PHYSICAL REVIEW VOLUME 115, NUMBER 4 AUGUST 15, 1959

Analytic Properties of Bloch Waves and Wannier Functions*

W. KOHN
Department of Physics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania
(Received March 16, 1959)

The one-dimensional Schrödinger equation with a periodic and symmetric potential is considered, under the assumption that the energy bands do not intersect. The Bloch waves, $\varphi_{n,k}$, and energy bands, $E_{n,k}$, are studied as functions of the *complex* variable, k. In the complex plane, they are branches of multivalued analytic and periodic functions, φ_k, and E_k, with branch points, k', off the real axis. A simple procedure is described for locating the branch points. Application is made to the power series and Fourier series developments of these functions. The analyticity and periodicity of $\varphi_{n,k}$ has some consequences for the form of the Wannier functions. In particular, it is shown that for each band there exists one and only one Wannier function which is real, symmetric or antisymmetric under an appropriate reflection, and falling off exponentially with distance. The rate of falloff is determined by the distance of the branch points k' from the real axis.

INTRODUCTION

1

THE motion of an electron in a crystal lattice is governed by a Schrödinger equation with a periodic potential. In one dimension we may write it as

$$[-d^2/dx^2+V(x)]\psi(x)=E\psi(x), \tag{1.1}$$

where

$$V(x+b)=V(x). \tag{1.2}$$

In the present paper, we assume further that $V(x)$ is symmetric,

$$V(-x)=V(x). \tag{1.3}$$

The nature of the solutions of (1.1) for real values of E has been described in a definitive paper by Kramers.[1] For certain so-called allowed ranges of E, (1.1) has solutions of the form

$$\varphi_{n,k}(x)=u_{n,k}(x)e^{ikx}, \quad n=0, 1, 2, \cdots \tag{1.4}$$

where $u_{n,k}(x)$ has the same periodicity as $V(x)$ and k is real. These are the well-known Bloch waves. The corresponding eigenvalues of (1.1) are the so-called energy bands,

$$E=E_{n,k}, \quad n=0, 1, 2, \cdots. \tag{1.5}$$

The allowed ranges of E are separated by forbidden ranges in which the solutions of (1.1) have the form (1.4), but with k purely imaginary. These solutions are seen therefore to have an exponential behavior. The present paper is restricted to cases in which all allowed bands are separated by forbidden bands of *finite* width.[2]

In some connections, the question of the behavior of $\varphi_{n,k}$ and $E_{n,k}$, regarded as functions of the *complex* variable

$$k=g+ih, \tag{1.6}$$

arises. Examples of such cases are the expansion of $E_{n,k}$ and $\varphi_{n,k}$ in powers of k,[3] and the theory of the motion of Bloch electrons in a magnetic field.[4]

The properties of $E_{n,k}$ and $\varphi_{n,k}$, regarded as analytic functions of k, are discussed in Secs. 3 and 4 of the present paper. One finds that the usual energy bands, $E_{n,g}$, are the traces on the $g-\mathrm{Re}(E)$ plane of a multivalued analytic function, E_k. The latter can be represented on a Riemann surface with an infinite sequence of sheets, S_n. Each sheet, S_n, is connected to S_{n-1} and S_{n+1} at a series of branch points of order 1[5] which lie off the real axis. Thus by going into the complex k-plane, one can pass continuously from one energy band to another. (See Fig. 4.) A similar, but slightly more complex, situation is found in the case of $\varphi_{n,k}$. One useful result is that the phase of $\varphi_{n,g}$ can be so chosen that it is a periodic function of g, with period $2\pi/b$ and, if continued into the complex k-plane, is analytic in a strip of finite width $2\bar{h}_n$, enclosing the real axis.

The analytic properties of $\varphi_{n,k}$ have some interesting consequencies concerning the properties of the Wannier function

$$a_n(x)\equiv\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\varphi_{n,g}(x)dg. \tag{1.7}$$

These are discussed in detail in Secs. 5–9. Here we mention only the following results. For each energy band, n, there exists one and only one Wannier function with all of the following properties: 1. It is real. 2. It is symmetric or antisymmetric about either $x=0$ or $x=b/2$. 3. It falls off exponentially as

$$a_n(x)\sim\exp(-\bar{h}_nx), \tag{1.8}$$

where $\bar{h}_n$ is the half-width of the strip of analyticity of $\varphi_{n,k}$. The magnitude of $\bar{h}_n$ is determined by a simple procedure. No other choice of phase leads to an exponential decrease more rapid than (1.8). On the other

* A preliminary note was published by W. Kohn and S. Michaelson, Proc. Phys. Soc. (London) **72**, 301 (1958).
[1] H. A. Kramers, Physica **2**, 483 (1935).
[2] The limiting case of completely free electrons is thereby excluded.
[3] J. Bardeen, J. Chem. Phys. **6**, 1367 (1938).
[4] W. Kohn, Proc. Phys. Soc. (London) **72**, 1147 (1958).
[5] The order of a branch point is defined as $\nu-1$, where ν is the number of different values the function can assume in its vicinity. Thus near a branch point of order 1 the function is double-valued.

hand, many choices of phase lead to a less rapid decrease.

While the results of this paper are obtained under fairly restrictive conditions, such as the symmetry of $V(x)$ and no intersection of energy bands, it is clear that some of them will continue to hold when one or the other of these conditions is relaxed. Many of our results may also be expected to carry over to the case of three dimensions.

I. BLOCH WAVES AND ENERGY BANDS

2. Preliminaries

We consider the Schrödinger equation

$$-d^2\psi/dx^2+V(x)\psi=E\psi, \tag{2.1}$$

where $V(x)$ is periodic with period b, symmetric about $x=0$, and sectionally continuous. We denote by $\psi_1(x,E)$ and $\psi_2(x,E)$ the two independent solutions of (2.1) which are defined by the initial conditions

$$\psi_1(0,E)=1, \quad \psi_1'(0,E)=0, \tag{2.2}$$

$$\psi_2(0,E)=0, \quad \psi_2'(0,E)=1. \tag{2.3}$$

It is then well known[6] that $\psi_1(x,E)$ and $\psi_2(x,E)$ are entire functions of the complex variable E, for all x.

We look for solutions of (2.1) which are multiplied by a constant factor λ when x is replaced by $x+b$, $\psi(x+b)=\lambda\psi(x)$. This is equivalent to requiring that

$$\psi(b)=\lambda\psi(0), \tag{2.5}$$

$$\psi'(b)=\lambda\psi'(0). \tag{2.6}$$

We can write

$$\psi=\alpha\psi_1+\beta\psi_2, \tag{2.7}$$

substitute into (2.5) and (2.6), and eliminate α and β. This gives the well-known result[1]

$$\lambda^2-2\mu(E)\lambda+1=0, \tag{2.8}$$

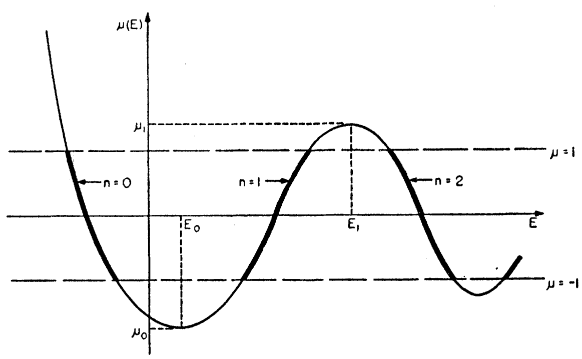

FIG. 1. Schematic plot of the function $\mu(E)$. The allowed energy ranges $n=0, 1, 2, \cdots$ correspond to $|\mu|\leqslant 1$ and are separated by forbidden ranges with $|\mu|>1$.

where

$$\mu(E)\equiv\tfrac{1}{2}[\psi_1(b,E)+\psi_2'(b,E)]. \tag{2.9}$$

In our case of a symmetric potential we can also, instead of (2.7), take $\psi_1(x)$ and $\psi_1(b-x)$ as fundamental system, which gives again a result of the form (2.8) with

$$\mu(E)=\psi_1(b,E).^7 \tag{2.10}$$

This expression is a little simpler to use than (2.9). We see that $\mu(E)$ *is an entire function of* E.

We can write λ in the form

$$\lambda=e^{ikb}, \tag{2.11}$$

where, by (2.8), k is determined as a function of E by the equation

$$\cos kb=\mu(E). \tag{2.12}$$

If k is real, it is called the wave number, and the corresponding function ψ is a Bloch wave of the form (1.4).

The properties of $\mu(E)$, considered as a function of the real variable E, have been established by Kramers.[1] For the case where no two allowed energy bands intersect, a schematic plot is shown in Fig. 1. The following properties are relevant for our purposes

$$\lim_{E\to-\infty}\mu(E)=+\infty\,; \tag{2.13}$$

$$\lim_{E\to+\infty}[\mu(E)-\cos(E^{\frac{1}{2}}b)]=0; \tag{2.14}$$

$$d\mu/dE=0 \quad \text{at} \quad E=E_n, \quad n=0,1,2,\cdots \tag{2.15}$$

where, if no two allowed energy regions touch—the case considered here—

$$\mu_{2m}\equiv\mu(E_{2m})<-1, \tag{2.16}$$

$$\mu_{2m+1}\equiv\mu(E_{2m+1})>+1, \tag{2.17}$$

and

$$\lim_{n\to\infty}\left[E_n-\left(\frac{(n+1)\pi}{b}\right)^2\right]=0. \tag{2.18}$$

The zeros E_n of $d\mu/dE$ are simple.

