

The results for the dispersion relations using the model $E(q)$ are summarized in Fig. 4. Nearly 900 reciprocal lattice points were included in the summations in Eqs. (13) and (14). Even so, the sums have not converged completely, as evidenced by the small splittings at the zone boundary in the [0001] direction. Comparing Figs. 1 and 4, it is clear that the model pseudopotential has generally been more successful in reproducing the observed frequencies than that computed from first principles. There are, however, important deviations as far as the transverse branches are concerned.

To summarize, phonon frequencies in magnesium computed using pseudopotential results obtained from first principles show poor agreement with experiment. A model pseudopotential involving two parameters has

proved more successful in this respect. Comparison of the pseudopotentials and $E(q)$ for the two cases shows a difference in the region beyond k_F . This suggests that better agreement with experiment could be obtained if the accuracy of the basic $E(q)$ were improved by computing the core energies and orbitals more carefully. We hope to examine this question shortly.

ACKNOWLEDGMENTS

It is a pleasure to thank Professor W. A. Harrison for encouraging us to undertake this calculation and for giving helpful advice while the work was in progress. We would also like to thank Dr. P. K. Iyengar for his keen interest in the work and Shri V. C. Sahni for a careful reading of the manuscript.

Some Analytic Properties of Finite-Band Models in Solids

J. B. KRIEGER*

Polytechnic Institute of Brooklyn, Brooklyn, New York

(Received 18 October 1966)

The work of Kohn is generalized to more than one dimension for a finite-band model by a simple algebraic procedure. Some results not previously derived for more than one dimension are obtained. The differences between the analytic properties of the model and those of the complete Hamiltonian are briefly discussed.

INTRODUCTION

IT is well known that the motion of an electron in a crystal is governed in the one-electron approximation by a Hamiltonian which is periodic in the lattice. From this it follows that the wave functions must have the form

$$\phi_n(\mathbf{r}, \mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}} U_n(\mathbf{r}, \mathbf{k}),$$

where U_n has the same periodicity in \mathbf{r} as the Hamiltonian. If the wave functions are to remain finite as $r \rightarrow \infty$ in any direction, then \mathbf{k} must have only real components. However, if the crystal has a boundary, i.e., say for $x > 0$ we have only free space, then we cannot restrict k_x in the crystal to be real since, if k_x has a negative imaginary part, $\phi_n(\mathbf{r}, \mathbf{k})$ will not diverge as $x \rightarrow -\infty$ and hence is an acceptable solution. Clearly then, these solutions, which are simply the analytic continuation of the Bloch solutions for complex \mathbf{k} , will have ramifications in problems involving surfaces such as the spectrum of allowed surface states or the matching of electronic wave functions at the boundary of a crystal in a low-energy electron-diffraction experiment. Furthermore, solutions with complex \mathbf{k} also appear in the theory of electron tunneling and in any physical

problem involving a "tailing off" of the wave function in some classically forbidden region. Finally, we should mention that the rate of decay of Wannier functions is intimately related to the analytic properties of the Bloch waves.

The analytic properties of Bloch waves and Wannier functions have been exhaustively studied by Kohn¹ for the one-dimensional case. However, his methods are based on the theory of ordinary, i.e., not partial differential equations, and cannot be extended to two or three dimensions, not even to a one-dimensional section of a two- or three-dimensional band structure. The latter follows from the fact that in one dimension, bands cannot overlap, whereas in more than one dimension, one-dimensional sections of the energy may overlap. More recently, Blount² and Heine³ have proved some general results concerning the analytic properties of the energy function, but it is not clear how to obtain the analytic properties of the Bloch waves from their work.

All the previously mentioned work makes liberal use of theorems concerning the analytic properties of

¹ W. Kohn, Phys. Rev. **115**, 809 (1959).

² E. I. Blount, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1962), Vol. 13, pp. 305-373.

³ V. Heine, Proc. Phys. Soc. (London) **81**, 300 (1963).

* Supported in part by National Aeronautics and Space Administration Grant No. NSG 589.

functions of a complex variable, which many workers in the field may find obscure. Furthermore, since in actual problems the analytic properties will often be obtained from a finite-band model, it is not *a priori* obvious that the properties of the approximate treatment reflect those of an exact treatment.

The purpose of the present work is to remedy this situation by showing that some analytic properties of an n -band model can be derived by simple algebraic means and that, furthermore, some results which have previously been derived only for the one-dimensional case are valid for an arbitrary number of dimensions.

