathbf{x}] b_q(\mathbf{x}; \mathbf{k}) \\ & = \sum_{\boldsymbol{\rho}} \exp [i\mathbf{k} \cdot \boldsymbol{\rho}] w_q(\boldsymbol{\rho}) \{ \exp [-\frac{1}{2}i(e/\hbar c) \\ & \cdot \mathbf{H} \times \boldsymbol{\rho} \cdot \mathbf{x}] b_q(\mathbf{x}; \mathbf{k} + \frac{1}{2}(e/\hbar c)\mathbf{H} \times \boldsymbol{\rho}) \}. \end{aligned} \quad (54)$$

The equation defines a Bloch function because the nonperiodic \mathbf{x} on the left now occurs in the periodic

²¹ R. Peierls, Z. Physik **80**, 763 (1933).

combination $\mathbf{x} + i \partial/\partial \mathbf{k}$. On the right the Bloch functions have a slightly shifted \mathbf{k} vector, which is, however, restored by a special exponential placed in front of it. It is somewhat easier to envisage realizing the solution by power series expansion in H if we first use the conventional splitup

$$b_q(\mathbf{x}; \mathbf{k}) = \exp [i \mathbf{k} \cdot \mathbf{x}] u_q(\mathbf{x}; \mathbf{k}), \quad (55)$$

which yields

$$\begin{aligned} \mathcal{H}_0[\mathbf{p} + \hbar \mathbf{k} - \frac{1}{2} i(e/c) \mathbf{H} \times \partial/\partial \mathbf{k}, \mathbf{x}] u_q(\mathbf{x}; \mathbf{k}) \\ = \sum_{\boldsymbol{\rho}} \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] w_q(\boldsymbol{\rho}) u_q(\mathbf{x}; \mathbf{k} + \frac{1}{2} (e/\hbar c) \mathbf{H} \times \boldsymbol{\rho}). \end{aligned} \quad (56)$$

Equation (56) is the equation for the periodic part of a Bloch function in the limit $H = 0$. Thereupon, power series expansion is possible in both positions containing H , yielding power series results for $u_q(\mathbf{x}; \mathbf{k})$ and $w_q(\boldsymbol{\rho})$. The corrections remain periodic in \mathbf{x} . Thus, the Bloch function exists, at least as a power series in H .

To proceed in the other direction toward an effective band Hamiltonian, we start from (53), multiply with $\exp [i \mathbf{k} \cdot \boldsymbol{\rho}]$ and sum over $\boldsymbol{\rho}$. We observe from (50) and (10) that

$$\sum_{\boldsymbol{\rho}} \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] A_q(\mathbf{x}; \boldsymbol{\rho}) = B_q(\mathbf{x}; \mathbf{k}), \quad (57)$$

where we define

$$B_q(\mathbf{x}; \mathbf{k}) = b_q[\mathbf{x}; \mathbf{k} - \frac{1}{2} (e/\hbar c) \mathbf{H} \times \mathbf{x}]. \quad (58)$$

These rather curious functions having the argument \mathbf{x} in two different places were first introduced by Harper.²² Their purpose is the same as that of the Houston functions (45), namely, to find a distortion of Bloch functions suitable for handling homogeneous fields. In the electric case the success is more direct. In the present case, combination of (53), (57), and (58) yields

$$\begin{aligned} \mathcal{H}_0[\mathbf{p} - \frac{1}{2} (e/c) \mathbf{H} \times \mathbf{x}, \mathbf{x}] B_q(\mathbf{x}; \mathbf{k}) \\ = \sum_{\boldsymbol{\rho}} \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] w_q(\boldsymbol{\rho}) B_q[\mathbf{x}; \mathbf{k} + \frac{1}{2} (e/\hbar c) \mathbf{H} \times \boldsymbol{\rho}]. \end{aligned} \quad (59)$$

In other words, we have a matrix representation of \mathcal{H} in the B_q 's which is free of interband elements, but not a direct solution of the time dependent Schrödinger equation as in the previous case. Thus, there remains more work to be done, and (59) is not a terminal result.