We shall now show that the real zeros E_n of the entire function $(d\mu/dE)$ are its only zeros. We begin by writing

$$E=\kappa^2, \tag{2.19}$$

and

$$\kappa=\sigma+i\tau, \tag{2.20}$$

and look for the zeros of

$$d\mu/d\kappa=2\kappa(d\mu/dE). \tag{2.21}$$

Now as E or $\kappa\to\infty$, it can be shown[6] that

$$\psi_1(b,E)=\cos\kappa b+O(e^{|\tau|b}/|\kappa|), \tag{2.22}$$

[6] See, for example, E. C. Titschmarch, *Eiquenfunction Expansions Associated with Second Order Differential Equations* (The Clarendon Press, Oxford, 1946), Chap. 1.

[7] I am indebted to Mr. L. Glasser for bringing this result to my attention. See also, E. Kamke, *Differentialgleichungen* (Akademische Verlagsgesellschaft, Leipzig, 1943), Vol. I, Art. 2.22.

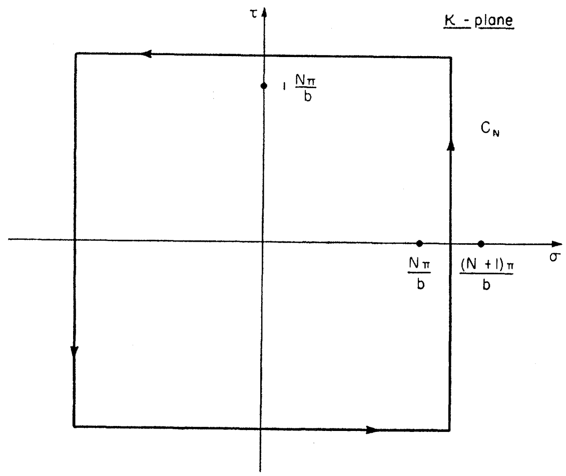

FIG. 2. Contour used to establish the reality of the roots of $d\mu/dE$.

and similarly

$$\partial\psi_1(b,E)/\partial\kappa = -b\sin\kappa b + O(e^{|\tau|b}/|\kappa|). \quad (2.23)$$

These equations are simply a quantitative expression of the fact that for large E (real or complex), $\psi_1(x,E) \sim \cos(E^{\frac{1}{2}}x)$. Because of Eq. (2.10), Eq. (2.23) implies that for large κ

$$d\mu/d\kappa = -b\sin\kappa b + O(e^{|\tau|b}/|\kappa|). \quad (2.24)$$

For perfectly free electrons we have, of course,

$$d\mu^{(0)}/d\kappa = -b\sin\kappa b. \quad (2.25)$$

We now define the function

$$F(\kappa) \equiv \frac{d\mu/d\kappa}{d\mu^{(0)}/d\kappa} = \frac{d\mu/d\kappa}{-b\sin\kappa b}. \quad (2.26)$$

This is a single-valued analytic function of κ with zeros at the zeros of $d\mu/d\kappa$ and poles at the zeros of $\sin\kappa b$, i.e., at

$$\kappa = j\pi/b, \quad j=0, \pm 1, \cdots. \quad (2.27)$$

Now consider $F(\kappa)$ on the square contour C_N of side $(N+\frac{1}{2})\pi/b$ shown in Fig. 2. As $N\to\infty$, κ on C_N approaches ∞. Furthermore, the contours C_N avoid the zeros (2.27) of the denominator of $F(\kappa)$. Hence, in view of (2.24) one sees easily that as $N\to\infty$, $F(\kappa)\to 1$ for all points on C_N. It follows that for sufficiently large N,

$$\oint_{C_N}\left[\frac{d}{d\kappa}\ln F(\kappa)\right]d\kappa = 0, \quad N \geqslant N_0. \quad (2.28)$$

Now by a well-known theorem of analysis

$$\frac{1}{2\pi i}\oint_{C_N}\left[\frac{d}{d\kappa}\ln F(\kappa)\right]d\kappa = Z_N - P_N, \quad (2.29)$$

where Z_N and P_N are the number of zeros and poles, respectively, of $F(\kappa)$ inside C_N. Further we know from (2.26) and (2.27) that $P_N = 2N+1$. Hence

$$Z_N = 2N+1, \quad N \geqslant N_0. \quad (2.30)$$

But in view of (2.18) and (2.21), the real zeros of $d\mu/dE$ and the zero contributed by the factor κ in (2.21) total exactly $2N+1$. Hence, $d\mu/dE$ can have no other zeros.

3. The Energy Function

The connection between E and k (real or complex) is given by Eq. (2.12),

$$\cos kb = \mu(E), \quad (3.1)$$

where the function $\mu(E)$ is defined by Eq. (2.9) or (2.10) and is a single valued, entire function of E. Equation (3.1) shows at once that

$$E_k = E_{-k}, \quad (3.2)$$

and

$$E_{k+2\pi/b} = E_k. \quad (3.3)$$

Further, since $\mu(E)$ is real for real E, we have

$$\mu(E^*) = [\mu(E)]^*. \quad (3.4)$$

Hence, on taking the complex conjugate of (3.1), one finds

$$E_{k^*} = (E_k)^*. \quad (3.5)$$

To obtain further insight into the analytic structure of E_k, let us for a moment consider the function $E(\mu)$, the inverse of the entire function $\mu(E)$. $E(\mu)$ is an analytic function of μ except where $d\mu/dE=0$. In the vicinity of such a point, we have

$$\mu = \mu_n + \alpha_n(E-E_n)^2 + \cdots, \quad (3.6)$$

where α_n does not vanish. Hence

$$E = E_n + \frac{1}{\alpha_n^{\frac{1}{2}}}(\mu-\mu_n)^{\frac{1}{2}}. \quad (3.7)$$

Thus each extremum μ_n of the $\mu(E)$-plot in Fig. 1 represents a branch point of order 1[5] of the function $E(\mu)$ (see Fig. 3). Since $d\mu/dE$ has no other zeros, these are the only singularities of $E(\mu)$ in the finite μ-plane. If we start on the real μ axis at $\mu=+\infty$, with a real value of E, proceed to the left to μ_0, around μ_0 to μ_1, around μ_1 to μ_2, etc., as indicated on Fig. 3, we trace

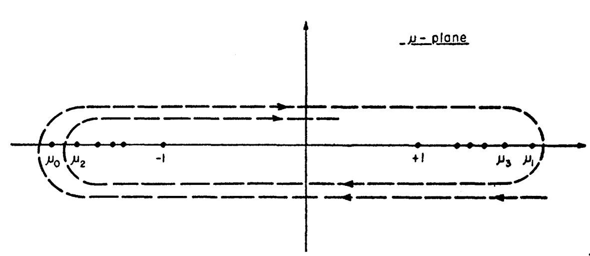

FIG. 3. The singularities of the function $E(\mu)$.

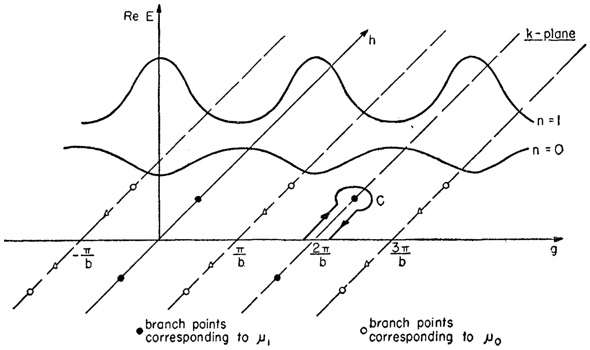

FIG. 4. Schematic representation of the k-plane ($k=g+ih$), the energy bands E_{ng}, and the branch points of E_k.

out the curve $\mu(E)$ of Fig. 1. It is clear that $E(\mu)$ can be represented on a Riemann surface with sheets $\bar{S}_n$ corresponding to the different bands n. $\bar{S}_0$ is connected to $\bar{S}_1$ by the branch point at μ_0, $\bar{S}_1$ to $\bar{S}_2$ by the branch point at μ_1, etc. The values of $E(\mu)$ on $\bar{S}_n$ for real μ between -1 and $+1$ correspond to the allowed energy band n of Fig. 1.