In particular, we have investigated the analytic behavior of the energy as a function of the complex variable k_x . We have also derived the analytic structure of both the Bloch waves and the crystal momentum representation of the operator x in the neighborhood of a singular point and found these results to be identical to the exact analysis for a one-dimensional crystal. The analysis is applicable to any finite band model in which one component of \mathbf{k} is treated as a complex variable and the other two are taken as real. The only requirement that it be valid at a given point in \mathbf{k} space is that no more than two bands meet at that point.

Differences between our results and the results obtained from treating the exact Hamiltonian are discussed in the conclusion.

THE n -BAND MODEL

Let H_0 be the one-electron Hamiltonian which is periodic in the crystal. We shall not specify whether we are dealing with one-, two-, or three-dimensional problems, or whether H_0 contains spin-orbit coupling, so that our results will be valid for the most general case.

The Schrödinger equation for the Bloch wave is then

$$H_0\phi_i(\mathbf{r},\mathbf{k}) = \epsilon_i(\mathbf{k})\phi_i(\mathbf{r},\mathbf{k}), \tag{1}$$

where i denotes the band and the spin state if spin-orbit coupling is included. Equation (1) may also be written in terms of the cell periodic function U_i

$$H(\mathbf{k})U_i(\mathbf{r},\mathbf{k}) = \epsilon_i(\mathbf{k})U_i(\mathbf{r},\mathbf{k}), \tag{2}$$

where

$$H(\mathbf{k}) \equiv e^{-i\mathbf{k}\cdot\mathbf{r}}H_0e^{i\mathbf{k}\cdot\mathbf{r}} \tag{3}$$

and is Hermitian for real \mathbf{k} . For example, if

$$H_0 = \hat{p}^2/2m + V(\mathbf{r}),$$

then

$$H(\mathbf{k}) = H_0 + \hbar\mathbf{k}\cdot\hat{\mathbf{p}}/m + \hbar^2k^2/2m.$$

If we include spin-orbit coupling, $H(\mathbf{k})$ is still a polynomial of second degree in components of \mathbf{k} . The $U_i(\mathbf{r},\mathbf{k}_0)$, for any \mathbf{k}_0 , span a complete set of orthonormal functions for any function that is periodic in a cell. Hence we may write

$$U_m(\mathbf{r},\mathbf{k}) = \sum_i A_i^{(m)}U_i(\mathbf{r},\mathbf{k}_0). \tag{4}$$

In this representation the eigenvalue equation becomes

$$\sum_j H_{ij}(\mathbf{k})a_j = \epsilon a_i, \tag{5}$$

where

$$A_i^{(m)}(\mathbf{k}) = a_i^{(m)}(\mathbf{k})/N_m^{1/2},$$

and where $a_i^{(m)}(\mathbf{k})$ is a solution of Eq. (5), with $\epsilon = \epsilon_m(\mathbf{k})$, and N_m is a normalization constant. In what follows we shall assume that the summations in Eqs. (4) and (5) go only from $i=1$ to $i=n$ instead of over all i . This is the mathematical statement of the n -band model, its justification being that if n is chosen large enough, we expect to approach the exact solution as closely as we want. Or, in the language of perturbation theory, we expect that the interaction of bands very far away in energy should have a negligible effect. Hence we expect that as $n \rightarrow \infty$ we should obtain the properties that are characteristic of the original Schrödinger equation. The limitations of this statement are more thoroughly examined in the conclusion. Furthermore, this method enables us to study the differences between a finite-band model, with which it is easiest to do actual calculations, and the infinite-band case which, presumably, reflects the true state of affairs.

ANALYTIC PROPERTIES OF $\epsilon(\mathbf{k})$

For convenience we shall treat only k_x as complex, all other components of \mathbf{k} taken as real.

It follows from Eq. (5) that since $H_{ij}(\mathbf{k})$ are the elements of an Hermitian matrix for real \mathbf{k} , then $\epsilon(\mathbf{k})$ is real for real \mathbf{k} . Furthermore, expanding the secular determinant we have

$$P(\epsilon) = \epsilon^n + \gamma_1(\mathbf{k})\epsilon^{n-1} + \gamma_2(\mathbf{k})\epsilon^{n-2} + \dots + \gamma_{n-1}(\mathbf{k})\epsilon + \gamma_n = 0, \tag{6}$$

where the γ_i are polynomials in components of \mathbf{k} . We can prove that for real \mathbf{k} all γ_i are real by noting that Eq. (6) can be written

$$P(\epsilon) = [\epsilon - \epsilon_1(\mathbf{k})][\epsilon - \epsilon_2(\mathbf{k})] \dots [\epsilon - \epsilon_n(\mathbf{k})] = 0 \tag{7}$$

and hence the γ_i are sums of products of the $\epsilon_i(\mathbf{k})$ which are real for real \mathbf{k} . Thus for any \mathbf{k} ,

$$\gamma_i^*(\mathbf{k}) = \gamma_i(\mathbf{k}^*). \tag{8}$$

Hence taking the complex conjugate of Eq. (6) and using Eq. (8), we have

$$\epsilon^*(\mathbf{k}) = \epsilon(\mathbf{k}^*), \tag{9}$$

even if spin-orbit coupling is included.

