attempt of the edges and corners to shrink the surface layer.

(3) We may include third and further neighbor interactions. The algebra then becomes tedious: The order of the difference equation for Δ_{N-n} rises with each further interaction. Only the limiting case of Coulomb interactions is of importance. This case has been treated by Lennard-Jones and Dent[13] and others.[14,15] They have included polarization effects, and interesting surface clustering tendencies have been found.[14] Our one-dimensional calculation should also be corrected for polarization effects.

ACKNOWLEDGMENT

We wish to thank Dr. M. Lax for a helpful discussion.

[13] J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. (London) **A121**, 247 (1928).

[14] K. Molière, W. Rathje, and I. N. Stranski, Discussions Faraday Soc. **5**, 21 (1949).

[15] M. M. Nicolson, Proc. Roy. Soc. (London) **A228**, 490 (1955).

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Decoupling of Bloch Bands in the Presence of Homogeneous Fields*

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Following up an earlier communication, wave functions are constructed in Sec. 2 of this paper which are valid if a charge moves in a superposition of a periodic electric potential and a uniform magnetic field. The wave functions are not themselves solutions of the Schroedinger equation, but yield the traditional effective Hamiltonian for this problem. Contrary to the electric field case the mainfold of states linked by the "band index" does not form a Bloch band; the reason is that the cellular transforms of the Bloch-like functions are modified by the Peierls phase. At present, the derivation of these results is in closed form, but justifiable only "to all powers of the magnetic field." This was also the case for the previous electric derivation. The limitation may not be genuine. The third section of the paper does in fact prove directly the existence of closed Bloch bands in the presence of a homogeneous electric field; the case of free electrons is given as an example. One expects from this that the new results for the magnetic field are at least in part also independent of the power series method used for their justification. The fourth section extends the procedure to crossed electric and magnetic fields.

1. INTRODUCTION

IN a previous communication having a similar title,[1] one of us has put forward the notion that homogeneous fields must have a very special relationship to the energy bands of a Bloch particle. The basis for this idea is that energy bands arise from the translational symmetry of the crystalline field and that this symmetry is not removed physically by the presence of the applied field. Commonly employed formalisms do not seem to support this viewpoint. The notion is, however, followed up in I for the case of a homogeneous electric field. It is shown that one can modify the Bloch functions in powers of the field in such a way that there is no interband coupling and the particle is confined to one band only. Within this band the particle moves according to the law

$$\mathbf{k}=\mathbf{k}_0+e\mathbf{E}t/\hbar. \tag{1}$$

The procedure yields, simultaneously with the wave functions, an effective one-band Hamiltonian $\mathcal{H}_q$ for the particle. This Hamiltonian reads

$$\mathcal{H}_q=W_q(\mathbf{k})-e\mathbf{E}\cdot\mathbf{r}. \tag{2}$$

Here $W_q(\mathbf{k})$ is the (modified) energy band function for the band of index q, and $\mathbf{r}$ is the lattice vector operator, an operator conjugate to $\mathbf{k}$ within the band q.

In the present paper the notions of reference 1 will be pushed further in two directions. First of all the analogous procedure is carried out in Sec. 2 for the case of a homogeneous magnetic field. It is seen that because of the presence of the Peierls phase[2] the ensemble of states linked together by the band index q ceases to be a band. Instead of this, it becomes a manifold of just a structure that its effective Hamiltonian takes the form

$$\mathcal{H}=W_q(\mathbf{P}/\hbar), \tag{3a}$$

where $\mathbf{P}$ is given by

$$\mathbf{P}=\mathbf{p}-(e/c)\mathbf{A}. \tag{3b}$$

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[1] Gregory H. Wannier, Phys. Rev. **117**, 432, (1960). In the following referred to as I. There is an error in the Eqs. (36)–(40) of that paper where x should be replaced by ξ throughout. This error was pointed out to us by E. Blount.

[2] R. Peierls, Z. Physik **80**, 763 (1933).

