Wave Functions and Effective Hamiltonian for Bloch Electrons in an Electric Field

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Following up an earlier communication, wave functions are constructed which satisfy the Schrödinger equation for a potential which is a sum of a periodic and a uniform field term. The wave functions are Houston modifications of Bloch type functions; the Bloch functions form an orthogonal set whose members are fully determined except for phase. The theory exhibits them in the form of power series in the field strength; the unmodified Bloch band functions form the zero order term of that series. The solutions themselves do not allow for a Zener effect, but the fact that they are only given as power series in E may imply that there is a remainder term causing interband transitions; it would have to be asymptotically smaller than any power of E. Instead of constructing time dependent solutions of the Schrödinger equation one can take the time independent functions to construct an effective Hamiltonian for electrons in one band; it has the form (16). Certain indeterminacies are attached to this form of representation; it is shown, however, that final physical answers are unique. The study furnishes an incidental proof that **k**-space is a finite space consisting in its entirety of what is customarily called the first Brillouin zone. An appendix treats the case of degenerate bands; such bands have singularities in **k**-space even in the absence of a field. The difficulty is circumvented by working with a set which is not yet diagonalized but free of singularities; these intermediate functions can be continued as power series in E in the same way as nondegenerate band functions.

1. INTRODUCTION

IN a recent paper, Kohn[1] has studied the motion of an electron moving under the simultaneous influence of a periodic potential and a uniform magnetic field. He showed that the nondegenerate bands originating from the periodic field can be modified in such a way that an electron moves only within one band under the influence of the applied field. The motion is describable by an effective Hamiltonian typical for that band. The Hamiltonian is obtained as a power series in the magnetic field H; it is perhaps only semiconvergent in that variable.

The result of Kohn is very probably due to the fact that a uniform magnetic field preserves the periodicity of the medium. It would then appear *a priori* probable that a uniform electric field has the same properties. It is the purpose of this paper to prove the correctness of this view and to derive this Hamiltonian. It will be seen that the derivation can be given quite a short and transparent form. It is hoped that this feature will throw some light on the magnetic case and open the way for a simpler derivation of Kohn's results.

The philosophy of constructing an effective Hamiltonian is to abandon temporarily the usual preoccupation with the eigenfunctions of the Hamiltonian. The result sought is still to contain side by side noncommuting variables; however, these variables must be such as to commute with the band index. To achieve this, one must primarily look for a base in which interband elements can be absorbed easily into the intraband part of the Hamiltonian. As this absorption is carried out the effective Hamiltonian gradually reveals itself as a power series in **E**.

The Hamiltonian to be studied has the form,

$$\mathfrak{H}=\tfrac{1}{2}\mathbf{p}^2+V(\mathbf{x})-Ex. \tag{1}$$

Here $V(\mathbf{x})$ is a potential periodic in $\mathbf{x}$ with periods **a**, **b**, **c**. Units have been chosen here in which $\hbar=m=1$ and in which e is absorbed in the electric field. The last term of (1) is the one coupling the bands. It will be shown that the decoupling of the bands is achieved by the equation

$$[\tfrac{1}{2}\mathbf{p}^2+V(\mathbf{x})-E(x+i\partial/\partial k_x)]B(\mathbf{x};\mathbf{k}) =W(\mathbf{k})B(\mathbf{x};\mathbf{k}), \tag{2}$$

which was proposed by me in 1955.[2] The properties of this equation and of its solutions will be studied in great detail in Part 2 since statements challenging its validity are actually in the literature.[3] In Part 3 the decoupled band functions are used as a base to derive equations of motion. For a nondegenerate band these equations have Hamiltonian form. The limitations of this formalism will be discussed. In Part 4 the states of constant energy of the Hamiltonian (1) will be studied and their connection with (2) analyzed.

2. THE WAVE FUNCTIONS

It should be said at the outset that Eq. (2) can only apply as it stands to nondegenerate bands. Generalizations of it must be written down if a number of bands share degenerate points. Since these generalizations are not representable by a quasi-classical Hamiltonian formalism of the type proposed here, they will be discussed in an appendix. In the main text the assumption of nondegeneracy will therefore be made.

I have found in the past that a heuristic justification of Eq. (2) is rarely convicing until the nature of the solutions is fully grasped. The difficulty is connected with the operator $i\partial/\partial k_x$. It is best to consider it at first simply as a derivative with respect to k_x of a Bloch type function depending on x, y, z, k_x, k_y, k_z. Adams[3] has understood $i\partial/\partial k_x$ to mean differentiation with respect to k_x in the basic set of unperturbed wave func-

[1] W. Kohn, Phys. Rev. **115**, 1460 (1959).

[2] G. H. Wannier, Phys. Rev. **100**, 1227 (1955); **101**, 1835 (1956). The equation proposed there for the case of a magnetic field is false.

[3] E. N. Adams, Phys. Rev. **107**, 698 (1957).

tions, and assumed the operator to be given by its transform in Hilbert space for other functions. With this interpretation decoupling is indeed only achieved to second order in E, as he points out. Once this point is clear it would appear that the definition is circular, because unless the Eq. (2) has Bloch type solutions, the operation $\partial/\partial k_x$ is entirely meaningless. A second question that needs an answer is the nature of the quantity $W(\mathbf{k})$. Its status as an eigenvalue is questionable because it is sensitive to the phase of B; when B is multiplied by a phase factor $e^{i\Phi(\mathbf{k})}$. $W(\mathbf{k})$ acquires an additive term $E\partial\Phi/\partial k_x$.