It also follows from Eq. (6) that since the $\epsilon_i(\mathbf{k})$ are solutions of an algebraic equation whose coefficients are analytic functions of components of \mathbf{k} , then the $\epsilon_i(\mathbf{k})$ will be analytic functions of \mathbf{k} except at a set of isolated singular points corresponding to the branch points of the energy functions. These branch points must always exist because the equation $\epsilon_i(\mathbf{k}) - \epsilon_j(\mathbf{k}) = 0$ must always have at least one solution, since $\epsilon_i - \epsilon_j$ is

an analytic function of \mathbf{k} which must assume every value including zero at least once (except, of course, the case $\epsilon_i - \epsilon_j = \text{const}$).

Let us now examine the behavior of $\epsilon_i(\mathbf{k})$ near a branch point, i.e., near a point such that $\epsilon_i(q) = \epsilon_j(q) \equiv \epsilon(q)$. Thus from Eq. (7),

$$\left. \frac{dP(\epsilon)}{d\epsilon} \right|_{\epsilon=\epsilon(q)} = 0,$$

so that expanding Eq. (6) about $k_x = q$, $\epsilon = \epsilon(q)$, we have

$$0 = P(\epsilon) = \frac{1}{2} [\epsilon - \epsilon(q)]^2 \left. \frac{d^2 P}{d\epsilon^2} \right|_{\epsilon=\epsilon(q), k_x=q} + \dots + (k_x - q) \left. \frac{\partial P}{\partial k_x} \right|_{\epsilon=\epsilon(q), k_x=q}.$$

Therefore in the neighborhood of $k_x = q$,

$$\epsilon = \epsilon(q) \pm (k_x - q)^{1/2} 2 \left. \frac{\partial P / \partial k_x}{d^2 P / d\epsilon^2} \right|_{k_x=q, \epsilon=\epsilon(q)}. \quad (10)$$

Hence ϵ_i meets ϵ_j in a simple branch point in the complex k_x plane. [Of course, if three bands meet at a point in complex k_x space, then $d^2 P / d\epsilon^2 = 0$ and instead of obtaining $(k_x - q)^{1/2}$ we would have $(k_x - q)^{1/3}$ etc. We shall consider this an accidental degeneracy³ and not treat this case here.] We also note from Eq. (9) that if $\epsilon(q)$ has a singularity, so does $\epsilon(q^*)$; thus the branch points come in complex conjugate pairs.

In general, $q = q(k_y, k_z)$ and if it is possible that as k_y and k_z are varied q approaches the real axis, then so does q^* and

$$\epsilon_i - \epsilon_j \sim [(k_x - q)(k_x - q^*)]^{1/2} \sim k_x - q \quad (11)$$

as $q \rightarrow q^*$. Hence when bands meet for real q , q is no longer a singularity of $\epsilon(\mathbf{k})$. Furthermore, in systems of high enough symmetry

$$\epsilon(k_x) = \epsilon(-k_x), \quad (12)$$

so that a branch point at q implies a branch point at $-q$. Then $\epsilon_i - \epsilon_j \sim [(k_x - q)(k_x - q^*)(k_x + q)(k_x + q^*)]^{1/2}$. Then if $q(k_y, k_z) \rightarrow 0$ we have $\epsilon_i - \epsilon_j \sim k_x^2$ as in germanium and silicon.

It has been previously noted by Heine^{3,4} that if a crystal is to have surface states, there must exist some eigenvalues for the energy that are real even for complex k_x . Lines in complex k_x space on which the energy is real are called real lines. To see how these are analytically connected to the real k_x axis we write for any point on the real axis,

$$\epsilon(k_x) = \epsilon_0 + \left. \frac{\partial \epsilon}{\partial k_x} \right|_{k_0} (k_x - k_0) + \frac{1}{2} \left. \frac{\partial^2 \epsilon}{\partial k_x^2} \right|_{k_0} (k_x - k_0)^2 + \dots,$$

⁴ V. Heine, Surface Sci. 2, 1 (1964).

where the derivatives are, of course, real. Then for k_x just off the real axis $\epsilon(k_x)$ is real only if $\partial \epsilon / \partial k_x|_0 = 0$ or else the second term would be complex. Furthermore, this condition is sufficient to make $\epsilon(k_x)$ real on a line which crosses the real k_x axis at right angles since $(k_x - k_0)^2$ is real there.