Here $\mathbf{p}$ is the momentum, $\mathbf{A}$ the vector potential and $W_q(\mathbf{k})$ an energy band function of $\mathbf{k}$ periodic in the reciprocal lattice. The result (3) has been postulated many times and is effectively proved in the article of Kohn.[3] The present work goes beyond the work of Kohn in giving in closed form the law of formation of $W_q(\mathbf{k})$ and exhibiting explicitly the base in which (3) is true. In other words, it treats the magnetic case in a manner equivalent to the electric case. This method can be generalized to the case of crossed electric and magnetic fields as is shown in Sec. 4.

That this type of procedure is not yet the final form for the theory of homogeneous fields is suggested in Sec. 3 in which the results of I are partly liberated from the need of proceeding in powers of the field. The operator

$$O(t)=\exp(-i\mathfrak{H}t/\hbar)$$

controls the development of a wave function in time. For this operator a time T can be found such that $O(T)$ becomes periodic in $\mathbf{x}$. This operator must then have Bloch functions as solutions

$$\exp(-i\mathfrak{H}T/\hbar)b_q(\mathbf{x};\mathbf{k})=e^{-i\phi_q}b_q(\mathbf{x};\mathbf{k}). \tag{4}$$

For these wave functions the motion becomes strictly periodic in time. They define therefore the Bloch bands closed in time discussed in I. The modifying phrase "to all powers of the field" can thus be removed for the theorems in I concerning the wave functions. The situation is less favorable with respect to the effective Hamiltonian. The new derivation in fact encompasses the case of free electrons for which no effective Hamiltonian of the type (2) can exist. It thus foreshadows a more complicated situation than the one envisaged in reference 1.

2. RESULTS FOR THE MAGNETIC CASE

In this section results will be derived for the magnetic case from an assumed starting equation. Our hamiltonian reads

$$\mathfrak{H}=\tfrac{1}{2}(\mathbf{p}-\tfrac{1}{2}\mathbf{H}\times\mathbf{x})^2+V(\mathbf{x}), \tag{5a}$$

with

$$V(\mathbf{x}+\boldsymbol{\varrho})=V(\mathbf{x}), \tag{5b}$$

$$\boldsymbol{\varrho}=l\mathbf{a}+m\mathbf{b}+n\mathbf{c}, \tag{5c}$$

where

$$l,\ m,\text{ and }n\text{ are integers.} \tag{5d}$$

The units used here are the same as in I: m, $\hbar$, and c equal unity, and e is absorbed in the electric field E and magnetic field H.

As in the previous case, there is a starting equation defining a set of Bloch type functions. As in that case, a heuristic argument for its structure can be given, but is not necessary for a logical presentation. The important feature is a derivation of its properties; in the course of this derivation some of the heuristic elements will appear. We therefore simply state the following defining equation:

$$\{\tfrac{1}{2}[\mathbf{p}-\tfrac{1}{2}\mathbf{H}\times(\mathbf{x}+i\partial/\partial\mathbf{k})]^2+V(\mathbf{x})\}b_q(\mathbf{x};\mathbf{k})$$
$$=\textstyle\sum_{\boldsymbol{\varrho}} w_q(\boldsymbol{\varrho})\exp(i\mathbf{k}\cdot\boldsymbol{\varrho})\{\exp(-\tfrac{1}{2}i\mathbf{H}\times\boldsymbol{\varrho}\cdot\mathbf{x})$$
$$\times b_q(\mathbf{x};\mathbf{k}+\tfrac{1}{2}\mathbf{H}\times\boldsymbol{\varrho})\}. \tag{6a}$$

The fact that this equation defines a Bloch type function is more easily visualized if one makes the conventional split-up

$$b_q(\mathbf{x};\mathbf{k})=e^{i\mathbf{k}\cdot\mathbf{x}}u_q(\mathbf{x};\mathbf{k}),$$

and writes out the analogous equation for the function u_q. A cancellation of exponentials occurs then on the right and one gets

$$\{\tfrac{1}{2}(\mathbf{p}+\mathbf{k}-\tfrac{1}{2}i\mathbf{H}\times\partial/\partial\mathbf{k})^2+V(\mathbf{x})\}u_q(\mathbf{x};\mathbf{k})$$
$$=\textstyle\sum_{\boldsymbol{\varrho}} w_q(\boldsymbol{\varrho})\exp(i\mathbf{k}\cdot\boldsymbol{\varrho})u_q(\mathbf{x};\mathbf{k}+\tfrac{1}{2}\mathbf{H}\times\boldsymbol{\varrho}). \tag{6b}$$