Closer examination of (59) shows that the matrix equation is of just such a structure as to produce the

Hamiltonian that Onsager²³ postulated for the magnetic problem. To obtain this we write an eigenfunction of (48) in the form of an integral over the B_q 's in the first Brillouin zone, taking advantage of the fact that only one band index is involved:

$$\psi(\mathbf{x}) = \int_{\omega^{**}} f_q(\mathbf{k}) B_q(\mathbf{x}; \mathbf{k}) d\mathbf{k}. \quad (60)$$

Thereupon we ask for the equation obeyed by the amplitude function $f_q(\mathbf{k})$. Substitution of (59) into (60) yields

$$\begin{aligned} \mathcal{H} \psi(\mathbf{x}) = \int_{\omega^{**}} f_q(\mathbf{k}) \sum_{\boldsymbol{\rho}} \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] w_q(\boldsymbol{\rho}) \\ \times B_q[\mathbf{x}; \mathbf{k} + \frac{1}{2} (e/\hbar c) \mathbf{H} \times \boldsymbol{\rho}] d\mathbf{k}, \end{aligned}$$

or with a shift in the integration variable \mathbf{k}

$$\begin{aligned} \mathcal{H} \psi(\mathbf{x}) = \int_{\omega^{**}} \sum_{\boldsymbol{\rho}} f_q[\mathbf{k} - \frac{1}{2} (e/\hbar c) \mathbf{H} \times \boldsymbol{\rho}] \\ \times \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] w_q(\boldsymbol{\rho}) B_q(\mathbf{x}; \mathbf{k}) d\mathbf{k}. \end{aligned} \quad (61)$$

The f 's will define an eigenfunction of \mathcal{H} if (61) differs from (60) by an energy multiplier ε only. Since the B 's are linearly independent, at least for small enough H , we can factor out their coefficients in the resultant expression and write

$$\sum_{\boldsymbol{\rho}} \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] w_q(\boldsymbol{\rho}) f[\mathbf{k} - (e/2\hbar c) \mathbf{H} \times \boldsymbol{\rho}] = \varepsilon f(\mathbf{k}). \quad (62)$$

The displaced argument of f is advantageously given the form

$$\begin{aligned} f[\mathbf{k} - (e/2\hbar c) \mathbf{H} \times \boldsymbol{\rho}] \\ = \exp [-(e/2\hbar c) \mathbf{H} \times \boldsymbol{\rho} \cdot (\partial/\partial \mathbf{k})] f(\mathbf{k}), \end{aligned}$$

so that (62) takes the form

$$\begin{aligned} \sum_{\boldsymbol{\rho}} w_q(\boldsymbol{\rho}) \exp [i \mathbf{k} \cdot \boldsymbol{\rho}] \\ \times \exp [-(e/2\hbar c) \mathbf{H} \times \boldsymbol{\rho} \cdot (\partial/\partial \mathbf{k})] f(\mathbf{k}) = \varepsilon f(\mathbf{k}). \end{aligned}$$

The two exponentials combine into a single one, because the derivative is always taken with respect to a component of \mathbf{k} at right angles to $\boldsymbol{\rho}$. The eigenvalue equation therefore takes the form

$$W_q[\mathbf{k} - \frac{1}{2} i(e/\hbar c) \mathbf{H} \times (\partial/\partial \mathbf{k})] f(\mathbf{k}) = \varepsilon f(\mathbf{k}), \quad (63)$$

where $W_q(\mathbf{k})$ is given by (8). This is exactly the result expressed through the equation pair (25) and (34) in Sec. 1. From this the Eqs. (30) will follow in the classical limit. It must be emphasized, of course, that our $W_q(\mathbf{K})$ is not the band-energy function for the field-free band, but a modified band-energy function constructed with the help of the auxiliary

²² P. J. Harper, Proc. Phys. Soc. (London) **A68**, 879 (1955).

²³ L. Onsager, Phil. Mag. **43**, 1006 (1952).

equation (54) or (56). Another point which needs emphasis here is that the basis functions $B_q(\mathbf{x};\mathbf{k})$ differ slightly from Bloch functions. Equation (58) associates a Bloch function with them, but they themselves have a different structure. The band of index q is therefore not quite a Bloch band but a slightly modified manifold.

Determination of the energy levels from (63) or from the equivalent operator problem (25) and (34) is not as simple as in the corresponding case for the electric field. The basic simplicity of the electric field case is its isochronism or, in quantum language, the even spacing of its energy states. This is evident from Eq. (46). This same feature is also the one which allows the more exact treatment of the electric field case given in Sec. 3. Magnetic levels show even spacing under a variety of circumstances, but not as a universal rule. Completion of the calculation thus requires real algebraic study, and will not be discussed here. In many cases the quasi-classical formula (33), together with the correspondence principle, allows at least the determination of the spacing of the magnetic levels.