Heine³ has investigated the properties of real lines using only the fact that $\epsilon(k_x)$ is real on the real k_x axis, without using the condition that $\epsilon(\mathbf{k})$ is an eigenvalue of a partial differential equation. Hence all his results can immediately be taken over for the $\epsilon(\mathbf{k})$ of the n -band model, the model being useful in actually determining the position of the real lines. We summarize his results by stating that a real line leaves the real axis at a saddle point of the band structure, is always symmetric about the real axis, and turns back to the real axis after going around one or more branch points. In this way, the maxima of one band are joined across the band gap by a real line to the minima of a higher band. If the energy is real at a branch point, then the real line goes up to the branch point and comes back down along the same path.

A simple example of this occurs if Eq. (12) is satisfied. Then $\partial \epsilon / \partial k_x = 0$ at $k_x = 0$ and a real line is perpendicular to the real k_x axis at $k_x = 0$. But from Eqs. (9) and (12), $\epsilon(k_x)$ will be real on the imaginary axis so the real line stays on the imaginary axis until it reaches a real branch point.

ANALYTIC PROPERTIES OF BLOCH WAVES

We see from Eq. (4) that the analytic properties of the Bloch waves are completely determined by the analytic properties of the A_i which are related to the a_i by a normalization constant.

Now consider the case in which $a_\alpha(\mathbf{k}) \neq 0$ for some \mathbf{k} and α . Since the eigenvalue equation is linear, we can set $a_\alpha(\mathbf{k}) = 1$. [We will find it more convenient to normalize in a different way after Eq. (13).] Equation (5) may then be written

$$\sum_{j \neq \alpha}^n (H_{ij} - \epsilon \delta_{ij}) a_j = - (H_{i\alpha} - \epsilon \delta_{i\alpha})$$

which represents n equations with n unknowns, the latter being the $(n-1)a_i$ ($i = 1, \dots, n; i \neq \alpha$) and $\epsilon(\mathbf{k})$.

We can solve the first $(n-1)$ equations by Cramer's theorem for the a_i in terms of ϵ and the H_{ij} . The n th equation is then used to determine ϵ . The solution by Cramer's rule is

$$a_i = a_i(\mathbf{k}, \epsilon), \quad (13)$$

where we obtain both $a_i^{(r)}$ and $a_i^{(s)}$ by substituting $\epsilon_r(\mathbf{k})$ and $\epsilon_s(\mathbf{k})$, respectively, for ϵ , provided only that $a_\alpha^{(r)}$ and $a_\alpha^{(s)}$ are both not zero at some \mathbf{k} .

Since by Cramer's rule all the a_i for a given ϵ have the same determinant of the coefficients in the denominator, we can multiply them all by this factor so that the resulting $a_i(\mathbf{k})$ are simply polynomials in ϵ

and components of H_{ij} and hence are polynomials in ϵ and components of \mathbf{k} . Thus, $a_i(\mathbf{k}, \epsilon)$ is an analytic function of \mathbf{k} everywhere ϵ is analytic. We recall that the only singularities of $\epsilon(\mathbf{k})$ occur at the branch points in complex k_x space connecting two energy functions. If q is a branch point, then near $k_x = q$

$$\begin{aligned}\epsilon_r(\mathbf{k}) &= \epsilon(q) + c(k_x - q)^{1/2} + \dots, \\ \epsilon_s(\mathbf{k}) &= \epsilon(q) - c(k_x - q)^{1/2} + \dots.\end{aligned}\quad (14)$$

Furthermore, if we treat ϵ as a function of \mathbf{k} in Eq. (6) and differentiate with respect to $\lambda = (k_x - q)^{1/2}$, since the γ_i are polynomials in \mathbf{k} we have

$$\frac{\partial \gamma_i}{\partial \lambda} = 2(k_x - q)^{1/2} \frac{\partial \gamma_i}{\partial k_x},$$

so that we may generate all the derivatives of ϵ at $k_x = q$ except the first. Hence we may write

$$\epsilon(\mathbf{k}) = \sum_{p=0}^{\infty} c_p (k_x - q)^{p/2} \quad (15)$$

which will be valid in the neighborhood of $k_x = q$.