Now let us return to the properties of E as a function of k, as defined by (3.1). Since

$$dE/dk=(dE/d\mu)(-b\sin kb), \tag{3.8}$$

we see that E is an analytic function of k except at those points for which $(d\mu/dE)$ vanishes, i.e., where

$$\cos k_n b=\mu_n. \tag{3.9}$$

Of course, for a given μ_n, (3.9) has many solutions. Since for even n, $\mu_n<-1$, and for odd n, $\mu_n>+1$, the k_n which solve (3.9) have the form

$$k_{2m}=\pm[(2j+1)\pi/b+ih_{2m}],\quad j=0,\pm1,\cdots \tag{3.10}$$

$$k_{2m+1}=\pm(2j\pi/b+ih_{2m+1}),\quad j=0,\pm1,\cdots \tag{3.11}$$

where

$$h_n=|\cosh^{-1}|\mu_n||. \tag{3.12}$$

From (3.7) and (3.1), we see that near one of the k_n

$$E=E_n+\beta_n(k-k_n)^{\frac{1}{2}}, \tag{3.13}$$

where β_n does not vanish. Hence, the k_n are also branch points of order 1. We see from (3.9) and (3.12) that the position of these branch points can be directly read off the "Kramers plot" in Fig. 1. In particular, since $\lim_{n\to\infty}|\mu_n|=1$, we see from (3.12) that

$$\lim_{n\to\infty} h_n=0, \tag{3.14}$$

so that for very high-lying bands the branch points lie very close to the real k-axis. Figure 4 shows a schematic diagram of the k-plane, the energy bands $E_{n,g}$ and the branch points of E_k.

Clearly, the function E_k may be represented on a Riemann surface with an infinite sequence of sheets S_n, in such a way that the energy bands, $E_{n,g}$, are the values of E_k for real k on the sheet S_n. Each sheet S_n is connected to S_{n+1} by the infinite sequence of the branch points k_n given by (3.10) and (3.11). Thus, if one starts at a real value of k on the energy band n, passes around one of the branch points k_n, and returns to the real axis, one is then on the band $n+1$ (see path C in Fig. 4, which would take one from $n=1$ to $n=2$). Similarly, by passing around one of the points k_{n-1} one arrives on band $n-1$. By drawing branch lines from each k_n to $\pm i\infty$ (away from the real axis; see Fig. 4), the Riemann surface is divided into elements on each of which E_k is periodic with period $2\pi/b$ and single valued.

It is useful to represent E as a function of yet another variable, namely, λ, Eq. (2.11). By (2.8) we have

$$\mu=\frac{1}{2}\left(\lambda+\frac{1}{\lambda}\right). \tag{3.15}$$

We write

$$E=E(\mu)=E(\tfrac{1}{2}(\lambda+1/\lambda))\equiv\mathcal{E}(\lambda), \tag{3.16}$$

defining the function $\mathcal{E}(\lambda)$. As

$$\frac{d\mathcal{E}(\lambda)}{d\lambda}=\frac{dE(\mu)}{d\mu}\frac{1}{2}\left(1-\frac{1}{\lambda^2}\right), \tag{3.17}$$

we see that $\mathcal{E}(\lambda)$ is an analytic function of λ except at $\lambda=0$ and ∞, and at those points $\lambda_n^{\pm}$ where $dE/d\mu$ is infinite. In view of (2.8), they are given by

$$\lambda_n^{\pm}=\mu_n[1\pm(1-\mu_n^{-2})^{\frac{1}{2}}],\quad n=0,1,2,\cdots \tag{3.18}$$

where we take the square root to be positive. Figure 5 shows the positions of the singularities in the λ-plane. (The unit circle corresponds to real values of k.) The points $\lambda_n^{\pm}$ are again branch points of order 1,[5] and $\mathcal{E}(\lambda)$ can be represented on a Riemann surface with one sheet corresponding to each band. This surface may be divided into elements on which $\mathcal{E}(\lambda)$ is single-valued by drawing on the nth sheet branch lines joining λ_{n-1}^{-} and λ_n^{-} to the origin, and λ_{n-1}^{+} and λ_n^{+} to $\pm\infty$ away from the origin. The function $\mathcal{E}_n(\lambda)$, corresponding to the nth sheet has a Laurent expansion

$$\mathcal{E}_n(\lambda)=\sum_{l=-\infty}^{\infty} a_{n;l}\lambda^l, \tag{3.19}$$

whose coefficients are clearly real. Its region of convergence is

$$1/\bar{\lambda}_n<|\lambda|<\bar{\lambda}_n, \tag{3.20}$$

where

$$\begin{aligned}\bar{\lambda}_n&\equiv\min[|\lambda_n^{+}|,|\lambda_{n-1}^{+}|]\\&=\min[|\mu_n|+(\mu_n^2-1)^{\frac{1}{2}},\ |\mu_{n-1}|+(\mu_{n-1}^2-1)^{\frac{1}{2}}].\end{aligned} \tag{3.21}$$

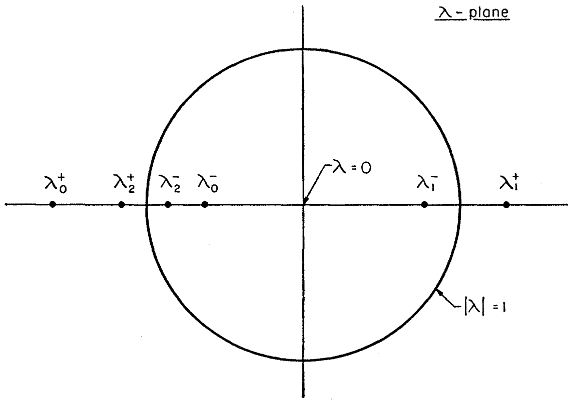

FIG. 5. Singularities of $\mathcal{E}(\lambda)$. The unit circle corresponds to real values of k.

In terms of the quantity

$$\bar{h}_n \equiv \min(h_n, h_{n-1}) \tag{3.22}$$

[see Eqs. (3.10) and (3.11)], we can also write

$$\exp(-b\bar{h}_n) < |\lambda| < \exp(-b\bar{h}_n). \tag{3.20'}$$

Finally, we see from Eq. (3.16) that $\mathcal{E}_n(\lambda) = \mathcal{E}_n(\lambda^{-1})$ so that (3.19) simplifies to

$$\mathcal{E}_n(\lambda) = a_{n;l} + \sum_{l=1}^{\infty} a_{n;l}\left(\lambda^l + \frac{1}{\lambda^l}\right). \tag{3.23}$$

Let us now mention some applications of our results.

Power Series Expansion of $E_{n,g}$

From what has been said about the function E_k, it is clear that the expansion of $E_{n,g}$ will converge for

$$|g| < r_n, \tag{3.24}$$

where

$$\begin{aligned} r_0 &= [(\pi/b)^2 + h_0^2]^{\frac{1}{2}}, \\ r_{2m} &= \min([(\pi/b)^2 + h_{2m}^2]^{\frac{1}{2}}, h_{2m-1}), \\ &\qquad m = 1, 2, \cdots \\ r_{2m+1} &= \min(h_{2m+1}, [(\pi/b)^2 + h_{2m}]^{\frac{1}{2}}), \\ &\qquad m = 0, 1, 2, \cdots. \end{aligned} \tag{3.25}$$

The h_n may be obtained from the "Kramers plot" of Fig. 1, by means of Eq. (3.12). In particular, for $n = 0$, the expansion converges over the entire first Brillouin zone, $|g| \leqslant \pi/b$.

For nearly free electrons ($V \to 0$), $h_n \to 0$ and, hence, the radius of convergence $r_n \to 0$ for all bands except the lowest. On the other hand, in the tight-binding limit ($b \to \infty$), it can be shown (see Appendix) that

$$\lim_{b\to\infty} h_n = (-\epsilon_n)^{\frac{1}{2}}, \tag{3.26}$$

where ϵ_n is the eigenvalue of the atomic wave function corresponding to band n. Hence

$$\lim_{b\to\infty} \frac{h_n}{(\pi/b)} = \infty, \tag{3.27}$$

so that for large enough b, the power series of $E_{n,g}$ for arbitrary n certainly converge over the entire first Brillouin zone.

Fourier Expansion of $E_{n,g}$

We have seen that the energy can be expressed as a Laurent expansion in λ [Eq. (3.23)]. Writing $\lambda = \exp(igb)$ gives the Fourier series

$$E_{n,g} = a_{n;l} + 2\sum_{l=1}^{\infty} a_{n;l} \cos(lgb). \tag{3.28}$$

Now from the region of convergence (3.22) of the Laurent expansion (3.23) we conclude that

$$\lim_{l\to\infty} a_{n;l}\lambda^l = \begin{cases} 0 & \text{if } |\lambda| < \bar{\lambda}_n \\ \infty & \text{if } |\lambda| > \bar{\lambda}_n, \end{cases} \tag{3.29}$$

where $\bar{\lambda}_n$, Eq. (3.21), can be directly obtained from the "Kramers plot," Fig. 1. Again, one finds good convergence in the tight-binding limit, poor convergence for nearly free electrons.

4. Bloch Functions

The term Bloch functions is usually applied to solutions of the Schrödinger equation (1.1) (with real E), which have the form (1.4) (with real $k = g$), and are normalized in the sense

$$(2\pi/b)\int_0^b |\varphi_{n,g}(x)|^2 dx = 1. \tag{4.1}$$

In the present context, we shall apply the term to the more general class of functions ψ, which have the following properties: They are solutions of (1.1) with complex E; they are quasi-periodic, in the sense that

$$\psi(b) = \lambda\psi(0); \quad \psi'(b) = \lambda\psi'(0); \tag{4.2}$$

and they are normalized in a manner which, for $|\lambda| = 1$ reduces to

$$(2\pi/b)\int_0^b |\psi(x)|^2 dx = 1, \quad |\lambda| = 1. \tag{4.3}$$

For $|\lambda| = 1$ (i.e., $\lambda = e^{igb}$), these functions are just the ordinary Bloch functions.