To answer these questions we convert Eq. (2) into a recursion relation proceeding in powers of E. This is the essentially new step over the previous publication on this subject.[2] Let us define

$$B_q(\mathbf{x};\mathbf{k})\approx\sum_{\nu=0}^{\infty} b_q^{(\nu)}(\mathbf{x};\mathbf{k})E^\nu, \tag{3}$$

$$W_q(\mathbf{k})\approx\sum_{\nu=0}^{\infty} w_q^{(\nu)}(\mathbf{k})E^\nu. \tag{4}$$

Here $b_q^{(0)}$ and $w_q^{(0)}$ are the qth band eigenfunctions and eigenvalues of the problem

$$\{\tfrac{1}{2}\mathbf{p}^2+V(\mathbf{x})\}b_q(\mathbf{x};\mathbf{k})=w_q(\mathbf{k})b_q(\mathbf{x};\mathbf{k}). \tag{5}$$

We shall usually omit the upper index 0 for these quantities. Through the choice of the starting function b_q the quantities B and W become also indirectly functions of q and are so designated in (3) and (4). If we substitute (3) and (4) into (2) and annul powers of E we get

$$\{\tfrac{1}{2}\mathbf{p}^2+V-w_q\}b_q^{(n)}=(x+i\partial/\partial k_x)b_q^{(n-1)}+\sum_{\nu=1}^{n} w_q^{(\nu)}b_q^{(n-\nu)}. \tag{6}$$

It is seen that Eq. (6) removes the circular character from the Eq. (2). The operator $(x+i\partial/\partial k_x)$ operates now on a function *already known* from the preceding recursion step. If we assume $b_q^{(n-1)}$ to have Bloch character with wave vector $\mathbf{k}$, then operation on it with $(x+i\partial/\partial k_x)$ retains that character; hence the entire right-hand side has that character also. We can therefore state:

Theorem 1

The Eqs. (6) define at every stage a feasible recursion system, that is, a quasi-periodic function $b_q^{(n)}(\mathbf{x};\mathbf{k})$ of wave vector $\mathbf{k}$ and a number $w_q^{(n)}(\mathbf{k})$ can be found satisfying the nth recursion relation (6).

Proof

Since the eigenfunctions of (5) form a complete set, other functions can be expressed in terms of them. In particular a function of the type assumed in Theorem 1 will have an expansion

$$b_q^{(n)}(\mathbf{x};\mathbf{k})=\textstyle\sum_s b_s(\mathbf{x};\mathbf{k})\beta_{sq}^{(n)}(\mathbf{k}), \tag{7}$$

involving the same wave vector $\mathbf{k}$ only. Substitution of this into (6) yields

$$(w_s-w_q)\beta_{sq}^{(n)}=\int b_s^*(x+i\partial/\partial k_x)b_q^{(n-1)}d\tau+\sum_{\nu=1}^{n} w_q^{(\nu)}\beta_{sq}^{(n-\nu)}. \tag{8}$$

Each equation contains only one unknown of order n. If $s\neq q$ the term on the right containing $w_q^{(n)}$ vanishes because $\beta_{sq}^{(0)}=\delta_{sq}$. On the other hand, the coefficient on the left for $\beta_{sq}^{(n)}$ is different from zero in that case, thanks to the assumption of nondegeneracy made for the band q. Hence solution with respect to it is always possible. For $s=q$ Eq. (8) takes the form

$$0=\int b_q^*(x+i\partial/\partial k_x)b_q^{(n-1)}d\tau+w_q^{(n)}+\sum_{\nu=1}^{n-1} w_q^{(\nu)}\beta_{qq}^{(n-\nu)}. \tag{9}$$

This equation is clearly soluble with respect to its only unknown $w_q^{(n)}$.

In order to carry out the same reasoning for degenerate bands the Eqs. (6) must first be generalized. This generalization, together with the feasibility proof, is found in Appendix I. We now continue with

Theorem 2

There is enough freedom in the recursion system (6) to allow maintenance of normalization to every power in E.

Proof

It is seen from (8) and (9) that there is no determining equation for the coefficients $\beta_{qq}^{(i)}$. This is to be expected in a perturbation calculation. Now the nth normalization condition reads

$$\int(b_q^*b_q^{(n)}+b_q^{(1)*}b_q^{(n-1)}+b_q^{(2)*}b_q^{(n-2)}+\cdots b_q^{(n)*}b_q)d\tau=0. \tag{10a}$$

It is of the form

$$\beta_{qq}^{(n)}+\beta_{qq}^{(n)*}+(\text{a known real expression})=0, \tag{10b}$$

and thus determines the real part of $\beta_{qq}^{(n)}$.

This normalization procedure is more important here than in related problems. For we have introduced in (2) the operator $i\partial/\partial\mathbf{k}$. Its conjugate complex $-i\partial/\partial\mathbf{k}$ will be its adjoint only within an orthonormal set. Thus by imposing normalization on B_q we make its

defining operator Hermitian for this particular B_q. This in turn will make $W_q(\mathbf{k})$ real. This reality is not directly evident from Eq. (9) which determines successive coefficients of the series (4).