Now since $a_i(\mathbf{k}, \epsilon)$ is a polynomial in \mathbf{k} and ϵ , it can be developed in a power series about any \mathbf{k} and ϵ . In particular, expanding about $k_x = q$ and $\epsilon = \epsilon(q)$

$$\begin{aligned}a_i(\mathbf{k}, \epsilon) &= a_i[q, \epsilon(q)] + \left. \frac{\partial a_i}{\partial \epsilon} \right|_{k_x=q, \epsilon=\epsilon(q)} [\epsilon - \epsilon(q)] + \dots \\ &+ \left. \frac{\partial a_i}{\partial k_x} \right|_{k_x=q, \epsilon=\epsilon(q)} (k_x - q) + \dots\end{aligned}\quad (16)$$

and substituting Eq. (14) we have

$$\begin{aligned}a_i^{(r)}(\mathbf{k}) &= t_i + w_i (k_x - q)^{1/2}, \\ a_i^{(s)}(\mathbf{k}) &= t_i - w_i (k_x - q)^{1/2},\end{aligned}\quad (17)$$

where t_i and w_i are independent of k_x .

To complete the derivation of the analytic structure of $U(\mathbf{r}, \mathbf{k})$ we must obtain the analytic structure of the normalization constant $N(\mathbf{k})$ near $k_x = q$. This can be done by writing $N(\mathbf{k})$ as a manifestly analytic function and then taking the analytic continuation. We note that this cannot be accomplished by simply taking the analytic continuation of the normalization condition

$$\int_{\text{cell}} U_r^*(\mathbf{r}, \mathbf{k}) U_s(\mathbf{r}, \mathbf{k}) d\mathbf{r} = \delta_{rs} \quad (18)$$

because complex conjugation is not an analytic operation. We circumvent this problem by writing

$$U_p(\mathbf{r}, \mathbf{k}) = f_p(\mathbf{r}, \mathbf{k}) + ig_p(\mathbf{r}, \mathbf{k}),$$

where both f and g are real for real \mathbf{k} . Then for real \mathbf{k}

$$U_p^*(\mathbf{r}, \mathbf{k}) = f_p(\mathbf{r}, \mathbf{k}) - ig_p(\mathbf{r}, \mathbf{k}).$$

Let us define, for real \mathbf{k} ,

$$\bar{U}_p(\mathbf{r}, \mathbf{k}) = f_p(\mathbf{r}, \mathbf{k}) - ig_p(\mathbf{r}, \mathbf{k}).$$

Then if U_p is an analytic function of \mathbf{k} , so is $\bar{U}_p(\mathbf{r}, \mathbf{k})$, which, unlike U_p^* , can be analytically continued for complex \mathbf{k} . (But for complex \mathbf{k} , we note that $\bar{U}_p \neq U_p^*$, so that the analytic continuation of the normalization condition will not necessarily lead to U_p being bounded for \mathbf{k} not on the real axis.)

The equation satisfied by the \bar{a}_i is obtained for real \mathbf{k} by taking the complex conjugate of Eq. (5). Using the property that $H_{ij}^* = H_{ji}$ we obtain for real \mathbf{k}

$$\sum_j H_{ji} \bar{a}_j = \epsilon \bar{a}_i$$

which is an analytic equation and can be used to determine \bar{a}_j even for complex \mathbf{k} . Also,

$$\begin{aligned}\bar{U}_p(\mathbf{r}, \mathbf{k}) &= \sum_i \bar{A}_i^{(p)} \bar{U}_i(\mathbf{r}, \mathbf{k}_0), \\ \bar{A}_i &= \bar{a}_i / N^{1/2}.\end{aligned}$$

Similar considerations to those made for the a_i lead to the conclusion that \bar{a}_i may be expanded such that

$$\begin{aligned}\bar{a}_i^{(r)}(\mathbf{k}) &= \bar{t}_i + \bar{w}_i (k_x - q)^{1/2} + \dots, \\ \bar{a}_i^{(s)}(\mathbf{k}) &= \bar{t}_i - \bar{w}_i (k_x - q)^{1/2} + \dots.\end{aligned}\quad (19)$$