Now let E be given and let us look for a solution of (1.1) which satisfies the quasi-periodic condition (4.2). Such a solution can be written as

$$\psi(x) = \alpha\psi_1(x) + \beta\psi_2(x). \tag{4.4}$$

Substitution into (4.2) gives the quadratic equation (2.8) for λ, and the ratio

$$\frac{\alpha}{\beta}=\frac{\psi_2(b)}{\lambda-\psi_1(b)}=\frac{\psi_2(b)}{\frac{1}{2}(\lambda-1/\lambda)}. \tag{4.5}$$

Hence, we may write

$$\psi(x)=\frac{1}{N^{\frac{1}{2}}}\left[\psi_2(b)\psi_1(x)+\frac{1}{2}\left(\lambda-\frac{1}{\lambda}\right)\psi_2(x)\right]$$
$$=\frac{1}{N^{\frac{1}{2}}}\chi(x), \tag{4.6}$$

thus defining the function $\chi(x)$. The normalization $N^{-\frac{1}{2}}$ has to be chosen in accordance with the requirement (4.3). One's first inclination would be to set N equal to

$$\left(\frac{2\pi}{b}\right)\int_0^b\left|\psi_2(b)\psi_1(x)+\frac{1}{2}\left(\lambda-\frac{1}{\lambda}\right)\psi_2(x)\right|^2dx. \tag{4.7}$$

However, this is not an analytic function of E. Instead, we choose

$$N=\frac{2\pi}{b}\int_0^b\left[\psi_2(b)\psi_1(x)+\frac{1}{2}\left(\lambda-\frac{1}{\lambda}\right)\psi_2(x)\right]$$
$$\times\left[\psi_2(b)\psi_1(x)+\frac{1}{2}\left(\frac{1}{\lambda}-\lambda\right)\psi_2(x)\right]dx, \tag{4.8}$$

which reduces to (4.7) for $|\lambda|=1$ and hence satisfies (4.3), and furthermore is an analytic function of E.

This expression for N can be considerably simplified. For this purpose we define

$$\chi(x,E)\equiv\psi_2(b,E)\psi_1(x,E)+\frac{1}{2}\left(\lambda(E)-\frac{1}{\lambda(E)}\right)\psi_2(x,E), \tag{4.9}$$

$$\tilde{\chi}(x,E)\equiv\psi_2(b,E)\psi_1(x,E)+\frac{1}{2}\left(\frac{1}{\lambda(E)}-\lambda(E)\right)\psi_2(x,E). \tag{4.10}$$

Here $\lambda(E)$ is one of the roots of Eq. (2.8). Clearly,

$$N=(2\pi/b)\int_0^b\chi(x,E)\tilde{\chi}(x,E)dx. \tag{4.11}$$

We now take the equations

$$\begin{gathered}[-d^2/dx^2+V-E]\chi(x,E)=0,\\ [-d^2/dx^2+V-E-\delta E]\tilde{\chi}(x,E+\delta E)=0,\end{gathered} \tag{4.13}$$

multiply the first by $\tilde{\chi}(x, E+\delta E)$, the second by $\chi(x,E)$, subtract and integrate from 0 to b. This gives

$$\begin{aligned}\delta E\int_0^b dx\,\chi(x,E)\tilde{\chi}(x,E+\delta E)&=\left[\tilde{\chi}(x,E+\delta E)\frac{\partial}{\partial x}\chi(x,E)-\chi(x,E)\frac{\partial}{\partial x}\tilde{\chi}(x,E+\delta E)\right]_0^b\\ &=\psi_2(b,E+\delta E)\frac{1}{2}\left(\lambda(E)-\frac{1}{\lambda(E)}\right)\left(\frac{\lambda(E)}{\lambda(E+\delta E)}-1\right)\\ &\quad-\psi_2(b,E)\frac{1}{2}\left(\frac{1}{\lambda(E+\delta E)}-\lambda(E+\delta E)\right)\\ &\quad\times\left(\frac{\lambda(E)}{\lambda(E+\delta E)}-1\right),\end{aligned} \tag{4.14}$$

where in the last step we have used the "periodicity" properties of χ and $\tilde{\chi}$. We now divide by δE and let $\delta E\rightarrow 0$. This gives

$$N=\frac{2\pi}{b}\psi_2(b,E)\left(\frac{1}{\lambda(E)^2}-1\right)\frac{d\lambda(E)}{dE}. \tag{4.15}$$

Finally, noting that

$$\frac{d\mu}{dE}=\frac{d}{dE}\left[\frac{1}{2}\left(\lambda+\frac{1}{\lambda}\right)\right]=\frac{1}{2}\left(1-\frac{1}{\lambda^2}\right)\frac{d\lambda}{dE}, \tag{4.16}$$

we obtain

$$N=-\frac{4\pi}{b}\psi_2(b,E)\frac{d\mu}{dE}, \tag{4.17}$$

and hence (4.6) becomes

$$\psi(x)=\chi(x)\bigg/\left[-\frac{4\pi}{b}\psi_2(b)\frac{d\mu}{dE}\right]^{\frac{1}{2}}, \tag{4.18}$$

where $\chi(x)$ is defined by Eq. (4.9). For $\lambda=e^{iqb}$, this function reduces to a familiar normalized Bloch wave whose phase is such that

$$\mathrm{Im}\psi(0)=0,\quad \lambda=e^{iqb}. \tag{4.19}$$

Bloch Waves Regarded as Analytic Functions of λ

We now wish to study the analytic behavior of $\psi(x)$ as a function of λ, from which the functional dependence on k is then easily deduced. Since E is a function of λ, we may regard ψ_1, ψ_2, and ψ as functions of λ.

$$\begin{gathered}\psi_1(x)\rightarrow\psi_1(x,\lambda);\quad \psi_2(x)\rightarrow\psi_2(x,\lambda);\\ \psi(x)\rightarrow\psi(x,\lambda).\end{gathered} \tag{4.20}$$

The possible singularities of $\psi(x,\lambda)$ are the points $\lambda_n{}^{\pm}$, where $d\mu/dE=0$ and $\mathcal{E}(\lambda)$ is singular, as well as the points where

$$\psi_2(b,\lambda)=0, \tag{4.21}$$

which makes N vanish.

We begin by showing that at the latter points $\psi(x,\lambda)$ is, in fact, regular. First we note that (4.21) can occur only for real E. For

$$E=\frac{\displaystyle\int_0^b \psi_2^*(x,\lambda)\left(-\frac{d^2}{dx^2}\right)\psi_2(x,\lambda)dx+\int_0^b V(x)|\psi_2(x,\lambda)|^2dx}{\displaystyle\int_0^b |\psi_2(x,\lambda)|^2dx}$$

$$=\frac{\displaystyle\int_0^b \left|\frac{\partial\psi(x,\lambda)}{\partial x}\right|^2 dx+\int_0^b V(x)|\psi_2(x,\lambda)|^2dx}{\displaystyle\int_0^b |\psi_2(x,\lambda)|^2dx}, \tag{4.23}$$

where (4.21) was used in the last integration by parts. Now since E is real, so is $\psi_2(x,\lambda)$. Further, in view of the symmetry of the potential [and of Eq. (4.21)], we must have

$$\psi_2(b-x,\ \lambda)=\pm\psi_2(x,\lambda). \tag{4.24}$$

Now differentiate this equation with respect to x and set $x=0$. This gives

$$-\psi_2'(b,\lambda)=\pm\psi_2'(0,\lambda)=\pm1. \tag{4.25}$$

Since also

$$-\psi_2(b,\lambda)=\pm\psi_2(0,\lambda)=0,$$

we see that $\psi_2(x,\lambda)$ is a periodic solution with $\lambda=\pm1$. Hence we have the preliminary conclusion that (4.21) can occur only at $\lambda=\pm1$.

Let us take $\lambda=+1$, and study $\psi_2(b,\lambda)$ in the vicinity of $\lambda=1$. We write

$$\frac{d\psi_2(b,\lambda)}{d\lambda}=\frac{\partial\psi_2(b)}{\partial E}\frac{dE}{d\mu}\frac{d\mu}{d\lambda}. \tag{4.26}$$

Now by differentiating the Schrödinger equation satisfied by $\psi_2(x)$ with respect to E, it is easily shown that at $\lambda=1$,

$$\partial\psi_2(b)/\partial E=\int_0^b \psi_2^2dx=N_0, \tag{4.27}$$

which is nonvanishing. Also $\partial E/\partial\mu$ is finite and nonvanishing. Finally

$$\frac{d\mu}{d\lambda}=\frac{\partial}{\partial\lambda}\left[\frac{1}{2}\left(\lambda+\frac{1}{\lambda}\right)\right]=\frac{1}{2}\left(1-\frac{1}{\lambda^2}\right). \tag{4.28}$$

Hence

$$\psi_2(b,\lambda)=\tfrac{1}{2}N_0\frac{dE}{d\mu}(\lambda-1)^2+\cdots, \tag{4.29}$$

and therefore

$$N=-\frac{2\pi}{b}N_0(\lambda-1)^2+\cdots. \tag{4.30}$$

Now we examine the function $\chi(x)$ of (4.18). At $\lambda=1$, $\psi_2(b)=0$ and $\psi_1(b)=\mu=1$, so that the numerator

$$\chi(x,\lambda)\equiv\psi_2(b)\psi_1(x)+\frac{1}{2}\left(\lambda-\frac{1}{\lambda}\right)\psi_2(x)=0,\quad \lambda=1. \tag{4.31}$$

To determine its behavior near $\lambda=1$, we note that by (4.29)

$$\partial\psi_2(b)/\partial\lambda=0. \tag{4.32}$$

Hence, near $\lambda=1$

$$\chi(x,\lambda)=(\lambda-1)\psi_2(x). \tag{4.33}$$

Combining with (4.30), we see that $\psi(x,\lambda)$ is regular near $\lambda=1$ and

$$\psi(x,1)=\pm\left(\frac{b}{2\pi N_0}\right)^{\frac{1}{2}} i\psi_2(x,1), \tag{4.34}$$

provided that $\psi_2(b,1)=0$. A completely analogous situation holds if $\psi_2(b,\lambda)$ vanishes at $\lambda=-1$.