We now come to the central theorem of Part 2:

Theorem 3

The wave function $B_q(\mathbf{x};\mathbf{k})$ is unique, except for a phase factor which can be a function of $\mathbf{k}$ and E.

Proof

It follows from the Eqs. (8) and (10) that the only indeterminacy left in the nth approximation is the imaginary part of $\beta_{qq}^{(n)}$. It will lead to a term of the form

$$i\gamma_q^{(n)}E^n b_q,$$

added to the wave function. Instead of adding this term at the nth stage we may multiply instead the zero-order wave function with a factor

$$\exp[i\gamma_q^{(n)}E^n],$$

and keep $\beta_{qq}^{(n)}$ real. The result will be a phase factor multiplying the entire wave function whose exponent is a power series in E, and a determinate set of coefficients $\beta_{sq}^{(n)}$. To make the proof complete we must show in addition that the quantities $b_q^{(n)}$ which are unique functions of $b_q^{(0)}$ are only multiplied by a phase factor if $b_q^{(0)}$ is so multiplied. Indeed, if $b_q^{(0)}$ is altered by a factor $e^{i\Phi(\mathbf{k})}$, $w_q^{(1)}$ from (9) increases by the additive constant $\partial\Phi/\partial k_x$. The invariance of the $b^{(n)}$'s is then seen from (6) and (9): the other $w_q^{(n)}$'s remain the same and the extra term in $\partial b_q^{(n-1)}/\partial k_x$ cancels at each stage with the extra contribution from $w_q^{(1)}$. This proves the theorem.

From what has been said earlier the idea of eigenstates forming a complete set is not obviously associated with Eq. (2) because W_q appears as a redundant variable capable of being transformed away. Yet some sort of completeness is needed if we want (2) to given an exhaustive description of electronic behavior in the presence of a field. The conversion of (2) to the recursion form (5) produces here a radical change which may be expressed in

Theorem 4

Two solutions B_q and B_s of (3) and (6) which are associated with different band solutions of (5) are orthogonal to each other in all powers of E.

Proof

We form Green's identity between a solution B_q of (2) and a solution B_s^* of the conjugate complex equation. We get

$$-iE\frac{\partial}{\partial k_x}\int B_s^* B_q d\tau = (W_q - W_s)\int B_s^* B_q d\tau. \quad (11)$$

The term on the left arises from the nonhermitian character of the operator $i\partial/\partial k_x$ and is sufficient to invalidate orthogonality for *arbitrary* solutions of (2). However, the situation is quite different for our special solutions arising from the recursion system (6). To see this we replace B_s^*, B_q, W_q, W_s by their power series expansions in E, and annul separately each power of E in (11). Let us denote by $O_{sq}^{(n)}E^n$ the terms in the orthogonality integral containing the nth power of E, that is explicitly

$$O_{sq}^{(n)} = \int (b_s^{(n)*} b_q + b_s^{(n-1)*} b_q^{(1)} + \cdots + b_s^* b_q^{(n)}) d\tau. \quad (12)$$

Then Eq. (11) takes the form

$$-i\partial O_{sq}^{(n-1)}/\partial k_x = (w_q - w_s)O_{sq}^{(n)} + \sum_{\nu=1}^{n} (w_q^{(\nu)} - w_s^{(\nu)})O_{sq}^{(n-\nu)}. \quad (13)$$

This is a recursion system in the quantities $O_{sq}^{(n)}$ with a nonvanishing coefficient for the highest order term at every stage. Hence, having started with an $O_{sq}^{(0)}$ equal to zero we find all quantities $O_{sq}^{(n)}$ equal to zero.

The proof given here must be generalized to cover degenerate bands. In Appendix II the proof will be found for the proposition that a solution of (3) and (6) is orthogonal to all degenerate Bloch-like functions evolved from a partially degenerate base by the procedure of Appendix I. One can also show that separate degenerate band systems are orthogonal to each other. Within a band system sharing degeneracy points orthogonality is of course not entirely automatic.

It follows from the preceding theorems that we are in possession of a complete set of Bloch like functions, insofar as their orthogonality and continuity with the complete set b_q guarantees this property. These Bloch functions obey Eq. (2). It is possible to terminate this development very straightforwardly by constructing Houston type[4] wave functions from them. They are

$$\Psi(\mathbf{x},t) = B_q(\mathbf{x}; k_0+Et, k_y, k_z) \times \exp\left[-i\int^t W_q(k_0+Et, k_y, k_z)dt\right]. \quad (14)$$

These functions obey

Theorem 5

The expressions $\Psi(\mathbf{x},t)$ defined in Eq. (14) obey the time dependent Schrödinger equation associated with the Hamiltonian (1) to all powers of E; the two positions at which E occurs multiplied with t are not to be included in this expansion.

[4] W. V. Houston, Phys. Rev. **57**, 184 (1940).