The derivation carried out here can be extended without difficulty to the case of simultaneous homogeneous electric and magnetic fields. The calculation is routine, and gives routine answers. Interested readers can find the derivation elsewhere.²⁴

3. THE ELECTRIC FIELD; EXACT THEORY

The results of Sec. 2 form a rounded and beautiful general theory of electron behavior. There is, however, some question concerning its mathematical validity. Until it was proved that Wannier functions of nondegenerate bands fall off exponentially at large distance,¹⁵ the doubt affected the theory as a whole. Since that time, the questions have become more specific. In particular, the fundamental equations of Sec. 2 are partial differential equations in more than three variables, and the method of solution assumes that the dependence of the solution on \mathbf{k} has a very special form. It seems likely that the general solution of these equations goes beyond this form. There is a way out of this difficulty. If one looks for solutions of (41) and (56) which proceed in powers of the field then the zero-order equation is the Bloch equation for field-free electrons. The extra derivative and difference operators occur then in perturbation, and it is relatively easy to show that the solutions so obtained have the right structure.¹⁸ Unfortunately, a proof based on a power-series ex-

pansion is only asymptotically valid for infinitesimally small expansion parameter. Thus, the work of Sec. 2 leaves open the possibility that a remainder term with entirely different properties might exist, and that the theory might only be asymptotic. We shall disprove this possibility now by giving a rigorous proof of one key element in the theory: *the existence of closed Bloch bands in a uniform electric field.*

Let us assume the Hamiltonian (38) and consider its effect on a wave function which has the value $\psi(\mathbf{x},0)$ at the time $t = 0$. We then know that

$$\psi(\mathbf{x},t) = \exp[-(i/\hbar)\mathcal{H}t]\psi(\mathbf{x},0) \quad (64)$$

is a solution of the Schrödinger equation at time t . Now if $\psi(\mathbf{x},0)$, instead of being arbitrary, happens to be a Bloch function of wave vector \mathbf{k}_0 then it follows from (44) that $\psi(\mathbf{x},t)$ is a Bloch function of wave vector $\mathbf{k}_0 + (e/\hbar)\mathbf{E}t$. If now the electric field is in a reciprocal lattice direction and if the period of the reciprocal lattice in that direction is a^* , then the original wave vector will have been restored after a time

$$T = \hbar a^*/eE. \quad (65)$$

It follows that the unitary operator $\exp[-i\mathcal{H}T/\hbar]$ preserves the reduced wave vector, and its eigenfunctions must be Bloch functions. This conclusion can be verified directly on the Hamiltonian (38). We find with (65)

$$\exp[-i\mathcal{H}T/\hbar] = \exp[-(i/\hbar)T\mathcal{H}_0(\mathbf{p},\mathbf{x}) - 2\pi i a^* \cdot \mathbf{x}]. \quad (66)$$

This operator has the lattice period in \mathbf{x} because the first term on the right has the period as stated in (4). The second term, on the other hand, is just such as to impart this property to any exponent of which it is a part. It follows that we can define a set of Bloch functions as eigenfunctions of the operator (66), writing

$$\exp[-i\mathcal{H}T/\hbar] b_q(\mathbf{x};\mathbf{k}) = e^{-i\phi_q} b_q(\mathbf{x};\mathbf{k}). \quad (67)$$

If we now start out at time $t = 0$ with one of those wave functions $b_q(\mathbf{x};\mathbf{k})$ then the wave function

$$\psi(\mathbf{x},t) = \exp[-i\mathcal{H}t/\hbar] b_q(\mathbf{x};\mathbf{k}_0)$$

will vary periodically in time because it returns to its original form (apart from a phase factor) after a time T . Thus, the bands generated by the operator Eq. (66) are closed in time.