We rewrite Eq. (18) for real \mathbf{k} as

$$\int_{\text{cell}} \bar{U}_r(\mathbf{r}, \mathbf{k}) U_s(\mathbf{r}, \mathbf{k}) d\mathbf{r} = \delta_{rs} \quad (20)$$

which can be analytically continued for complex \mathbf{k} . If we express the U and \bar{U} in terms of the \mathbf{k} , ϵ by Eq. (13), then for Eq. (20) to hold, ϵ must be a root of Eq. (6) [i.e., a continuation of the $\epsilon(\mathbf{k})$ for real \mathbf{k}] as in Eqs. (17) and (19). Substituting for U and \bar{U} in Eq. (20) and using the orthonormality of the $U(\mathbf{r}, \mathbf{k}_0)$ yields

$$\sum_i \bar{a}_i^{(r)}(\mathbf{k}) a_i^{(s)}(\mathbf{k}) = 0, \quad r \neq s.$$

Therefore, using Eqs. (17) and (19), we obtain to $O(k_x - q)^{1/2}$ near $k_x = q$,

$$\sum_i \bar{t}_i t_i + (k_x - q)^{1/2} \sum_i (\bar{t}_i w_i - t_i \bar{w}_i) = 0.$$

Hence

$$\begin{aligned}\sum_i \bar{t}_i t_i &= 0, \\ \sum_i (\bar{t}_i w_i - t_i \bar{w}_i) &= 0.\end{aligned}\quad (21)$$

N_p is also analytic, since for real \mathbf{k} , choosing the arbitrary phase to be zero, we have

$$N_p = f_p^2 + g_p^2,$$

which can be analytically continued.

The normalization constant is then given by

$$\begin{aligned}N_s &= \sum_i \bar{a}_i^{(s)} a_i^{(s)} \\ &= \sum_i \bar{t}_i t_i + \sum_i (w_i \bar{t}_i + \bar{w}_i t_i) (k_x - q)^{1/2} + \dots\end{aligned}\quad (22)$$

and hence by Eq. (21)

$$N_s \sim (k_x - q)^{1/2} \tag{23}$$

which gives

$$A_i^{(s)}(\mathbf{k}) = a_i^{(s)}(\mathbf{k}) / N_s^{1/2} \sim (k_x - q)^{-1/4}.$$

Similarly,

$$N_r = \sum_i \bar{t}_i t_i - \sum_i (w_i \bar{t}_i + \bar{w}_i t_i) (k_x - q)^{1/2} + \dots$$

and hence

$$N_r / N_s \rightarrow -1 \quad \text{as } k_x \rightarrow q.$$

Furthermore, it is easy to see that when we go to higher orders in the expansion of $a_i^{(s)}$ as given by Eq. (16) we have terms like $[\epsilon_s - \epsilon_s(q)]^m (k_x - q)^j$. Since $[\epsilon_s - \epsilon_s(q)]$ can be written as a series in powers of $(k_x - q)^{1/2}$, then the series for $a_i^{(s)}$ analogous to Eq. (15) will have terms like $(k_x - q)^{p/2} (k_x - q)^j$. Hence we can break the series into two parts, i.e., even p and odd p , and finally obtain

$$a_i^{(s)}(\mathbf{k}) = V_i^{(s)}(\mathbf{k}) + (k_x - q)^{1/2} W_i^{(s)}(\mathbf{k})$$

or

$$A_i^{(s)}(\mathbf{k}) = a_i^{(s)} / N_s^{1/2} = (k_x - q)^{-1/4} F_i^{(s)}(\mathbf{k}) + (k_x - q)^{1/4} G_i^{(s)}(\mathbf{k}), \tag{24}$$

where both $F_i^{(s)}$ and $G_i^{(s)}$ are analytic functions of k_x in the neighborhood of $k_x = q$.

Equation (24) was previously obtained by Kohn for the one-dimensional system, from the properties of the Schrödinger equation. We see, however, that its validity does not depend on the very special properties of ordinary differential equations, but instead comes directly from the fact that the eigenfunctions corresponding to different eigenvalues are orthogonal.

In concluding this section we point out that Eq. (24) does not violate the finiteness of $a_i^{(s)}$ on the real k_x axis since we have used the condition that q is a branch point of ϵ , which, by Eq. (11), is not true if q is real. In fact, when q is real it is easy to see from Eqs. (11) and (16) that $a_i^{(s)}$ and $N_s^{1/2}$ are series in powers of $(k_x - q)$, which makes $U_s(\mathbf{r}, \mathbf{k})$ finite and nonzero for $k_x = q$.