Proof

We get from (1) and (14)

$$(\mathfrak{H}-i\partial/\partial t)\Psi=\exp\left[-i\int^{t}W_q(k_0+Et,\,k_y,\,k_z)dt\right]$$
$$\times[\tfrac{1}{2}\mathbf{p}^2+V-Ex-W_q(k_0+Et,\,k_y,\,k_z)-i\partial/\partial k_x]$$
$$\times B_q(\mathbf{x};\,k_0+Et,\,k_y,\,k_z).$$

The square bracket is the operator in (2); hence the expression equals zero to all powers in E. The distinction between E occurring alone (or more precisely divided by an energy denominator) and E occurring multiplied with t is familiar from Kohn's work[1]; in his case H was treated as small unless it occurred multiplied with x.

3. THE HAMILTONIAN

In order to develop an effective Hamiltonian for electrons located in the nondegenerate band q we refrain from the last step of Part 2. We do not integrate the Schrödinger equation with respect to time but use instead the wave functions B_q as a base in which to express the equations of motion for the dynamical variables.

In order to do this we must take a fundamental step. Up to now $-i\partial/\partial k_x$ was defined as a straight derivative. It is not in general a Hermitian operator. However with respect to the basic functions B_q it has as its adjoint operator $+i\partial/\partial k_x$. Hence we can now introduce the *lattice vector operator* for this set by the definition

$$\mathbf{r}B_q(x;\,k)=-i(\partial/\partial\mathbf{k})B_q(\mathbf{x};\,\mathbf{k}). \tag{15}$$

The adjoint form is $+i\partial/\partial\mathbf{k}$. Outside the basic set of the B_q's $\mathbf{r}$ is to be considered defined by the normal transformation properties of Hermitian operators. The operator $\mathbf{r}$ is particularized among all possible operators conjugate to the wave vector $\mathbf{k}$ in that it must also commute with the band index q in the set on which it is defined.[5] Its eigenvalue spectrum is the totality of all possible lattice vectors of the crystal; these eigenvalues are realized through the so-called Wannier functions.[6] In our present study the operator $\mathbf{E}\cdot\mathbf{r}$ forms the difference between the true Hamiltonian occurring in Eq. (1) and the defining operator for the wave functions in Eq. (2). This latter operator is simply $W_q(\mathbf{k})$ in the set of wave functions B_q and has no interband elements to finite powers of E. Since $\mathbf{r}$ has no interband elements either the entire Hamiltonian is free of interband terms [except for degeneracies already present in (5)]. In particular, the projection $\langle q|\mathfrak{H}|q\rangle$ of $\mathfrak{H}$ into the band q takes the form

$$\langle q|\mathfrak{H}|q\rangle=W_q(\mathbf{k})-\mathbf{E}\cdot\mathbf{r}, \tag{16}$$

where $W_q(\mathbf{k})$ is given by (2) and $\mathbf{r}$ by (15).

Since the expression (16) explicitly contains the conjugate variables $\mathbf{k}$ and $\mathbf{r}$ equations of motion are immediately written down:

$$d\mathbf{k}/dt=(1/i)(\mathfrak{H}\mathbf{k}-\mathbf{k}\mathfrak{H})=\mathbf{E}, \tag{17}$$

$$d\mathbf{r}/dt=(1/i)(\mathfrak{H}\mathbf{r}-\mathbf{r}\mathfrak{H})=\partial W_q/\partial\mathbf{k}. \tag{18}$$

These equations are of Hamiltonian form with $W_q(\mathbf{k})$ playing the role of an effective kinetic energy.

In principle, the subject could be dropped at this point. However, the Eqs. (15)–(18) have certain unsatisfactory features which must be taken up to get physical understanding. The wave functions are unique, but the function $W_q(\mathbf{k})$ is not. It was pointed out already that multiplication of $B_q(\mathbf{k})$ by a factor $e^{i\Phi(\mathbf{k})}$ modifies W_q by an additive term $E\partial\Phi/\partial k_x$. This indeterminacy arises from an intrinsic indeterminacy in the definition of the lattice vector operator $\mathbf{r}$.[7] The present instance is an example of this; while (17) is a well known universal relation (18) refers to an imperfectly defined operator; the identification of $d\mathbf{r}/dt$ with the expectation value of the velocity is therefore debatable.

A simple way to shed light on this question is to calculate the intraband matrix elements of the true velocity. In other words we write

$$\langle q|d\mathbf{x}/dt|q\rangle=(1/i)\langle q|\mathfrak{H}\mathbf{x}-\mathbf{x}\mathfrak{H}|q\rangle$$
$$=(1/i)\{\mathfrak{H}_q\langle q|\mathbf{x}|q\rangle-\langle q|\mathbf{x}|q\rangle\mathfrak{H}_q\}.$$

Here $\langle q|\mathbf{x}|q\rangle$ and $\langle q|d\mathbf{x}/dt|q\rangle$ are the projections of these operators into the subspace q. We now employ for $\mathbf{x}$ the decomposition[8,2]

$$\mathbf{x}=\mathbf{r}+\mathbf{X}. \tag{19}$$

This yields for $\mathbf{X}$, from (15)

$$\mathbf{X}B_q(\mathbf{x};\,\mathbf{k})=(\mathbf{x}+i\partial/\partial\mathbf{k})B_q(\mathbf{x};\,\mathbf{k}). \tag{20}$$

$\mathbf{X}$ is a periodic operator which conserves $\mathbf{k}$. We can say *a posteriori* that it enters into the defining Eq. (2) of B_q. It arises because the center of gravity of a Bloch function does not always coincide with a lattice point but has a definite shift for each q and $\mathbf{k}$ which equals

$$\langle q,\mathbf{k}|\mathbf{X}|q,\mathbf{k}\rangle=X_q(\mathbf{k}). \tag{21}$$

In the presence of a field this shift in position produces an energy shift with respect to which the functions B_q

[5] G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), pp. 173–177.