For $H=0$ the equation (6b) is just the defining equation for the periodic part of the unperturbed Bloch functions of the crystal. This starting point has the usual hazards arising from overlapping and degenerate bands; these hazards can only be taken care of by generalizing (6) to a set of simultaneous equations. We shall ignore this difficulty in the following and assume that the variables in (6b) exist in the limit $H=0$. We may then collect linear terms in H, substitute in these terms the zero order solution and get a first order correction for u_q and w_q. Proceeding in this fashion we get a power series expansion for these quantities in power of H. At each stage the perturbation is periodic and thus yields a periodic u_q in the next following stage. In detail the procedure is very much like the procedure followed in I, except that it is more cumbersome. For the equation (I,2) the justification of these steps was carefully outlined in a series of theorems. Rather than repeat such a treatment we shall take these results for granted, except for orthogonality. The structure of (6) throws some doubt on the orthogonality of the functions b_q, and we shall in fact avoid making use of this postulate. Linear independence will, on the other hand, be valid at least for a certain range of H since it is valid for $H=0$. As a result we are thus in possession of a set of Bloch functions $b_q(\mathbf{x};\mathbf{k})$ and an "energy band function" $W_q(\mathbf{k})$ which is given by

$$W_q(\mathbf{k})=\textstyle\sum_{\boldsymbol{\varrho}} w_q(\boldsymbol{\varrho})\exp(i\mathbf{k}\cdot\boldsymbol{\varrho}). \tag{7}$$

Both these quantities are given to us as power series in H, and solve equation (6b) in powers of H. They are related to the band index through the zero order term of this expansion. Equation (6) is similar to, but different from the equation proposed by one of us in 1955[4]; the left-hand side is the same, but the right has a more involved structure; only when the energy band function reduces to a constant is the older form justified.

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

[4] Gregory H. Wannier, Phys. Rev. **100**, 1227 (1955).

As the next step we consider the following function

$$B_q(\mathbf{x};\mathbf{k})=b_q(\mathbf{x};\mathbf{k}-\tfrac{1}{2}\mathbf{H}\times\mathbf{x}). \tag{8}$$

Functions of this type were first introduced by Harper.[5] They bring us back to the Hamiltonian (5a) because they satisfy the following identity

$$\{\mathbf{p}-\tfrac{1}{2}\mathbf{H}\times\mathbf{x}\}B_q(\mathbf{x};\mathbf{k}) =[\{\mathbf{p}-\tfrac{1}{2}\mathbf{H}\times(\mathbf{x}+i\partial/\partial\mathbf{k})\}b_q(\mathbf{x};\mathbf{k})]_{\mathbf{k}\to\mathbf{k}-\frac{1}{2}\mathbf{H}\times\mathbf{x}}. \tag{9}$$

On the right hand side of (6) this same substitution $\mathbf{k}\to\mathbf{k}-\frac{1}{2}\mathbf{H}\times\mathbf{x}$ just removes one of the exponentials, yielding with (5)

$$\mathcal{H}B_q(\mathbf{x};\mathbf{k})=\sum_{\varrho} w_q(\varrho)\exp(i\mathbf{k}\cdot\varrho)B_q(\mathbf{x};\mathbf{k}+\tfrac{1}{2}\mathbf{H}\times\varrho). \tag{10}$$

Equation (10) achieves the essential goal of finding a set of functions which the Hamiltonian couples only to other functions of the same "band index" q. In the pursuit of this goal the functions have admittedly lost their Bloch character. This loss had to occur because it is implied in the old observation of Peierls[2] concerning the phase factor bearing his name. To bring this out we pass over to a Wannier representation. Define a Wannier type function by the obvious transformation of the solutions of (6)[6]

$$a_q(\mathbf{x}-\varrho)=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}\exp(-i\mathbf{k}\cdot\varrho)b_q(\mathbf{x};\mathbf{k}). \tag{11}$$