ANALYTIC PROPERTIES OF THE REPRESENTATION OF x IN THE CRYSTAL MOMENTUM REPRESENTATION

It can be shown^{2,5} that if any function $\phi(\mathbf{r})$ is written in terms of the Bloch functions, i.e.,

$$\phi(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{r}} \sum_n U_n(\mathbf{r}, \mathbf{k}) f_n(\mathbf{k}) \tag{25}$$

then

$$x f_n = i \frac{\partial}{\partial k_x} f_n + \sum_{n'} X_{nn'}(\mathbf{k}) f_{n'}, \tag{26}$$

where

$$X_{nn'}(\mathbf{k}) = \int_{\text{cell}} U_n^*(\mathbf{r}, \mathbf{k}) i \frac{\partial}{\partial k_x} U_{n'}(\mathbf{r}, \mathbf{k}) d\mathbf{r}. \tag{27}$$

⁵ E. N. Adams, J. Chem. Phys. **21**, 1013 (1953).

The behavior of $X_{nn'}(\mathbf{k})$ for complex k_x will be important in problems that involve the representation of the wave function in a region in which it is exponentially decreasing as in tunneling problems.⁶

To find the analytic structure of X_{rs} we first write Eq. (26) as

$$\begin{aligned} X_{rs}(\mathbf{k}) &= i \int_{\text{cell}} \bar{U}_r(\mathbf{r}, \mathbf{k}) \frac{\partial}{\partial k_x} U_s(\mathbf{r}, \mathbf{k}) d\mathbf{r} \\ &= i \sum_i \bar{a}_i^{(r)} N_r^{-1/2} \frac{\partial}{\partial k_x} [a_i^{(s)} N_s^{-1/2}] \\ &= i \sum_i \bar{a}_i^{(r)} N_r^{-1/2} N_s^{-1/2} \frac{\partial}{\partial k_x} a_i^{(s)} \\ &\quad + (i \sum_i \bar{a}_i^{(r)} a_i^{(s)}) N_r^{-1/2} \frac{\partial N_s^{-1/2}}{\partial k_x}. \end{aligned} \tag{28}$$

The second term is zero for $r \neq s$ by orthogonality. Using Eqs. (17) and (19) in the first term we have near $k_x = q$

$$X_{rs} = i N_r^{-1/2} N_s^{-1/2} (-\frac{1}{2}) (k_x - q)^{-1/2} \sum_i \bar{t}_i w_i. \tag{29}$$

But from Eqs. (21) and (22),

$$\sum_i w_i \bar{t}_i + \bar{w}_i t_i = 2 \sum_i \bar{t}_i w_i = N_s / (k_x - q)^{1/2}.$$

Substituting this in Eq. (27) gives

$$X_{rs} = -i \left(\frac{N_s}{N_r} \right)^{1/2} \frac{1}{4(k_x - q)}$$

and using

$$N_r / N_s \rightarrow -1 \quad \text{for } k_x \rightarrow q$$

we obtain

$$X_{rs} = \pm 1 / [4(k_x - q)] \quad \text{for } k_x \rightarrow q \quad r \neq s, \tag{30}$$

which generalizes Keldysh's⁷ one-dimensional result to an arbitrary number of dimensions.

We note that, unlike Blount, we do not find X_{rs} undetermined up to an arbitrary phase factor because in writing (28) we have made use of the condition that for real \mathbf{k}

$$N_r = \bar{N}_r,$$

i.e., the normalization constant is real for real \mathbf{k} .

For the diagonal element we find

$$X_{ss}(\mathbf{k}) = i \int_{\text{cell}} \bar{U}_s(\mathbf{r}, \mathbf{k}) \frac{\partial}{\partial k_x} U_s(\mathbf{r}, \mathbf{k}) d\mathbf{r},$$

which, using

$$(\partial / \partial k_x) \int_{\text{cell}} \bar{U}_s U_s d\mathbf{r} = 0,$$

⁶ E. O. Kane, J. Phys. Chem. Solids, **12**, 181 (1959).

⁷ L. V. Keldysh, Zh. Eksperim. i Teor. Fiz. **33**, 994 (1957) [English transl.: Soviet Phys.—JETP **6**, 763 (1958)].

can be written

$$X_{ss}(\mathbf{k}) = \frac{i}{2} \left[\int_{\text{cell}} \bar{U}_s \frac{\partial U_s}{\partial k_x} d\mathbf{r} - \int_{\text{cell}} U_s \frac{\partial \bar{U}_s}{\partial k_x} d\mathbf{r} \right] \\ = \frac{i}{2} N_s^{-1} \sum_i \left[\bar{a}_i^{(s)} \frac{\partial a_i^{(s)}}{\partial k_x} - a_i^{(s)} \frac{\partial \bar{a}_i^{(s)}}{\partial k_x} \right]. \quad (31)$$