[6] G. H. Wannier, Phys. Rev. **52**, 191 (1937); J. C. Slater, Phys. Rev. **76**, 1592 (1949).

[7] As an illustration of this indeterminacy we may modify $b(\mathbf{x};\,\mathbf{k})$ by multiplication with $e^{i\mathbf{k}\cdot\mathbf{a}}$, where $\mathbf{a}$ is some vector of the Bravais lattice. It is then seen that all Wannier functions are shifted by this vector $\mathbf{a}$ from their fiducial positions. The lattice vector operator $\mathbf{r}$ thus can convey a certain amount of misinformation which is not present in the basic wave functions.

[8] E. N. Adams, J. Chem. Phys. **21**, 2013 (1953); R. Karplus and J. N. Luttinger, Phys. Rev. **95**, 1154 (1954).

are defined self-consistently. This same interpretation will be helpful in the discussion below.

We see that with (16) and (19) both $\mathcal{H}_q$ and $\langle q|\mathbf{x}|q\rangle$ are decomposed into two terms, one a function of $\mathbf{k}$, the other of $\mathbf{r}$. As corresponding terms commute the commutator of $\mathbf{x}$ and $\mathcal{H}_q$ takes the form

$$\langle q|d\mathbf{x}/dt|q\rangle=(1/i)\{W_q\mathbf{r}-\mathbf{r}W_q\}-(E/i)\{r_x\mathbf{X}_q-\mathbf{X}_q r_x\}. \quad (22)$$

The result is

$$\langle q,\mathbf{k}|d\mathbf{x}/dt|q,\mathbf{k}'\rangle=\delta_{\mathbf{k},\mathbf{k}'}\left[\frac{\partial W_q(\mathbf{k})}{\partial\mathbf{k}}+E\frac{\partial\mathbf{X}_q(\mathbf{k})}{\partial k_x}\right], \quad (23)$$

or in components, using (2)

$$\frac{dx_q(\mathbf{k})}{dt}=\frac{\partial}{\partial k_x}\langle q,\mathbf{k}|\tfrac{1}{2}\mathbf{p}^2+V|q,\mathbf{k}\rangle, \quad (24)$$

$$\frac{dy_q(\mathbf{k})}{dt}=\frac{\partial}{\partial k_y}\langle q,\mathbf{k}|\tfrac{1}{2}\mathbf{p}^2+V|q,\mathbf{k}\rangle+E\left(\frac{\partial Y_q(\mathbf{k})}{\partial k_x}-\frac{\partial X_q(\mathbf{k})}{\partial k_y}\right). \quad (25)$$

Equations (24) and (25) are independent of the phase of B_q. In (24) this is self-evident. To prove it for (25) we start out with (20) and (21)

$$\mathbf{X}_q(\mathbf{k})=\int B_q^*(\mathbf{x}+i\partial/\partial\mathbf{k})B_q d\tau.$$

Now set

$$B_q\rightarrow e^{i\Phi}B_q,$$

Then we get

$$X_q\rightarrow X_q-\partial\Phi/\partial k_x,$$
$$Y_q\rightarrow Y_q-\partial\Phi/\partial k_y,$$
$$(\partial X_q/\partial k_y)-(\partial Y_q/\partial k_x)\rightarrow(\partial X_q/\partial k_y)-(\partial Y_q/\partial k_x),$$

which proves the proposition.

It is also true that the equations (24) and (25) agree with (18) when averaged over time. The difference between the two velocities is seen from (23) to equal

$$\frac{d\mathbf{x}}{dt}-\frac{d\mathbf{r}}{dt}=E\frac{\partial\mathbf{X}}{\partial k_x}.$$

This quantity is zero when averaged over time because k_x varies linearly in time and $\mathbf{X}$ is periodic in reciprocal space. Hence the two types of velocities are compatible as arising from two position vectors differing locally.

The question arises whether we can dispose of the phase in B_q in such a way that the similarity between (18) and (23) becomes greater. An approach to this is suggested by the fact that Eq. (24) has obvious Hamiltonian form. We may dispose of the phase in B_q in such a way as to make (24) coincide with the corresponding Eq. (18). This is done by making the component of X_q a constant along the field direction. To do this we make the substitution

$$B_q\rightarrow B_q\exp i\int^{k_x}d\kappa\,\{X_q(\kappa,k_y,k_z)-\bar{X}_q(k_y,k_z)\}. \quad (26)$$

Here X_q is defined by (20) and (21) and $\bar{X}_q$ is its average along k_x for fixed k_y and k_z.[9] This brings (18) in the form

$$\frac{dr_x}{dt}=\frac{\partial}{\partial k_x}\langle q,\mathbf{k}|\tfrac{1}{2}\mathbf{p}^2+V|q,\mathbf{k}\rangle, \quad (27)$$

$$\frac{dr_y}{dt}=\frac{\partial}{\partial k_y}[\langle q,\mathbf{k}|\tfrac{1}{2}\mathbf{p}^2+V|q,\mathbf{k}\rangle-E\bar{X}_q]. \quad (28)$$

There is now exact agreement of (27) and (24). However, (28) and (25) still differ by a term which averages to zero in time.