The sum here is really an integral but it is written in the Born-vonKarman fashion for convenience. If we apply the same unitary transformation to the functions (8) and define $A_q(\mathbf{x};\varrho)$ by the equation

$$A_q(\mathbf{x};\varrho)=\frac{1}{\sqrt{N}}\sum_{\mathbf{k}}\exp(-i\mathbf{k}\cdot\varrho)B_q(\mathbf{x};\mathbf{k}), \tag{12}$$

we get with (8)

$$A_q(\mathbf{x};\varrho)=\exp(-\tfrac{1}{2}i\mathbf{H}\cdot\mathbf{x}\times\varrho)a_q(\mathbf{x}-\varrho). \tag{13}$$

In other words, the functions (8) are not quite Bloch functions because their cellular transforms are not quite Wannier functions, but differ from each other by the Peierls phase factor. In order to get the cellular form of Eq. (10) we multiply with $(N^{-\frac{1}{2}})\exp(-i\mathbf{k}\cdot\varrho)$ and sum over $\mathbf{k}$. The result is

$$\mathcal{H}A_q(\mathbf{x};\varrho)=\sum_{\varrho''}A_q(\mathbf{x};\varrho'')w_q(\varrho-\varrho'') \times\exp(-\tfrac{1}{2}i\mathbf{H}\cdot\varrho''\times\varrho). \tag{14}$$

The form of the magnetic Hamiltonian postulated in the past results from (10) in the following way. Suppose we write an eigenfunction of the Hamiltonian (5a) in the form

$$\psi(\mathbf{x})=\sum_{\mathbf{k}} f(\mathbf{k})B_q(\mathbf{x};\mathbf{k}), \tag{15}$$

where the B's are defined by (6) and (8). We can then ask for the equations obeyed by the amplitude function $f(\mathbf{k})$. Applying (10) to (15) we get

$$\mathcal{H}\psi(\mathbf{x})=\sum_{\mathbf{k},\varrho} f(\mathbf{k})\exp(i\mathbf{k}\cdot\varrho)w_q(\varrho)B_q(\mathbf{x};\mathbf{k}+\tfrac{1}{2}\mathbf{H}\times\varrho),$$

or with a shift in the summation index $\mathbf{k}$

$$\mathcal{H}\psi(\mathbf{x})=\sum_{\mathbf{k},\varrho} w_q(\varrho) \times\exp(i\mathbf{k}\cdot\varrho)f(\mathbf{k}-\tfrac{1}{2}\mathbf{H}\times\varrho)B_q(\mathbf{x};\mathbf{k}). \tag{16}$$

The f's will define an eigenfunction of $\mathcal{H}$ if (16) differs from (15) by an energy multiplier $\mathcal{E}$ only. Since the B's are linearly independent in the same sense as the b's we can factor out their coefficients in the resultant expansion and write

$$\sum_{\varrho} w_q(\varrho)\exp(i\mathbf{k}\cdot\varrho)f(\mathbf{k}-\tfrac{1}{2}\mathbf{H}\times\varrho)=\mathcal{E}f(\mathbf{k}). \tag{17a}$$

The displaced argument of f is advantageously given the form

$$f(\mathbf{k}-\tfrac{1}{2}\mathbf{H}\times\varrho)=\exp(-\tfrac{1}{2}\mathbf{H}\times\varrho\cdot\partial/\partial\mathbf{k})f(\mathbf{k}),$$

so that (17a) takes the form

$$\sum_{\varrho} w_q(\varrho)\exp(i\mathbf{k}\cdot\varrho)\exp(-\tfrac{1}{2}\mathbf{H}\times\varrho\cdot\partial/\partial\mathbf{k})f(\mathbf{k})=\mathcal{E}f(\mathbf{k}).$$

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 ϱ. The eigenvalue equation therefore takes the form

$$W_q(\mathbf{K})f(\mathbf{k})=\mathcal{E}f(\mathbf{k}), \tag{17b}$$

where $W(\mathbf{k})$ is given by (7) and the operator $\mathbf{K}$ by

$$\mathbf{K}=\mathbf{k}-\tfrac{1}{2}i\mathbf{H}\times\partial/\partial\mathbf{k}. \tag{18}$$

