Analytical Properties of n-Dimensional Energy Bands and Wannier Functions

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If, in an n-dimensional crystal, the structure of a simple ($d=1$) or complex ($d>1$) energy band fulfills proper symmetry conditions, the band can be spanned by a set of Wannier functions and, in many cases, the following statements can be established. (1) There exists a set of Bloch waves ($d=1$) or quasi Bloch waves ($d>1$) which are periodic and analytic functions of the complex wave vector $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ in a domain of the complex $\mathbf{K}$ space defined by an equation of the form $|\mathbf{K}''|<A$ where A is a positive constant. (2) The corresponding Wannier functions fall off exponentially at infinity.

I. INTRODUCTION

THE eigenstates of a one-electron Hamiltonian H which is invariant with respect to the transformation of a space group G_H, can be expressed linearly in terms of orthonormal local orbitals by using group theoretical methods. A precise definition of such orbitals[1] and a complete description of their symmetry properties have been given by the author in a previous work[2] (paper I). Unfortunately, this method does not show how to build really localized orbitals because the nature of the problem is rather analytical and topological and has very little to do with group theory. Actually, the answer to this question seems far from simple; it depends on our definition of the localizability properties of the orbitals and also on the specific properties of the Hamiltonian H. However, if G contains a subgroup T of translations, the system can be considered as a cyclic crystal (or infinite crystal) and this case which is especially interesting, seems also easier to treat. In crystals, local orbitals are called Wannier functions and the present work deals with the localizability properties of these functions. Infinite linear crystals with a center of symmetry have been studied by Kohn.[3] He showed that there is always a unique way of associating with each band, a single set of symmetric or antisymmetric Wannier functions falling off exponentially at infinity. This property results from the analyticity of the Bloch waves with respect to the wave number $K=K'+iK''$ in a strip of the complex K space; this strip is defined by an equation of the form $|K''|<A$ where A is a positive constant characteristic of the band.

Here, we want to generalize these results for two- or three-dimensional crystals. However, as the Schrödinger equation, in this case, is no longer an ordinary but rather a partial differential equation, the problem is much more difficult to solve and Kohn's approach cannot be used. In an n-dimensional crystal ($n>1$), the structure of the energy bands is also more complicated than in the linear case. In general, a band is made of several branches which touch each other. By definition, if two branches are connected, they belong to the same band; on the contrary, a given band $\mathcal{B}$ never touches any other band; it is isolated. The number of Bloch waves which, for each (real) value of the wave vector $\mathbf{K}$, belong to $\mathcal{B}$ is a constant d. Thus, the band can be simple ($d=1$) or complex ($d>1$). If the band $\mathcal{B}$ is simple, it contains, for each value of $\mathbf{K}$, only one Bloch state; in this case, it seems, *a priori*, possible to build a Bloch wave which is an analytic function of the wave vector $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ in a strip of the complex $\mathbf{K}$ space; this strip could be defined by an equation of the form $|\mathbf{K}''|<A$ where A is a positive constant. In this case, the existence of Wannier functions with exponential tails can be directly related to this property of analyticity of the Bloch waves. However, if the band $\mathcal{B}$ is complex ($d>1$), the Bloch waves which belong to $\mathcal{B}$ cannot be analytic functions of the wave vector $\mathbf{K}$ for real values of $\mathbf{K}$; in this case, the energy is a multivalued function of $\mathbf{K}$; the points where several branches touch each other are branch points of this function and, of course, they are also branch points for the Bloch waves. This remark does not imply the impossibility of representing a complete band $\mathcal{B}$ by a set of localized Wannier functions; it indicates only that a generalization of Kohn's results is not trivial and that a different method of approach is needed. The Bloch waves of wave vector $\mathbf{K}$ belonging to a given band $\mathcal{B}$ span a subspace $\mathcal{S}(\mathbf{K})$ of dimension d, which can be defined by the operator $P(\mathbf{K})$ of projection on $\mathcal{S}(\mathbf{K})$. This operator $P(\mathbf{K})$ can be expressed directly in terms of Bloch waves and has also nice analyticity properties. Actually, we showed in a preceding work[4] (paper II) that the matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$ of $P(\mathbf{K})$ are in general continuous functions of $\mathbf{r}$ and $\mathbf{r}'$, that they can be defined for complex values of $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ and that they remain analytic in a strip of the complex $\mathbf{K}$ space; this strip is defined by an equation of the form $|\mathbf{K}''|<A$ where A is a positive constant which depends on the characteristics of $\mathcal{B}$. This result is valid for any kind of band and for this reason, we use the operator $P(\mathbf{K})$ to build Bloch waves (when $d=1$) or so called quasi Bloch waves (when $d>1$), which are analytic functions of $\mathbf{K}$ in a strip of the complex $\mathbf{K}$ space. The existence of Wannier functions with exponential tails turns out to be a consequence of these analyticity properties.

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[1] This question has been discussed by E. I. Blount, Solid State Phys. **13**, 305 (1962).
[2] J. des Cloizeaux, paper I, Phys. Rev. **129**, 554 (1963).
[3] W. Kohn, Phys. Rev. **115**, 809 (1959).
[4] J. des Cloizeaux, paper II, Phys. Rev. **135**, A685 (1964).