We shall conclude this part by carrying out the power series expansions of B_q and W_q a certain way, proceeding to square terms in Eq. (3) and to cubic terms in Eq. (4). The equations employed are (8), (9), and (10). For simplicity we shall make the system determinate by the phase prescription indicated under Theorem 3.

$$\beta_{qq}^{(n)}=\text{real}. \quad (29)$$

Let us also introduce the definition[8]

$$\int b_s^*(x+i\partial/\partial k_x)b_s d\tau=(s|\xi|s). \quad (30)$$

We find then with $s\neq q$

$$w_q^{(0)}=w_q, \quad (31)$$

$$\beta_{qq}^{(0)}=1, \quad (32)$$

$$\beta_{sq}^{(0)}=0, \quad (33)$$

[9] It is very suggestive to leave off the term $\bar{X}_q$ in (26). The expressions in the rest of this chapter would then become much simpler since X_q and $\bar{X}_q$ can then be replaced by 0 in the rest of this discussion. That this is incorrect is proved from the equation of motion (28) which does then not reproduce (25) in the mean. The error committed in leaving off $\bar{X}_q$ is that B_q ceases to be periodic in reciprocal space; this requirement seems to me essential *a priori* because $\mathbf{k}$ is defined through the lattice displacement operators $\exp(i\mathbf{k}\cdot\boldsymbol{\varrho})$ with $\boldsymbol{\varrho}$ a lattice vector. Distinction of different cells in reciprocal space is not consistent with this definition. It is gratifying to see this viewpoint on this somewhat controversial question confirmed here in the sense that the looser interpretation of the meaning of $\mathbf{k}$ space gives actually wrong results. The error would also be very serious in Part 4, which deals with stationary states. Allowing a phase shift upon return to the starting position in $\mathbf{k}$ space is perhaps tolerable for a moving wave packet but makes the selection of constant energy wave functions quite impossible.

$$w_q^{(1)} = -(q|\xi|q), \tag{34}$$

$$\beta_{qq}^{(1)} = 0, \tag{35}$$

$$\beta_{sq}^{(1)} = \frac{(s|x|q)}{w_s - w_q}, \tag{36}$$

$$w_q^{(2)} = -\sum_{r\neq q} \frac{|(r|x|q)|^2}{w_r - w_q}, \tag{37}$$

$$\beta_{qq}^{(2)} = -\tfrac{1}{2}\sum_{r\neq q} \frac{|(r|x|q)|^2}{(w_r - w_q)^2}, \tag{38}$$

$$\beta_{sq}^{(2)} = \sum_{r\neq s,q} \frac{(s|x|r)(r|x|q)}{(w_s - w_q)(w_r - w_q)} + \frac{\{(s|\xi|s) - (q|\xi|q)\}(s|x|q)}{(w_s - w_q)^2} + \frac{i}{w_s - w_q}\frac{\partial}{\partial k_x}\left[\frac{(s|x|q)}{w_s - w_q}\right], \tag{39}$$

$$w_q^{(3)} = -\sum_{s\neq q, r\neq q, r\neq s} \frac{(q|x|s)(s|x|r)(r|x|q)}{(w_s - w_q)(w_r - w_q)} - \sum_{r\neq q} \frac{|(q|x|r)|^2\{(r|\xi|r) - (q|\xi|q)\}}{(w_r - w_q)^2} + \tfrac{1}{2}i\sum_{r\neq q} \frac{(q|x|r)[\partial(r|x|q)/\partial k_x] - [\partial(q|x|r)/\partial k_x](r|x|q)}{(w_r - w_q)^2}. \tag{40}$$

One can verify that the phase dependencies in the second and third term of (39) cancel as proved earlier for the wave functions generally. Phase independence holds actually for all terms $w_q^{(n)}$ except $w_q^{(1)}$ as was already discussed in connection with Theorem 3. All other indeterminacies of the $w_q^{(n)}$'s are suppressed here through Eq. (29). It is clear that the expression for W derived from (29) is not the same as the one suggested by Eqs. (27) and (28). In crystals with a center of symmetry all matrix elements (30) can be made to vanish by a suitable choice of phase.[10] The first order pseudoenergy $w^{(1)}$ is then zero and corresponding simplifications arise later in the sequence.

We see from this discussion that a Bloch electron acted upon by a uniform electric field has an effective Hamiltonian of the form (16). It has a field term of the usual type and a new kinetic energy term which equals the band energy function $w_q(k)$ for small field. If this function is modified for larger fields in a certain way interband elements are suppressed to all powers in E. The modification contains a certain amount of indeterminacy. The expressions (31), (34), (37), and (40), together with (4) define one of the possible explicit forms of the effective kinetic energy $W_q(k)$. It is possible that the effective Hamiltonian so obtained is only asymptotic for small fields and that interband elements are not really absent from the full Hamiltonian.