The operator $i\partial/\partial\mathbf{k}$ occurring in (18) is a coordinate type variable conjugate to $\mathbf{k}$. The vector $\mathbf{K}$ thus obeys the commutation relation

$$\mathbf{K}\times\mathbf{K}=i\mathbf{H}. \tag{19}$$

This is also the commutation relation obeyed by the vector $\mathbf{P}$ defined in (3b). The diagonalization of $W_q(\mathbf{K})$ will therefore proceed in exactly the same fashion as the diagonalization of (3a). In addition to confirming this traditional guess the present derivation also provides through Eqs. (6)–(8) the basis in which this form is realized and an explicit recipe for the construction of $W_q(\mathbf{k})$.

3. SUPPLEMENTARY RESULTS FOR THE ELECTRIC CASE

In reference 1 results similar to the preceding are worked out for a homogeneous electric field. Proofs are carried through in rather greater detail than here, and the result is that the theory as presented is clearly justified only if proceeding in powers of the field, even though the formulas are in closed form. This opens up the possibility that the results might be only correct in an asymptotic sense, and that a remainder term with

[5] P. J. Harper, Proc. Phys. Soc. (London) **A68**, 879 (1955).
[6] Gregory H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), Eqs. (6.15) and (6.16).

entirely different properties might exist The work of this section excludes this possibility in the electric field case, as far as the modified Bloch functions are concerned.

Suppose we take an arbitrary initial wave function $\psi(\mathbf{x},0)$ at the time $t=0$. We then know that

$$\psi(\mathbf{x},t)=\exp(-i\mathfrak{H}t)\psi(\mathbf{x},0) \tag{20}$$

is a solution of the Schroedinger equation in time. Now if $\mathfrak{H}$ is the hamiltonian $(I,1)$ and if $\psi(\mathbf{x},0)$ happens to be a Bloch function of reduced wave vector $\mathbf{k}_0$, then it follows from (1) that $\psi(\mathbf{x},t)$ is a Bloch function of wave vector $\mathbf{k}_0+\mathbf{E}t$. If now the electric field is in a reciprocal lattice direction and if the period of the reciprocal lattice in that direction is $\mathbf{a}^*$ then the original wave vector will have been restored after a time[7]

$$T=2\pi(\mathbf{a}^*/E). \tag{21}$$

It follows that the unitary operator $\exp(-i\mathfrak{H}T)$ preserves the reduced wave vector, and its eigenfunctions must be Bloch functions. This conclusion can be verified directly on the Hamiltonian (I,1). We find with (21)

$$\exp(-i\mathfrak{H}T)=\exp\{-iT[\tfrac{1}{2}\mathbf{p}^2+V(\mathbf{x})]-2\pi i\mathbf{a}^*\cdot\mathbf{x}\}. \tag{22}$$

This operator has the lattice period in $\mathbf{x}$ because the square bracket has that period and the factor of $\mathbf{x}$ in the last term is just such as to increase it by a multiple of 2π whenever $\mathbf{x}$ is increased by a lattice vector.

It follows that we can define a set of Bloch functions with the help of the operator (22), writing

$$\exp(-i\mathfrak{H}T)B_q(\mathbf{x};\mathbf{k})=e^{-i\phi_q}B_q(\mathbf{x};\mathbf{k}). \tag{23}$$

If we now start out at the time $t=0$ with one of these wave functions $B_q(\mathbf{x};\mathbf{k}_0)$ then the wave function

$$\psi(\mathbf{x};t)=\exp(-i\mathfrak{H}t)B_q(\mathbf{x};\mathbf{k}_0)$$

will vary periodically in time because it returns to its original form (apart from a phase factor) after a time T. A very obvious assignment of the band index and phase will then create a band closed in time with wave functions periodic in reciprocal space. The assignment is

$$B_q(\mathbf{x};\mathbf{k}_0+\mathbf{E}t)=\exp(-i\mathfrak{H}t)B_q(\mathbf{x};\mathbf{k}_0)\exp(i\phi_q t/T), \tag{24}$$

and the time dependent wave function may be given the form

$$\psi(\mathbf{x};t)=\exp(-i\phi_q t/T)B_q(\mathbf{x};\mathbf{k}_0+\mathbf{E}t). \tag{25}$$