Then using Eqs. (17) and (19) we have near $k_x = q$,

$$X_{ss} = \frac{1}{2} i N_s^{-1} \left[\sum_i (\bar{t}_i w_i - t_i \bar{w}_i) (k_x - q)^{-1/2} + O(k_x - q)^0 \right].$$

But by Eq. (21) the coefficient of $(k_x - q)^{-1/2}$ is zero. Hence

$$X_{ss} \sim N_s^{-1} \sim (k_x - q)^{-1/2} \quad (32)$$

for k_x near q . Furthermore, if for all i , $a_i^{(s)}(\mathbf{k})$ is real for real \mathbf{k} , then from Eq. (31), $X_{ss}(\mathbf{k}) = 0$ for real \mathbf{k} and hence is zero for the analytic continuation. This will be the case if the basis functions $U_j(\mathbf{r}, \mathbf{k}_0)$ can be chosen so that all H_{ij} are real. We also note that if we let $N_s^{-1/2} \rightarrow (N_s')^{-1/2} = N_s^{-1/2} \exp i \int_0^{k_x} X_{ss}(k_x') dk_x'$, then $X_{ss}' = 0$. Hence X_{ss} can always be made to vanish by choosing the arbitrary phase conveniently.

The representation of higher powers of x can be accomplished by repeated use of Eqs. (25), (26), and (30). For example, if we define

$$x^2 \phi(\mathbf{r}) = x \phi^{(1)}(\mathbf{r})$$

then

$$x f_n^{(1)} = i \frac{\partial}{\partial k_x} f_n^{(1)} + \sum_{n'} X_{nn'} f_{n'}^{(1)}, \quad (33)$$

but

$$f_{n'}^{(1)} = x f_{n'} = i \frac{\partial}{\partial k_x} f_{n'} + \sum_{n''} X_{n'n''} f_{n''}. \quad (34)$$

Then substituting Eq. (34) into Eq. (33) gives $x^2 f_n$ in terms of the $X_{nn'}$ and $\partial X_{nn'}/\partial k_x$ whose analytic structure is known. Similarly, we can investigate the singularities of the representations of x^p by this method.

CONNECTION WITH WANNIER FUNCTIONS

It is easily seen² that

$$a_n(\mathbf{r}) \sim \exp[-|\text{Im}q x|]$$

for large x where $a_n(\mathbf{r})$ is the Wannier function. This is a generalization of a result of Kohn.

In the one-dimensional case, this leads to the Wannier functions being localized in a few cells. However, in more than one dimension there is nothing to prevent the singularities from approaching the real k_x axis and

thus in these cases the Wannier functions are not well localized as one generally assumes. In such cases, the assumption that potentials and envelope wave functions vary little over one cell is not sufficient to justify the usual derivations in the Wannier representation.

CONCLUSION

The original motivation of this work was to obtain the analytic properties of Bloch waves and other related quantities by diagonalizing a finite block of the original Hamiltonian and then letting the dimensions of the finite block become infinite. In this way we hoped to find the difference between the properties of a finite-band approximation and the complete Hamiltonian. We have found, however, that none of our results depend on letting the dimensions of our finite block become infinite, so that our conclusions concerning the general properties of $\epsilon(\mathbf{k})$ and the analytic properties of wave functions and matrix elements near branch points are valid in either case. Furthermore, we have derived certain results in general, i.e., Eqs. (24) and (30), which had previously been obtained only for the one-dimensional case by methods not capable of being generalized to n dimensions.

Finally, we note two limitations of the n -band model. First of all, the model does not give rise to the result that in one dimension two bands cannot overlap, which readily follows from the Schrödinger equation. Second, the model cannot yield the fact that the energy is periodic in \mathbf{k} space because $\epsilon(\mathbf{k})$ is the solution of an algebraic equation rather than a transcendental equation. The first difficulty is unimportant for real crystals. The second is irrelevant because we usually restrict ourselves to the first Brillouin zone which is finite in every direction, and within this zone we can approximate the energy as closely as we want by including more bands in the model. This problem is intimately related to the fact that although the general theorems we have proved do not change as we add more bands, the positions of the branch points do change—the more bands we include, the more accurately the model gives q in terms of the interband matrix elements H_{ij} . In general, the interband matrix elements will not be known but rather will be deduced by diagonalizing the finite-band model and determining these parameters by measurements pertaining to real \mathbf{k} . The q are then determined by these parameters and the analytic form of $\epsilon(\mathbf{k})$. Hence in practice it would not be necessary to include more than just a few bands to find the branch points of interest.