The only singularities of $\psi(x,\lambda)$ occur then at the points $\lambda_n^{\pm}$ given by Eq. (3.18). Let us examine $\psi(x,\lambda)$ in the vicinity of such a point,

$$\lambda_n^{\pm}\equiv\lambda'. \tag{4.35}$$

For a given x, the function $\chi(x,\lambda)$ in (4.18) behaves like

$$\chi(x,\lambda)=A_1(x)+B_1(x)(\lambda-\lambda')^{\frac{1}{2}}+\cdots, \tag{4.36}$$

as ψ_1 and ψ_2 are entire functions of E, but the function $E=\mathcal{E}(\lambda)$ has a branch point of order 1 at λ'. In the denominator the factor ψ_2 behaves as

$$\psi_2(b)=A_2+B_2(\lambda-\lambda')^{\frac{1}{2}}+\cdots, \tag{4.37}$$

while

$$d\mu/dE=2\alpha_n(E-E_n)=A_3(\lambda-\lambda')^{\frac{1}{2}}. \tag{4.38}$$

Hence $\psi(x,\lambda)$ behaves as

$$\psi(x,\lambda)=\frac{C(x)}{(\lambda-\lambda')^{\frac{1}{4}}}[1+D(x)(\lambda-\lambda')^{\frac{1}{2}}+\cdots]. \tag{4.39}$$

Thus we see that the points $\lambda_n^{\pm}$ are branch points of order 1[5] of the un-normalized function $\chi(x,\lambda)$, but branch points of order 3[5] of the normalized function $\psi(x,\lambda)$.

Now let us go back to Fig. 5 of the λ-plane. The function $\chi(x,\lambda)$ has branch points of order 1 at the same locations $\lambda_n^{\pm}$ as $\mathcal{E}(\lambda)$. It may be represented on the same Riemann surface as $\mathcal{E}(\lambda)$, with one sheet corresponding to each energy band n. If, for instance, we start at $\lambda=1$ with $\chi(x,1)$ corresponding to band $n=1$, go around λ_1^+ and return to $\lambda=1$, we then have the value of $\chi(x,1)$ for $n=2$.

On the other hand, the function $\psi(x,\lambda)$ requires a Riemann surface with twice as many sheets as $\mathcal{E}(\lambda)$. For each sheet on which ψ has the values $\psi_n(x,\lambda)$, there is a second sheet on which it has the values $-\psi_n(x,\lambda)$. Each branch point λ' connects four sheets, $\sigma_n^{\pm}$ and $\sigma_{n+1}^{\pm}$. Suppose we start at $\lambda=1$ with $\psi(x,1)$ corresponding to band $n=1$, on sheet σ_1^+. Passing once around λ_1^+ and returning to $\lambda=1$ gives $\psi(x,1)$ for band $n=2$, on σ_2^+; two encirclements give $-\psi(x,1)$ for band $n=1$, on σ_1^-; three give $-\psi(x,1)$ for band $n=2$, on σ_2^-; and four give again $\psi(x,1)$ for band $n=1$, on σ_1^+.

Behavior of $\psi(x,\lambda)$ in the Vicinity of the Unit Circle $\lambda=1$

As the unit circle corresponds to real values of k, it is of special interest.

Suppose we start on the unit circle with a particular value of $\mathcal{E}(\lambda)$ and a corresponding $\psi(x,\lambda)$. If we remain in the vicinity of the unit circle, $\mathcal{E}(\lambda)$ remains single valued, hence so does $\psi_1(x,\mathcal{E}(\lambda))$ and $\psi_2(x,\mathcal{E}(\lambda))$ and therefore also the un-normalized function $\chi(x,\lambda)$, Eq. (4.6).

We now turn to the normalizing factor $N^{-\frac{1}{2}}$. Since for $|\lambda|=1$, E is real and λ of the form $\exp(igb)$ we see from the original definition, Eq. (4.8), that N is real and $\geqslant 0$. Furthermore, by Eq. (4.17), since $d\mu/dE\neq 0$ on $|\lambda|=1$, we see that N can vanish only where $\psi_2(b)$ vanishes. As we have seen, this can only occur at $\lambda=\pm1$, and where it occurs $\psi_2(b,\lambda)$ has a double root in λ.

This leads one to distinguish two cases: (A) $\psi_2(b)$ vanishes at neither $\lambda=\pm1$, or at both; (B) $\psi_2(b)$ vanishes at either $\lambda=\pm1$, but not at both. In case (A), $N^{-\frac{1}{2}}(\lambda)$ and hence $\psi(x,\lambda)$ returns to its original value on going around the unit circle. Hence, we can write $\psi(x,\lambda)$ as a Laurent expansion in λ

$$\psi(x,\lambda)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\sum_{l=-\infty}^{\infty}\alpha_n^{(l)}(x)\lambda^l, \tag{4.40}$$

which converges in the ring (3.20′). In case (B), $N^{-\frac{1}{2}}(\lambda)$ and hence $\psi(x,\lambda)$ change sign on going around the unit circle. Therefore, we can write $\psi(x,\lambda)$ as a Laurent series of the following form in $\lambda^{\frac{1}{2}}$,

$$\psi(x,\lambda)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\sum_{l=-\infty}^{\infty}\beta_n^{(l)}(x)\lambda^{(2l+1)/2} \tag{4.41}$$

converging again in the ring (3.20′).

Behavior of $\varphi_{n,k}$ as a Function of k

This is easily obtained from the functional dependence of $\psi(x,\lambda)$ on λ by the substitution $\lambda=\exp(ibk)$.

We find that $\varphi_{n,k}$ is a branch of a many-valued function φ_k, whose branch points have the same locations as those of E_k (see Sec. 3 and Fig. 4). In the vicinity of such a branch point, k',

$$\varphi_k\approx C'/(k-k')^{\frac{1}{4}}. \tag{4.42}$$

Thus four Riemann sheets are connected at each branch point. Two of these correspond to a band n and two to the band $n+1$. On the two sheets corresponding to a given n, φ_k differs only by sign.

We now have to distinguish several cases, corresponding to different possible behavior of $\varphi_{n,k}$ at $k=0$ and π/b (or $\lambda=\pm1$).

Case A. $\varphi_{n,0}(0)$ and $\varphi_{n,\pi/b}(0)$ both not zero or both zero. From (4.40) we have the Fourier expansion

$$\varphi_{n,k}(x)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\sum_{l=-\infty}^{\infty}\alpha_n^{(l)}(x)e^{ilbk}, \tag{4.43}$$

which represents an analytic function of k in the strip

$$|\mathrm{Im}k|<\bar{h}_n, \tag{4.44}$$

where $\bar{h}_n$ is defined in Eq. (3.22). Clearly, $\varphi_{n,g}(x)$ is *periodic* in g with period $2\pi/b$:

$$\varphi_{n,g+2\pi/b}(x)=\varphi_{n,g}(x). \tag{4.45}$$

Now let us further distinguish two subcases.

(A1) $\qquad \varphi_{n,0}(0)\neq 0, \quad \varphi_{n,\pi/b}(0)\neq 0.$

Then from (4.6) and the fact that $N^{-\frac{1}{2}}(\lambda)=N^{-\frac{1}{2}}(\lambda^{-1})$, we find directly the following symmetry properties

$$\varphi_{n,g}^*(x)=\varphi_{n,g}(-x), \tag{4.46}$$

$$\varphi_{n,-g}(x)=\varphi_{n,g}(-x). \tag{4.47}$$

(A2) $\qquad \varphi_{n,0}(0)=0, \quad \varphi_{n,\pi/b}(0)=0.$

Here, since $N^{-\frac{1}{2}}(\lambda)=-N^{-\frac{1}{2}}(\lambda^{-1})$, we find

$$\varphi_{n,g}^*(x)=\varphi_{n,g}(-x), \tag{4.48}$$

$$\varphi_{n,-g}(x)=-\varphi_{n,g}(-x). \tag{4.49}$$

Case B. $\varphi_{n,0}(0)$ or $\varphi_{n,\pi/b}(0)$ is zero, but not both. From (4.41) we have the Fourier expansion

$$\varphi_{n,k}(x)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\sum_{l=-\infty}^{\infty}\beta_n^{(l)}(x)\exp\left(i\frac{2l+1}{2}bk\right), \tag{4.50}$$

which represents an analytic function of k in the strip (4.44). In this case $\varphi_{n,g}(x)$ is *antiperiodic* in g with period $2\pi/b$:

$$\varphi_{n,g+2\pi/b}(x)=-\varphi_{n,g}(x). \tag{4.51}$$

We may again distinguish two subcases.