Finally, one can derive from (24) the starting equation of reference 1 by differentiation with respect to time. One finds, using Eq. (1)

$$\mathbf{E}\cdot\partial B_q/\partial\mathbf{k}=-i\mathfrak{H}B_q+i(\phi_q/T)B_q. \tag{26}$$

If one substitutes (I,1) for $\mathfrak{H}$ Eq. (26) is seen to be identical with (I,2), as indicated.

[7] See reference 6, pp. 191–192 for a physical interpretation of this periodicity.

Once one is in possession of Bloch functions obeying Eq. (I,2) and conforming to Theorems I,4 and I,5 without reference to power series expansion one might think that direct derivation of the remainder of that paper would be a mere formality. This idea is not correct. The effective Hamiltonian in I cannot be derived by the new method. In fact the Hamiltonian does not always exist. An easy way to show this is by the counterexample method. The counterexample is the case of free electrons; it is sufficient to treat this example in one dimension.

In the case of free electrons the introduction of a period d is of course artificial. Nevertheless, a Stark ladder with spacing Ed and arbitrary first member can be picked out of the continuum of states, and the wave functions thereof superimposed according to (I,42). Denote by $A(x)$ the function

$$A(-x)=(2x^{\frac{1}{2}}/3)K_{\frac{1}{3}}(2x^{\frac{3}{2}}/3^{\frac{1}{2}}), \tag{27}$$

with the proper analytic continuation for positive x. Then we get from (I,42)

$$B_q(x;k)=\sum_{\nu=-\infty}^{+\infty}e^{-ik\nu d}A\left[(6E)^{\frac{1}{3}}\left(x+\frac{\mathcal{E}}{E}+\nu d\right)\right], \tag{28}$$

where $\mathcal{E}$ is the energy of some member of the chosen Stark ladder. The summation can be carried out by the Poisson summation formula[8] and yields with a change of factor

$$B_q(x;k)=\sum_{\nu=-\infty}^{+\infty}\exp i\left[\left(k+\frac{2\pi\nu}{d}\right)\left(x+\frac{\mathcal{E}}{E}\right)-\frac{1}{6E}\left(k+\frac{2\pi\nu}{d}\right)^3\right]. \tag{29}$$

The formal divergence of the series need not bother us since the accelerated oscillation in phase for large ν will produce absolute convergence if we just assume a small range of error in k.

It is to be observed that the wave functions (29) obey all criteria laid down for the band eigenfunctions. Each term of it obeys separately Eq. (26) with

$$\phi_q=2\pi(\mathcal{E}/Ed). \tag{30}$$

Hence a time dependent solution of the Schroedinger equation can be constructed by formula (25). The periodicity requirement in reciprocal space is taken care of by the succession of terms. $\mathcal{E}$ acts as the band index as is seen from (30) All possible bands are reached if $\mathcal{E}$ varies through the interval $\langle 0,Ed\rangle$. Thus, the Bloch bands exist, and are closed in time. Yet the Hamiltonian (I,16) cannot be constructed because the power series method is clearly inapplicable and direct construction of the square bracket in (I,28) yields divergent results.

[8] R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Verlag Julius Springer, Berlin, 1931), Vol. I, p. 65.

In fact, a divergence for the expectation value of $\dot{p}^2$ has to occur because only through it can we reconcile the existence of closed bands with the indefinite increase of p with time which we know to be present for a free particle in a uniform field.

It is clear for physical reasons that the divergences just found for free electrons must still be present when the crystalline field is everywhere weaker than the applied field. Whether they are also present in the weak field limit cannot be decided at this time. In any case, the existence of closed Bloch bands is neatly illustrated by this example.

4. RESULTS FOR CROSSED FIELDS

It is implicit in the philosophy of the present work that we should be capable of handling simultaneous electric and magnetic fields in a solid. In discussing such a possibility we may assume the two fields perpendicular because the effects of an electric field parallel to a magnetic field are kinematically separable. Let us therefore assume an $\mathbf{E}$ field along the x direction and an $\mathbf{H}$ field along the z direction.