4. ENERGY STATES

Energy states in the electric field case do not have much intrinsic interest because they are *a priori* known to be not normalizable and hence not truly stationary. We wish to discuss them mainly to show their relationship to the wave functions $B_q(\mathbf{x};\mathbf{k})$ discussed in Part 2. This discussion proceeds more easily in one dimension, to which discussion will at first be limited.

It is well to show up first the status of Eq. (2) in the constant energy problem. Suppose we assume a constant energy solution for the Hamiltonian (1)

$$[\tfrac{1}{2}p^2 + V - Ex]A(x) = \mathcal{E}A(x). \tag{41}$$

Let the period of V be d, that is

$$V(x+d) = V(x).$$

Then $A(x+d)$ is also a solution of (41) with energy $\mathcal{E}+Ed$. This is the familiar "Stark ladder" associated with constant energy solutions of (41). It is the image of the periodicity of the Houston functions in k space, which through $k = k_0 + Et$, becomes a periodicity in time. Now superimpose the solutions of (41) in the following way

$$B(x;k) = \sum_{-\infty}^{+\infty} e^{iknd}A(x-nd). \tag{42}$$

Let this be for the moment a formal operation. Then B obeys the equation

$$[\tfrac{1}{2}p^2 + V - E(x + i\partial/\partial k)]B = \mathcal{E}B,$$

which is a special case of Eq. (2).

To prove the existence of B we must supplement the formal manipulations with a convergence proof for the series (42). To do this we must know the behavior of A for large x. For such values V is negligible compared to Ex and the behavior is of the free electron type. This means good convergence in the up field direction, and

[10] W. Kohn, Phys. Rev. **115**, 809 (1959).

behavior as

$$A\sim\frac{\exp[\pm\frac{2}{3}i(2E)^{\frac{1}{2}}x^{\frac{3}{2}}]}{x^{\frac{1}{4}}},\tag{43}$$

in the down field direction. The contributions to the series (42) from large n diminish therefore in magnitude and oscillate more and more rapidly in phase, hence converge. Thus an existence proof for Bloch type solutions of (2) has been given. There is to be sure no proof that these solutions are identical with the power series type of Part 2. It would be, however, a very surprising accident if the solutions which were proved to exist here were somehow different from the power series solutions which we constructed explicitly in Part 2.

If the reader permits me to make this identification then the connection just made can be inverted. We can Fourier analyze the solutions (14) with respect to time to get the energy. These solutions are quasi-periodic in $k_x=k_0+Et$ with period $2\pi/d$ and Floquet factor

$$\exp\left[-\frac{i}{E}\int_0^{2\pi/d}W_q(k_x,k_y,k_z)dk_x\right].$$

The energy values are therefore

$$\mathcal{E}_q(n)=\frac{d}{2\pi}\int_0^{\pi/d}W_q(k)dk+nEd.\tag{44}$$

This is again the Stark ladder discussed previously with a definite value for the energy constant. The constant is phase independent if we remember to treat reciprocal space as discussed in footnote 9. The W's then differ from each other only by the derivative of a periodic function and definite values result for $\mathcal{E}$. The same result can be arrived at also by the method of Part 3. In this case we construct a wave function in k space from the Hamiltonian (16). The appropriate wave equation results from insertion of (15) into (16) and reads

$$iEd\psi/dk+W_q(k)\psi=\mathcal{E}\psi,\tag{45}$$

which solves to

$$\psi=\exp\left(-i\int\frac{\mathcal{E}-W_q(k)}{E}dk\right).\tag{46}$$

The demand of periodicity in k space for ψ yields again the condition (44).

It is interesting to note that identification of B as obtained from (2) and (42) yields a tentative result for the limitation of the one band idea in the presence of a field. It is seen from (43) that the series for B converges but that the one for $\partial B/\partial k$ does not, for the magnitude of the terms increases in the latter case as $n^{\frac{1}{4}}$. Since convergence is restored by a factor $e^{-\alpha|n|}$ with α arbitrarily small we are actually at the limiting circle of convergence for the Laurent series (42). Hence there must be actually some value of e^{ikd} on the unit circle for which B is singular. This singularity can be guessed at from the case of free electrons to which the analysis applies also. If free electron wave functions are forced into a lattice scheme with an artificially indeterminate k the wave functions and energies acquire singularities at the Bragg positions. The present analysis suggests that these singularities appear for all bands as soon as a field is present except that transitions from band to band are generally very much harder. It is thus possible that the sequence (6) converges even in the presence of a Zener effect; the Zener effect would in this view manifest itself through the appearance of singular points in k space rather than actual divergence of the sequence for all k.

Very little will be said here about constant energy states in three dimensions. If the field direction is a lattice vector direction of the reciprocal lattice, say k_x, then the period a^* of the reciprocal lattice in the field direction can be chosen as one of the basis vectors of the primitive cell in reciprocal space. The components k_y and k_z out of this direction are then constants of the motion and the wave functions in $\mathbf{k}$ space extend along a line only. Analysis proceeds then as previously for each fixed k_y and k_z. It is seen that the spacing of the Stark levels is proportional to the spacing $1/a^*$ of lattice planes perpendicular to E. Analysis now gets into difficulty if the direction of E is not mathematically fixed with respect to the crystal. For we deal now with a Stark pattern varying erratically for infinitely small variation in angle. The constant energy states loose thereby a great deal of their physical reality. A description by wave functions of the type (2) or (14), on the other hand, does not suffer from this defect. Their dependence on the field is such that a small change in field or angle produces only a small change in the wave functions. Their use would thus seem preferable for continuity reasons; one might expect that any well defined physical problem will permit a way of being looked at in this frame of reference.