(B1) $\qquad \varphi_{n,0}(0)\neq 0, \quad \varphi_{n,\pi/b}(0)=0.$

In this case one finds that $\varphi_{n,g}(x)$ has the symmetry relations (4.46), (4.47).

(B2) $\qquad \varphi_{n,0}(0)=0, \quad \varphi_{n,\pi/b}(0)\neq 0.$

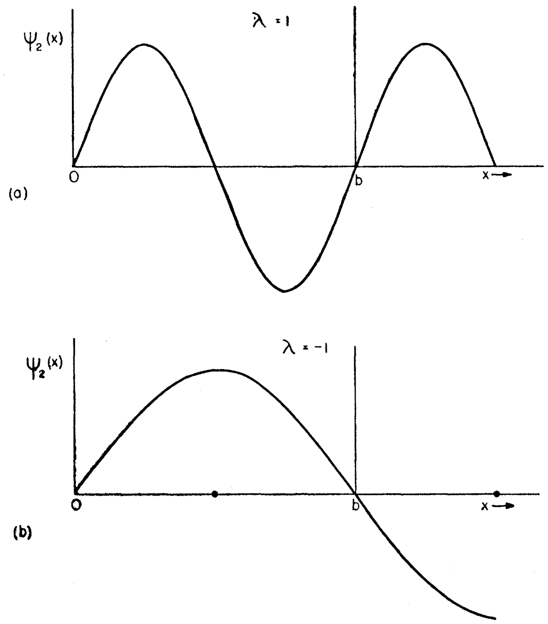

FIG. 6. Schematic plots of $\psi_2(x)$ for $\lambda=\pm1$ and $\psi_2(b)=0$.

In this case one finds that $\varphi_{n,g}(x)$ has the symmetry relations (4.48) and (4.49).

Power Series Expansion of $\varphi_{n,g}$

Since the singularities of $\varphi_{n,k}$ have the same locations as those of $E_{n,k}$, our remarks about the power series expansion of $E_{n,g}$ can be taken over without change.

Coordinate Shift Through Half Period

Let us consider a new pair of basis functions, $\bar{\psi}_1(x)$ and $\bar{\psi}_2(x)$, referring to the other center of symmetry of $V(x)$, namely $b/2$:

$$\bar{\psi}_1(b/2)=1, \quad \bar{\psi}_1'(b/2)=0, \tag{4.52}$$

$$\bar{\psi}_2(b/2)=0, \quad \psi_2'(b/2)=1. \tag{4.53}$$

Elementary considerations using the symmetry of the potential give the following results: At $\lambda=+1$, $\psi_2(b)$ and $\bar{\psi}_2(\frac{1}{2}b+b)$ are either both zero or both not zero [see Fig. 6(a)]; while at $\lambda=-1$, one and only one of $\psi_2(b)$ and $\bar{\psi}_2(\frac{1}{2}b+b)$ [see Fig. 6(b) and use the fact that bands do not intersect]. Hence, if the normalized Bloch waves $\bar{\varphi}_{n,g}$ are defined by the requirement that $\bar{\varphi}_{n,g}(b/2)$ be real and that $\bar{\varphi}_{n,k}(x)$ be analytic for $k=g$, then depending on whether

$$\varphi_{n,g+2\pi/b}(x)=\pm\varphi_{n,g}(x), \tag{4.54}$$

$\bar{\varphi}_{ng}$ has the property

$$\bar{\varphi}_{n,g+2\pi/b}(x)=\mp\bar{\varphi}_{n,g}(x). \tag{4.55}$$

Thus in all cases one of the functions, $\varphi_{n,g}$ and $\bar{\varphi}_{n,g}$, is periodic with period $2\pi/b$, while the other is antiperiodic.

Remark on Other Choices of Phase

We have discussed two particular assignments of phase suggested by the symmetries of $V(x)$ about $x=0$ and $b/2$. Other choices are of course possible. For complex k we can write the most general Bloch function as

$$\Phi_{n,k}(x)=e^{i\theta(k)}\varphi_{n,k}(x), \tag{4.56}$$

where, to preserve the normalization for real k, we must have

$$\mathrm{Im}\theta(g)=0. \tag{4.57}$$

However, it is obvious that all possible $\Phi_{n,k}$ have singularities at the singularities of $E_{n,k}$. For suppose the contrary, i.e., that $\Phi_{n,k}$ is regular at such a point. Then so would be the function

$$\frac{(-d^2/dx^2+V)\Phi_{n,k}}{\Phi_{n,k}}=E_{n,k}, \tag{4.58}$$

which is a self-contradiction. On the other hand, $\theta(k)$ can of course introduce singularities of its own.

II. WANIER FUNCTIONS

5. Preliminaries

Wannier functions,[8] $a_n(x)$, are localized linear combinations of all the Bloch waves of a given band. In the following paragraphs, we shall be speaking only about one band at a time and, therefore, generally suppress the band index, n. Let then $\Phi_g(x)$ be a normalized Bloch wave of as yet arbitrary phase. Then the corresponding Wannier function is defined

$$a(x)\equiv\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{\pi/b}^{\pi/b}\Phi_g(x)dg. \tag{5.1}$$

Its shape depends on the variation with g of the phase of Φ_g. From the form (1.4) of Φ_g, we deduce that

$$a(x-lb)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_g(x)e^{-ilbg}dg. \tag{5.2}$$

We shall use the notation

$$a^{(l)}(x)\equiv a(x-lb). \tag{5.3}$$

If we multiply (5.2) by $e^{ilbg'}$ and sum over l, using the fact that

$$\sum_l e^{ilb(g'-g)}=(2\pi/b)\delta(g'-g), \tag{5.4}$$

we obtain

$$\Phi_g(x)=(b/2\pi)^{\frac{1}{2}}\sum_l a^{(l)}(x)e^{ilbg}. \tag{5.5}$$

By means of (5.2) and (5.5), the Wannier functions, $a^{(l)}(x)$, and Bloch waves, $\Phi_g(x)$, can be expressed in terms of one another.

Of course, (5.1) assumes sufficient regularity of $\Phi_g(x)$ for the integral to exist and (5.5) assumes the con-

[8] G. Wannier, Phys. Rev. **52**, 191 (1947).

vergence of the sum over l. To avoid irrelevant mathematical subleties, let us assume from here on that the phases of $\Phi_g(x)$ are so chosen that $\Phi_g(x)$ is a sectionally continuous function of g in the interval $-\pi/b\leqslant g\leqslant\pi/b$. Then the integral (5.1) exists and the sum in (5.5) converges to $\frac{1}{2}(\Phi_{g-0}+\Phi_{g+0})$ for $-\pi/b<g<\pi/b$ and to $\frac{1}{2}(\Phi_{(\pi/b)-0}+\Phi_{(-\pi/b)+0})$ at $g=\pm\pi/b$.

From their definition, the well-known ortho-normality of the $a^{(l)}(x)$ may be verified at once,

$$\int_{-\infty}^{\infty} a^{(l')}(x)^* a^{(l)}(x)dx=\delta_{ll'}. \tag{5.6}$$

6. Reality and Symmetry

In discussing the reality and symmetry of $a(x)$, we must distinguish two cases.

Case A1 or B1:

$$\Phi_0(0)\neq 0.$$

Here we choose the phase of Φ_g such that $\Phi_g(0)$ is real and $\Phi_k(x)$ is analytic for $k=g$. Then $\Phi_g(x)$ is (apart from a possible factor -1) identical to the $\varphi_g(x)$ of Sec. 4. Therefore, on using Eqs. (4.46) and (4.47) in Eq. (5.1), we find

$$a(-x)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_{-g}(x)dg=a(x), \tag{6.1}$$

and

$$a^*(x)=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_{-g}(x)dg=a(x). \tag{6.2}$$

Thus $a(x)$ is both symmetric about $x=0$ and real.

Case A2 or B2:

$$\Phi_0(0)=0.$$

Here we choose the phase of Φ_g such that $\Phi_g(0)$ is purely imaginary and $\Phi_k(x)$ is analytic for $k=g$. This Φ_g is related to the φ_g of Sec. 4 by

$$\Phi_g(x)=\pm i\varphi_g(x). \tag{6.3}$$

Therefore, using Eqs. (4.48) and (4.49), we obtain

$$a(-x)=-\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_{-g}(x)dg=-a(x), \tag{6.4}$$

and

$$a^*(x)=+\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_{-g}(x)dg=a(x). \tag{6.5}$$

This time $a(x)$ is antisymmetric about $x=0$ and real.

Uniqueness

We shall now show that no other choice of phase, which has the property that the corresponding Bloch waves are continuous functions of g, leads to a Wannier function which is both real and either symmetric or antisymmetric about $x=0$.[9]

[9] Apart, of course, from a trivial factor -1; see Eq. (6.15).