At the present time we can only generalize the power series method because the magnetic equivalent of the operator (22) is not yet known. Once this restriction is made, generalization is rather easy because the procedures for the electric and magnetic case can be superimposed without mutual interference. The Bloch function for the crossed fields results therefore from superposition of (6a) and (I,2)

$$\{\tfrac{1}{2}[\mathbf{p}-\tfrac{1}{2}\mathbf{H}\times(\mathbf{x}+i\partial/\partial\mathbf{k})]^2+V(\mathbf{x})-E(x+i\partial/\partial k_x)\}\times b_q(\mathbf{x};\mathbf{k})=\sum_{\varrho} w_q(\varrho)\exp(i\mathbf{k}\cdot\varrho)\times\{\exp(-\tfrac{1}{2}i\mathbf{H}\times\varrho\cdot\mathbf{x})b_q(\mathbf{x};\mathbf{k}+\tfrac{1}{2}\mathbf{H}\times\varrho)\}. \quad (31)$$

It is seen from previous work that superfluous magnetic terms are removed by a phase correction, while the superfluous electric term is simply subtracted. These procedures again do not interfere with each other so that we end with the following generalization of (10)

$$\mathcal{H}B_q(\mathbf{x};\mathbf{k})=\sum_{\varrho} w_q(\varrho)\exp(i\mathbf{k}\cdot\varrho)B_q(\mathbf{x};\mathbf{k}+\tfrac{1}{2}\mathbf{H}\times\varrho)+iE\frac{\partial B_q(\mathbf{x};\mathbf{k})}{\partial k_x}. \quad (32)$$

We now write an energy eigenfunction in the form (15). If we recognize that the summation indicated there is actually an integration, and that both $f(\mathbf{k})$ and $B_q(\mathbf{x};\mathbf{k})$ are periodic in k_x then we see that the operation $\partial/\partial k_x$ can be transferred to $f(\mathbf{k})$ with a change in sign. The reduction of the first term on the right proceeds as before to the form (17). The generalization of (17) thus reads

$$\{W_q(\mathbf{k}-\tfrac{1}{2}i\mathbf{H}\times\partial/\partial\mathbf{k})-iE\partial/\partial k_x\}f(\mathbf{k})=\mathcal{E}f(\mathbf{k}). \quad (33)$$

We see that we are dealing here also with a generalization of Eq. (2). Further simplification of the problem can proceed by operator methods as in I. We may thus write

$$\mathcal{H}_{\text{eff}}=W_q(\mathbf{K})-Er_x. \quad (34)$$

Here $\mathbf{K}$ is defined by (18). r_x is the x component of the lattice vector operator and obeys the relations

$$r_xK_x-K_xr_x=i, \quad (35a)$$

$$r_xK_y-K_yr_x=0, \quad (35b)$$

$$r_xK_z-K_zr_x=0. \quad (35c)$$

The commutation relations (19), on the other hand read

$$K_xK_y-K_yK_x=iH, \quad (36a)$$

$$K_yK_z-K_zK_y=0, \quad (36b)$$

$$K_zK_x-K_xK_z=0. \quad (36c)$$

It follows from these two sets of equations that K_y+Hr_x commutes with all variables of the system and thus is a constant of the motion

$$K_y+Hr_x=C. \quad (37)$$

Substituting (37) into (34) we get, apart from a constant

$$\mathcal{H}_{\text{eff}}=W_q(\mathbf{K})+\frac{E}{H}K_y. \quad (38)$$

This is a correct substitution. However, the new expression is the correct Hamiltonian only for motion in $\mathbf{K}$ space. For motion in $\mathbf{r}$ space one must return to equation (34).

5. CONCLUSIONS

This paper, together with reference 1, shows that the wave functions arising from the superposition of a periodic potential and a homogeneous field have indeed special properties. In the case of a homogeneous electric field bands filling the first Brillouin zone exist which are closed in time (even for free electrons). The existence of an effective Hamiltonian is not as well assured. There are in fact certainly cases in which there is no Hamiltonian, and the evidence for it remains linked to the power series method. On the other hand, it exists in a practical sense in many cases.