APPENDIX I

It is known that diagonalization of the Hamiltonian in degenerate band systems introduces algebraic singularities.[11] Appearance of such singularities is not consistent with the employment of the lattice vector operator because its eigenfunctions loose their localized character.[10] To avoid these difficulties imperfectly diagonalized Bloch type functions are advantageously employed for which the Hamiltonian is represented by a finite matrix with nonsingular elements[12]:

$$\{\tfrac{1}{2}\mathbf{p}^2+V\}b_{s;\sigma}=\textstyle\sum_\rho w_{s;\sigma\rho}b_{s;\rho}.\tag{a}$$

What must be discussed now is the feasibility of solving

[11] G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), p. 146.
[12] W. Shockley, Phys. Rev. **78**, 173 (1950).

the equation

$$\left\{\tfrac{1}{2}\mathbf{p}^2+V-E\left(x+i\frac{\partial}{\partial k_x}\right)\right\}B_{s,\sigma}=\sum_\rho W_{s,\sigma\rho}B_{s,\rho}, \quad \text{(b)}$$

in successive powers of E. This means proving the feasibility of the recursion system

$$(\tfrac{1}{2}\mathbf{p}^2+V)b_{s;\sigma}^{(n)}-\sum_\rho w_{s;\sigma\rho}b_{s;\rho}^{(n)}=(x+i\partial/\partial k_x)b_{s;\sigma}^{(n-1)}$$
$$+\sum_\rho\sum_{\nu=1}^{n} w_{s;\sigma\rho}^{(\nu)}b_{s;\rho}^{(n-\nu)}. \quad \text{(c)}$$

Multiplication with a basis function $b_{s;\tau}^*$ *inside* the quasidegenerate set yields after integration

$$\sum_{\pi,\rho}(w_{s;\pi\tau}-w_{s;\sigma\rho})\int b_{s;\pi}^*b_{s;\rho}^{(n)}d\tau$$
$$=\int b_{s;\tau}^*(x+i\partial/\partial k_x)b_{s;\sigma}^{(n-1)}d\tau+w_{s;\sigma\tau}^{(n)}$$
$$+\sum_\rho\sum_{\nu=1}^{n-1} w_{s;\sigma\rho}^{(\nu)}\int b_{s;\tau}^*b_{s;\rho}^{(n-\nu)}d\tau.$$

Satisfaction of this equation is always possible because of the appearance of the isolated constant $w_{s;\sigma\tau}^{(n)}$. It is therefore immaterial whether the left-hand side vanishes or not. Multiplication with a basis function b_q^* *outside* the quasidegenerate starting basis yields

$$\sum_\rho(w_q\delta_{\sigma\rho}-w_{s;\sigma\rho})\int b_q^*b_{s;\rho}^{(n)}d\tau$$
$$=\int b_q^*(x+i\partial/\partial k_x)b_{s;\sigma}^{(n-1)}d\tau$$
$$+\sum_\rho\sum_{\nu=1}^{n-1} w_{s;\sigma,\rho}^{(\nu)}\int b_q^*b_{s;\rho}^{(n-\nu)}d\tau.$$

This is a system of simultaneous linear equations for the expansion coefficients of $b_{s;\rho}^{(n)}$ with respect to b_q. The number of equations is given by the number of quasidegenerate bands in s. The determinant Δ of the coefficients equals

$$\Delta=\begin{vmatrix} w_{s;11}-w_q & w_{s;12} & w_{s;13} \\ w_{s;21} & w_{s;22}-w_q & \cdots \\ \cdots & \cdots & \cdots \end{vmatrix}, \quad \text{(d)}$$

or

$$\Delta=\prod_i(w_{s;i}-w_q). \quad \text{(e)}$$

Since w_q is by assumption outside the set $w_{s;i}$ the determinant Δ never vanishes and the simultaneous system can be solved with respect to the expansion coefficients in question.

APPENDIX II

In order to prove the orthogonality of the solutions of (b) to a solution of (2) to all orders in E we construct Green's identity between the two equations as was done in the text. We get

$$\sum_\rho(W_q\delta_{\sigma\rho}-W_{s;\sigma\rho})\int B_q^*B_{s;\rho}d\tau$$
$$-Ei\frac{\partial}{\partial k_x}\int B_q^*B_{s;\sigma}d\tau=0.$$

As previously, this equation has to be sorted out according to powers of E; we define therefore by $O_\rho^{(n)}$ the coefficient in the power E^n of the integral $\int B_q^*B_{s;\rho}d\tau$. The nth recursion stage reads then

$$\sum_\rho(w_q\delta_{\sigma\rho}-w_{s;\sigma\rho})O_\rho^{(n)}$$
$$=\text{material involving } O_\rho^{(\nu)} \text{ with } \nu<n.$$

All the terms on the right have been set equal to zero in previous recursion stages. The determinant of the $O_\rho^{(n)}$'s is the Δ defined in (d) and (e) which cannot vanish. Therefore all quantities $O_\rho^{(n)}$ are zero.