Consider then a possible alternative set of Bloch waves,

$$\Phi_g'=e^{i\theta(g)}\Phi_g,\quad -\pi/b\leqslant g\leqslant\pi/b, \tag{6.6}$$

leading to a real and (anti-) symmetric Wannier function. We write

$$e^{i\theta(g)}=\sum_{m=-\infty}^{\infty}A_m e^{-imgb},\quad -\pi/b\leqslant g\leqslant\pi/b. \tag{6.7}$$

The corresponding Wannier function is

$$\begin{aligned} a'(x)&=\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_g'(x)dx\\ &=\sum_{m=-\infty}^{\infty}A_m\left(\frac{b}{2\pi}\right)^{\frac{1}{2}}\int_{-\pi/b}^{\pi/b}\Phi_g(x)e^{-imgb}dg\\ &=\sum_{m=-\infty}^{\infty}A_m a(x-mb). \end{aligned} \tag{6.8}$$

Now using the reality of $a(x)$, we have

$$[a'(x)]^*=\sum_{m=-\infty}^{\infty}A_m^* a(x-mb). \tag{6.9}$$

Since the $a(x-mb)$ form an orthonormal set, we see that $a'(x)$ is real only if

$$A_m=\text{real}. \tag{6.10}$$

Further

$$\begin{aligned} a'(-x)&=\sum_{m=-\infty}^{\infty}A_m a(-x-mb)\\ &=\sum_{m=-\infty}^{\infty}A_{-m}a(-x+mb)\\ &=\pm\sum_{m=-\infty}^{\infty}A_{-m}a(x-mb), \end{aligned} \tag{6.11}$$

depending on whether $a(x)$ is symmetric or antisymmetric. Therefore, if $a(-x)$ is to be symmetric or antisymmetric, we must have

$$A_{-m}=\pm A_m. \tag{6.12}$$

Now using (6.10) and (6.12) in (6.7) gives

$$e^{i\theta(g)}=\begin{cases} A_0+2\sum_{m=1}^{\infty}A_m\cos mgb\\ -2i\sum_{m=1}^{\infty}A_m\sin mgb,\end{cases} \tag{6.13}$$

depending on the sign in (6.12). The second line in (6.13) can be ruled out at once by setting $g=0$. The first line implies that $e^{i\theta(g)}$ is real and hence, because of the assumed continuity of φ_g,

$$e^{i\theta(g)}\equiv\pm 1. \tag{6.14}$$

Therefore,

$$\Phi_g' = \pm \Phi_g. \tag{6.15}$$

7. Asymptotic Behavior of $a(x)$

We begin by discussing the particular Wannier functions of the preceding section, which are real and (anti-) symmetric about $x=0$.

Case A. $\varphi_0(0)$ *and* $\varphi_{\pi/b}(0)$ *Both Nonzero or Both Zero*

In this case φ_g is a periodic function of g with period $2\pi/b$. The Φ_g with which we constructed our Wannier functions was related to φ_g of Sec. 4 by a constant ϵ,

$$\Phi_g = \epsilon \varphi_g, \tag{7.1}$$

where $\epsilon = \pm 1$ or $\pm i$ depending on whether $\varphi_0(0)$ did not or did vanish. Since

$$\Phi_g = (b/2\pi)^{\frac{1}{2}} \sum_l a^{(l)}(x) e^{ilbg}, \tag{7.2}$$

we see by comparison with Eq. (4.43) that

$$a^{(l)}(x) \equiv \epsilon \alpha^{(l)}(x). \tag{7.3}$$

Now the functions, $\alpha^{(l)}(x)$, were the coefficients of the Laurent expansion (4.40) which converged for

$$\exp(-b\bar{h}_n) < \lambda < \exp(b\bar{h}_n), \tag{7.4}$$

where $\bar{h}_n$ is defined in Eq. (3.22). Hence

$$\lim_{l\to\infty} \alpha^{(l)}(x)\lambda^l = \begin{cases} 0, & |\lambda| < \exp(b\bar{h}_n) \\ \infty, & |\lambda| > \exp(b\bar{h}_n). \end{cases} \tag{7.5}$$

In view of the connection

$$\alpha^{(l)}(x) = \frac{1}{\epsilon} a(x-lb), \tag{7.6}$$

this is equivalent to

$$\lim_{x\to\infty} a(x) e^{qx} = \begin{cases} 0, & q < \bar{h}_n \\ \infty, & q > \bar{h}_n. \end{cases} \tag{7.7}$$

More loosely speaking, $a(x)$ falls off like $\exp(-\bar{h}_n x)$.

Case B. One and Only One of $\varphi_0(0)$ *and* $\varphi_{\pi/b}(0)$ *is Zero*

In this case, φ_g and hence Φ_g is an antiperiodic function of g. The asymptotic behavior of the corresponding Wannier function can be found from (5.2) by performing an integration by parts. For fixed x and large l we find

$$a(x-lb) = \frac{1}{l}\left[\left(\frac{2}{\pi b}\right)^{\frac{1}{2}} (-1)^l i \Phi_{\pi/b}(x)\right] + O\left(\frac{1}{l^2}\right). \tag{7.8}$$

Thus $|a(x)|$ falls off only as x^{-1}.

For many applications such slowly decreasing Wannier functions are most inconvenient. It is therefore fortunate that we find that in Case B, $\varphi_0(b/2)$ and $\varphi_{\pi/b}(b/2)$ are either both nonzero or both zero [see Eqs. (4.54) and (4.55)]. Hence with respect to this new origin we have Case A and can therefore construct Wannier functions $\bar{a}(x)$ with the following properties.

$$\bar{a}(\tfrac{1}{2}b+x) = \pm \bar{a}(\tfrac{1}{2}b-x), \tag{7.9}$$

$$\bar{a}^*(x) = \bar{a}(x), \tag{7.10}$$

$$\lim_{x\to\infty} \bar{a}(x) e^{qx} = \begin{cases} 0, & q < \bar{h}_n \\ \infty, & q > \bar{h}_n. \end{cases} \tag{7.11}$$

8. Existence and Uniqueness of Real, (Anti-) Symmetric, and Short Range Wannier Function

We are now in a position to prove the following theorem: For every band there exists one and only one Wannier function[9] which has all three of the following properties:

1. It is real.
2. It is either symmetric or antisymmetric about either $x=0$ or $x=b/2$.
3. It falls off exponentially.

The quantitative rate of exponential decay of the function which has these properties is given by Eq. (7.7).

To fix our ideas let us take, for example, a band with the following properties: $\varphi_0(0) \neq 0$, $\varphi_{\pi/b}(0)=0$. This is case B1 of Sec. 4 [Eq. (4.51) ff.]. Now in Sec. 6 we have seen that there exists only one choice of $\Phi_g(x)$ which is continuous in g, with the property of leading, via (5.1), to a Wannier function which is real and symmetric or antisymmetric about $x=0$. This Wannier function did not fall off exponentially but like x^{-1}. If we consider also Bloch waves, $\Phi_g(x)$, which are *not* continuous functions of g, the corresponding Wannier function certainly cannot fall off exponentially with x [see Eq. (5.2)]. Thus we conclude that in this case there exists no Wannier function which is real, (anti-) symmetric about $x=0$, and falling off exponentially with x.

However, in the present case we have $\varphi_0(\frac{1}{2}b) \neq 0$ and $\varphi_{\pi/b}(\frac{1}{2}b+b) \neq 0$. Hence relative to $x=\frac{1}{2}b$ this band corresponds to case A1 of Sec. 4. Now in Sec. 6 we have shown that there exists one and only one choice of Φ_g which is continuous in g, with the property of leading via (5.1) to a Wannier function which is real and symmetric or antisymmetric about $x=b/2$. In Sec. 7, we saw that this function fell off exponentially for large x, according to Eq. (7.7). Any other choice of Φ_g, leading to a Wannier function real and symmetric or antisymmetric about $x=b/2$, is necessarily discontinuous in g and hence the corresponding Wannier function does not fall off exponentially.

This completes the proof of our theorem for a band of this type. For the other three types of band exactly similar proofs can be given.

For convenience we list below, for the four possible types of band, the symmetry properties of the corresponding unique Wannier function which has the three properties listed at the beginning of this section.

$$\text{(A1)}\quad \varphi_0(0)\neq 0,\quad \varphi_{\pi/b}(0)\neq 0:\quad a(-x)=a(x), \tag{8.1}$$

$$\text{(A2)}\quad \varphi_0(0)=0,\quad \varphi_{\pi/b}(0)=0:\quad a(-x)=-a(x), \tag{8.2}$$

$$\text{(B1)}\quad \varphi_0(0)\neq 0,\quad \varphi_{\pi/b}(0)=0:\quad \bar{a}(\tfrac{1}{2}b-x)=\bar{a}(\tfrac{1}{2}b+x), \tag{8.3}$$

$$\text{(B2)}\quad \varphi_0(0)=0,\quad \varphi_{\pi/b}(0)\neq 0:\quad \bar{a}(\tfrac{1}{2}b-x)=-\bar{a}(\tfrac{1}{2}b+x). \tag{8.4}$$

The question may be asked if one can possibly obtain a Wannier function falling off more rapidly than Eq. (7.7) by relaxing the requirements of reality and (anti-)symmetry. The answer is clearly "no." For, by Eq. (5.5), the corresponding Bloch waves would be analytic functions of k in a strip wider than Eq. (4.44), and this was shown to be impossible.