The question arises whether the wave functions b_q defined here are identical with the solutions of (41). This can be answered in the affirmative, be-

²⁴ See reference 19, Sec. 4.

cause (41) follows from (66) and (67). To do this we must complete the latter definition by specifying the phase of the Bloch functions. Let us write it as follows:

$$b_q(\mathbf{x}; \mathbf{k}_0 + e\mathbf{E}t/\hbar) = \exp [i\chi(\mathbf{k}_0 + e\mathbf{E}t/\hbar)] \\ \times \exp [-i\mathcal{E}t/\hbar] b_q(\mathbf{x}; \mathbf{k}_0). \quad (68)$$

Here $\chi(\mathbf{k}_0 + e\mathbf{E}t/\hbar)$ is a phase which is largely undetermined but which is known to take on the value 0 if $t = 0$ and the value ϕ_q when $t = T$. Let us differentiate this relation with respect to time, using (44)

$$e\mathbf{E} \cdot [\partial b_q(\mathbf{x}; \mathbf{k}) / \partial \mathbf{k}] \\ = ie\mathbf{E} \cdot [\partial \chi(\mathbf{k}) / \partial \mathbf{k}] b_q(\mathbf{x}; \mathbf{k}) - i\mathcal{E} b_q(\mathbf{x}; \mathbf{k})$$

or with (38)

$$\{\mathcal{E} - e\mathbf{E} \cdot (\mathbf{x} + i\partial / \partial \mathbf{k})\} b_q(\mathbf{x}; \mathbf{k}) \\ = e\mathbf{E} \cdot (\partial \chi / \partial \mathbf{k}) b_q(\mathbf{x}; \mathbf{k}). \quad (69)$$

This is Eq. (41) with the identification

$$\chi = \frac{1}{eE} \int W_q(\mathbf{k}) dk_x. \quad (70)$$

Equation (70) is the Houston determination of the phase factor, as one sees by comparing (45), (68), and (70). Equations (64) and (41) are therefore equivalent. It should be emphasized at this point that the identification establishes only the validity of the five theorems of reference 18. It does not prove the validity of the power-series expansion itself, nor does it establish the existence of an effective Hamiltonian of the type (47).

4. CONCLUSIONS

In Sec. 1 of this paper there is sketched a Hamiltonian formalism for the study of the motion of electrons in solids. The formalism is closely associated with the energy bands within the solid. In Sec. 2 the formalism is proved under the assumption that arbitrary uniform static fields are present. The proof is an asymptotic proof only, even though results are in closed form. It is very fortunate that we have in Sec. 3 a rigorous proof of one central piece of the general theory. The proof lays to rest the notion that we are dealing only with an asymptotic theory which has no bearing on practical questions. The theory must have its limits of validity, but these limits have yet to be determined. One might hopefully try to assume that the entire treatment of Sec. 2 is always valid at finite fields. This is also incorrect. For it is shown in reference 18 that the proof of Sec. 3 is

applicable to free electrons. For such electrons the effective Hamiltonian (47) cannot be constructed because the energy of an electron increases indefinitely in time. The same situation must prevail if the periodic field is weak compared with the uniform field. Nothing can be said at this time about the case of a weak field. If the theory of the atomic Stark effect is any clue then all power series results must be expected to have only asymptotic validity.

In view of the symmetry between electric and magnetic results, it seems highly likely that closed bands exist for finite magnetic fields as well, even though we have today only an asymptotic proof for it. The magnetic field does not have the intrinsic divergences which arise in the electric field case so that it may even be true that the effective Hamiltonian formalism (63) holds for finite fields. The opposite possibility is, however, also open.

A case worth studying is the case of time dependent, but uniform fields. The case is intermediate between the case treated here and the case of non-uniform fields. The question one would like to see answered there is whether the modified bands are adiabatically connected to the bands whose "label" they have at zero field. Evidence on this point is conflicting. The author has a nontrivial two-band model for which this is the case. He also has another one for which it is not, but that one has discontinuities in the energy-band function. The problem is associated with degeneracies in the angle ϕ_q between different bands. It follows from (67) and (70) that

$$\phi_q = \frac{1}{eE} \int_{k_{0x}}^{k_{0x} + 2\pi a^*} W_q(\mathbf{k}) dk_x. \quad (71)$$

The form of this angle yields an infinity of degeneracies between any two bands as the field becomes small. The evidence from two-band calculations is that these degeneracies have no practical significance, but that we may not have true analytic continuation.

If the field varies rapidly during a certain time interval then interband transitions must certainly occur. For it follows from this paper that the Bloch functions are field dependent. If the field changes too fast this dependence cannot be realized in time, and transitions take place. This type of transition is easily amenable to calculation. What this paper brings out is that in order to have such transitions *the field must be changing in time or space*. An unchanging field does not produce interband transitions.