In the case of a homogeneous magnetic field the manifold linked by a "band index" does not form a band. When one looks at the Bloch type functions their modification appears obscure, but in the cellular representation its meaning becomes clear; we deal with Wannier functions modified by the Peierls phase. This manifold is just such as to allow the conventional treatment (3) for the band in the presence of a magnetic field. In fact, for free electrons Eq. (6b) has the trivial solution $u_q(\mathbf{x};\mathbf{k})=1$ which yields in turn $W(\mathbf{k})=\frac{1}{2}\mathbf{k}^2$, so that (17) is, in this case, just the usual magnetic Schroedinger equation in the momentum representation. The success of the magnetic field formalism inde-

pendently of the presence of a crystal field, unlike the situation for the electric field formalism, where the effective Hamiltonian idea fails without a sufficiently strong crystal field, is understandable on simple physical grounds, and suggests that the magnetic field formalism should, if anything, be better founded than the electric field formalism. Nevertheless, all our magnetic field results must be qualified, in this paper, as being true "to all powers in the field," and we have been unable, so far, to do anything for the magnetic field problem analogous to Sec. 3. The difficulty here is, perhaps, related to the greater richness of phenomena produced by a magnetic field in a solid, compared to the basic simplicity of most electric field effects. It would, however, be very desirable to be free of the power series limitation, since the recent work of Cohen and Falicov[9] on "magnetic breakdown" suggests that there might be specific difficulties with the band index q as the field is varied, and the power series might only be an asymptotic representation of electron behavior.

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[9] M. H. Cohen and L. M. Falicov (unpublished).

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Microwave Losses in Strontium Titanate above the Phase Transition*

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The microwave losses in both pure and doped $SrTiO_3$ have been investigated as a function of frequency and temperature. It is found that the loss tangent is proportional to frequency in the range 3–36 kMc/sec. Above the phase transition at 112°K, the temperature dependence of the loss tangent is well represented by $\tan\delta=(T-T_c)^{-1}(\alpha+\beta T+\gamma T^2)$, where the Curie temperature, $T_c=37$°K. The parameter α is shown to be determined by lattice imperfections and vanishes for pure single-crystalline material. The parameters β and γ, which are related to third- and fourth-order anharmonic terms in the interionic potential, are shown to be intrinsic properties of the perfect lattice and are unaffected by imperfections.

INTRODUCTION

MICROWAVE losses in ferroelectric materials have been the subject of many studies in the past years. Powles and Jackson[1] and others[2] have measured the losses of barium and strontium titanate mixtures as a function of temperature and composition. At 3 kMc/sec, Davis and Rubin[3] have investigated the loss tangent of certain mixtures of $Ba_xSr_{1-x}TiO_3$ above and below the Curie temperature. Work on single crystals of $BaTiO_3$ has been published by Benedict and Durand.[4] In all these cases the microwave losses were relatively high even above the Curie temperature, obviously the main reason why such attractive properties like the nonlinearity of the dielectric constant have not yet been utilized in such materials to any appreciable extent. Recently we have shown that the microwave losses in single crystalline strontium titanate are surprisingly low above the Curie temperature, and that $SrTiO_3$ is potentially a good substance to study the loss mechanism in dielectric materials.[5]

$SrTiO_3$ is commercially available in relatively high purity as single crystals.[6] In the low-frequency range at room temperature Linz[7] has reported a loss tangent of 2.5×10^{-4} which is independent of frequency in the range between 10^2 and 10^7 cps.

It is the purpose of this paper to report in some detail on the functional dependence of the loss tangent at microwave frequency on parameters such as temperature, frequency, and lattice imperfections, and hereby strive for an answer to the question: Are the observed microwave losses intrinsically connected with the property of ferroelectricity and therefore unavoidable, or are they in part due to lattice imperfections and other disturbing factors? Many of the following experiments described below were carried out on single crystalline $SrTiO_3$. The data presented have been taken above the Curie temperature and will be evaluated in

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