9. Nearly Free and Tightly Bound Electrons

If the potential $V(x)$ is weak or if we consider electrons of high energy, the Kramers plot $\mu(E)$ is close to that for free electrons

$$\mu_0(E)=\cos(E^{\frac{1}{2}}b). \tag{9.1}$$

In the free-electron case, the extrema μ_n of $\mu(E)$ occur all at $\mu=\pm 1$. Hence in the "nearly free" case we have

$$|\mu_n|=1+\delta_n, \tag{9.2}$$

where δ_n is a small positive quantity. Therefore, the singularities of E_k and φ_k lie very close to the real axis,

$$h_n=\sqrt{2}\delta_n \tag{9.3}$$

[see Eqs. (3.10) and (3.11)], and hence the exponential decay of the Wannier functions is very slow. This is in accord with the fact that for perfectly free electrons (which are not included in our considerations because their bands intersect), the Wannier function falls off only as x^{-1}.

For very tightly bound electrons of binding energy ϵ_n, it is shown in the Appendix that $\bar{h}_n\rightarrow(-\epsilon_n)^{\frac{1}{2}}$. Therefore, for large x their Wannier function behaves as

$$a_n(x)\sim\exp[-(-\epsilon_n)^{\frac{1}{2}}x], \tag{9.4}$$

that is, it falls off at the same exponential rate as the wave function of an isolated potential well.

ACKNOWLEDGMENTS

The writer takes great pleasure in thanking Mr. S. Michaelson for valuable help with several phases of this paper. The work here reported was begun at the Imperial College of Science and Technology, London, England, while the writer was a National Science Foundation Senior Post-doctoral Fellow. Later it was supported at Carnegie Institute of Technology by the Office of Naval Research. The assistance of these organizations is acknowledged with thanks. The writer also is glad to avail himself of this opportunity to thank the staff of the Department of Mathematics at the Imperial College for the hospitality which he enjoyed during his stay there.

APPENDIX. TIGHTLY BOUND ELECTRONS

Let $V_0(x)$ be a cutoff, symmetric potential,

$$V_0(x)\equiv 0,\quad |x|>c, \tag{A.1}$$

with a number of bound states with eigenvalues

$$\epsilon_n=-q_n^2,\quad n=0,1,\cdots. \tag{A.2}$$

We now consider the solutions of the Schrödinger equation (1.1) corresponding to the periodic potential

$$V(x)\equiv\sum_{l=-\infty}^{\infty}V_0(x-lb) \tag{A.3}$$

in the so-called tight-binding limit,

$$b\rightarrow\infty. \tag{A.4}$$

We wish to determine the magnitude of $\mu(E)$ at those energies E_n where $d\mu/dE=0$. This enables us to locate the singularities of the energy function E_k in the complex k-plane.

For the present purposes it is convenient to use as fundamental system of solutions of the Schrödinger equation (1.1) the functions $u_1(x,E)$ and $u_2(x,E)$ where

$$u_1(-c,E)=1,\quad u_1'(-c,E)=0, \tag{A.5}$$

$$u_2(-c,E)=0,\quad u_2'(-c,E)=1. \tag{A.6}$$

μ is given by the relation [see Eq. (2.9)]

$$\mu(E)=\tfrac{1}{2}[u_1(b-c,E)+u_2'(b-c,E)]. \tag{A.7}$$

Now let us define

$$f_1(E)\equiv u_1(c,E);\quad f_1'(E)\equiv u_1'(c,E), \tag{A.8}$$

$$f_2(E)\equiv u_2(c,E);\quad f_2'(E)\equiv u_2'(c,E). \tag{A.9}$$

Then since in the interval $c<x<b-c$, $V(x)=0$, one finds by matching solutions at $x=c$, that

$$u_1(b-c,E)=\frac{1}{2}\left(f_1+\frac{f_1'}{q}\right)e^{q(b-2c)}+\frac{1}{2}\left(f_1-\frac{f_1'}{q}\right)e^{-q(b-2c)}, \tag{A.10}$$

$$u_2'(b-c,E)=\tfrac{1}{2}(f_2q+f_2')e^{q(b-2c)}-\tfrac{1}{2}(f_2q-f_2')e^{-q(b-2c)}, \tag{A.11}$$

where

$$q=(-E)^{\frac{1}{2}}; \tag{A.12}$$

q is taken positive for negative E. By means of (A.10) and (A.11), we can express μ in terms of f_1, f_1', f_2, and f_2'.

Now let us define the function

$$G(E)\equiv f_1(E)+\frac{f_1'(E)}{q}+f_2(E)q+f_2'(E). \quad (A.13)$$

Substituting (A.10) and (A.11) into (A.7), we find that as $b\rightarrow\infty$, the condition $d\mu/dE=0$ or $d\mu/dq=0$ gives the following equation for the determination of the E_n, Eq. (2.15):

$$G(E)+\frac{1}{(b-2c)}\frac{d}{dq}G(E)=O(e^{-2qb}). \quad (A.14)$$

On the other hand, the band edges, where $\mu=\pm1$, are given by

$$G(E)=O(e^{-qb}). \quad (A.15)$$

Since in the tight-binding limit the band edges coincide with the "atomic" energies, ϵ_n, we must have

$$G(E)=0 \quad \text{at } E=\epsilon_n; \quad (A.16)$$

this may also be directly verified.

For large b, the solutions E_n of (A.14) differ only slightly from those of (A.16)

$$E_n=\epsilon_n+\frac{2q_n}{b}+O\left(\frac{1}{b^2}\right). \quad (A.17)$$

Substituting these values into the expression (A.7) for μ gives, with the aid of (A.10), (A.11), and (A.13)

$$\begin{aligned}\mu(E_n)&=G(E_n)\exp[(-E_n)^{\frac{1}{2}}(b-2c)]+O(e^{-2q_nb})\\&=\exp[(-E_n)^{\frac{1}{2}}(b-2c)]\\&\quad\times\left[\frac{2q_n}{b}G'(E_n)+O\left(\frac{1}{b^2}\right)\right]. \quad (A.18)\end{aligned}$$

From this we can now determine the distance h_n of the singularities of E_k from the real k-axis [see Eq. (3.12)]:

$$\lim_{b\to\infty}h_n=(-\epsilon_n)^{\frac{1}{2}}. \quad (A.19)$$

As $\bar{h}_n=\min(h_n,h_{n-1})$ and $\epsilon_n>\epsilon_{n-1}$, we also have

$$\lim_{b\to\infty}\bar{h}_n=(-\epsilon_n)^{\frac{1}{2}}. \quad (A.20)$$

PHYSICAL REVIEW VOLUME 115, NUMBER 4 AUGUST 15, 1959

Electrodynamics of Charge Carriers of Negative Effective Mass in Crystals

SERGIO RODRIGUEZ*
Department of Physics, University of Washington, Seattle, Washington
(Received March 23, 1959)

The transport properties of negative-effective-mass carriers in crystals are studied. The electrical conductivity of a sample in which the electron distribution function is weakly-perturbed from its thermal equilibrium value is always positive, even in the presence of a magnetic field. Therefore, cyclotron resonance experiments in equilibrium should display energy absorption, although the negative-mass carriers will circulate in the sense opposite to that of positive-mass carriers of the same charge.

I. INTRODUCTION

THE energy bands of crystals exhibit, in general, regions in wave-vector space where the effective mass of the charge carriers is negative. Such carriers are accelerated by electric and magnetic fields in a direction opposite to that of the acceleration of positive effective mass carriers of the same charge. A cyclotron resonance experiment with circularly polarized radiation would enable us to distinguish between positive- and negative-mass carriers.

Kittel[1] has shown, on the basis of a general thermodynamic argument, that a system of carriers all having a negative effective mass cannot exist in thermal equilibrium with a bath at a positive temperature. However, it is possible for carriers of positive and negative effective mass to be in thermal equilibrium with each other. He has also shown that a distribution of negative- and positive-mass carriers in thermal equilibrium will always absorb energy from an external electromagnetic field. If this were not the case we would be able to construct a device which could perform work and produce no effect other than cooling a heat reservoir. This would, of course, be in contradiction with the second law of thermodynamics.

Kittel also shows that the standard Boltzmann transport theory leads to the same result as the more general thermodynamic argument. In fact, consider that we have a conductor with one conduction band defined by $E(\mathbf{k})$. Here $E(\mathbf{k})$ is the energy associated with the state with wave-vector $\mathbf{k}$. Let $f_0(\mathbf{k})$ be the distribution function in thermal equilibrium. If we apply a constant electric field $\boldsymbol{\mathcal{E}}$ the steady-state distribution function f is given, to first order in $\boldsymbol{\mathcal{E}}$, by the

* Present address: Department of Physics, University of Illinois, Urbana, Illinois.
[1] C. Kittel, Proc. Natl. Acad. Sci. **45**, 744 (1959).