In Sec. II, the main properties of $P(\mathbf{K})$ are summarized. In Sec. III, simple energy bands are studied. Relations connecting Bloch waves and Wannier functions are given in Sec. IIIA. Bloch waves are built in Sec. IIIB with the help of the operator $P(\mathbf{K})$; trial Wannier functions are used to determine the phases of the Bloch waves corresponding to different values of $\mathbf{K}$. The normalization of these waves introduces a difficulty. However, as we show in Sec. IIIC, the difficulty is not very serious if the crystal has a center of inversion, and it is also possible to overcome it in other special cases. In Sec. IV, a generalization of the method is applied to complex bands. In this case, the Bloch waves cannot be analytic with respect to $\mathbf{K}$ for real values of $\mathbf{K}$ and we are obliged to introduce a new set of waves called quasi Bloch waves; these waves may be analytic but are not eigenfunctions of the Hamiltonian H. A survey of the group theoretical aspects of the problem is made in Sec. IVA. Quasi Bloch waves are defined in Sec. IVB in terms of the corresponding Wannier functions and the general properties of these waves are listed in Sec. IVC. In Sec. IVD, we build quasi Bloch waves directly by using the operator $P(\mathbf{K})$ of the band and trial Wannier functions. In general, the analyticity of the operator $P(\mathbf{K})$ entails the analyticity of the Bloch waves. Finally, the orthonormalization difficulty is discussed in Sec. IVE.

II. REVIEW OF THE MAIN PROPERTIES OF THE OPERATORS $P(K)$ AND $P=\int P(K)d^nK$ (INTEGRATION ON THE BRILLOUIN ZONE)

The eigenstates of the Hamiltonian H are Bloch states $|\varphi(l,\mathbf{K})\rangle$. The index l characterizes both the band and the branch to which the state belongs. Thus, if $\mathbf{t}$ is a translation vector of the crystal, we have by definition

$$\langle \mathbf{r}+\mathbf{t}|\varphi(l,\mathbf{K})\rangle = e^{i\mathbf{K}\mathbf{t}}\langle \mathbf{r}|\varphi(l,\mathbf{K})\rangle. \tag{1}$$

Dirac-type normalization is used for these states

$$\langle\varphi(l,\mathbf{K})|\varphi(l',\mathbf{K}')\rangle = \delta_c(\mathbf{K}-\mathbf{K}')\delta_{ll'}. \tag{2}$$

The function $\delta_c(\mathbf{K}-\mathbf{K}')$ is given by

$$\delta_c(\mathbf{K}-\mathbf{K}') = \sum_{\mathbf{u}} \delta(\mathbf{K}-\mathbf{K}'+\mathbf{u}), \tag{3}$$

where the summation is made over all the translations $\mathbf{u}$ of the reciprocal lattice.

The operator $P(\mathbf{K})$ which is associated with a given band $\mathcal{B}$ can be defined for real values of $\mathbf{K}$ by

$$P(\mathbf{K}) = \sum_{l\in\mathcal{B}} |\varphi(l,\mathbf{K})\rangle\langle\varphi(l,\mathbf{K})|. \tag{4}$$

The Bloch states which appear in this formula are those which belong to $\mathcal{B}$. The operator $P(\mathbf{K})$ can be defined by its matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$ and according to Eq. (1), we have

$$\langle\mathbf{r}+\mathbf{t}|P(\mathbf{K})|\mathbf{r}'\rangle = \langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'-\mathbf{t}\rangle = e^{i\mathbf{K}\mathbf{t}}\langle\mathbf{r}|P(\mathbf{K})\mathbf{r}'\rangle. \tag{5}$$

On the other hand, the fact that $P(\mathbf{K})$ is a projection operator appears in the following relation:

$$P(\mathbf{K})P(\mathbf{K}') = \delta_c(\mathbf{K}-\mathbf{K}')P(\mathbf{K}), \tag{6}$$

which is a direct consequence of Eq. (2).

In paper II, it was shown that the matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$ can be defined also for complex values of $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ and that they remain analytic in a strip of the complex K plane; this domain is defined by an equation $|\mathbf{K}''|<A$ where A is a positive constant independent of $\mathbf{K}'$, $\mathbf{r}$ and $\mathbf{r}'$. Of course, for values of $\mathbf{K}$ belonging to this region, Eq. (5) remains valid but $P(\mathbf{K})$ is not an Hermitian operator if $\mathbf{K}$ is complex.

In paper II, we introduced also the operator P which is an integral of $P(\mathbf{K})$ over the Brillouin zone,

$$P = \int_{B.Z.} P(\mathbf{K})d^n\mathbf{K}. \tag{7}$$

According to Eq. (6) P is a projection operator and we have

$$P^2 = P. \tag{8}$$

This operator is periodic, in the following sense:

$$\langle\mathbf{r}+\mathbf{t}|P|\mathbf{r}'+\mathbf{t}\rangle = \langle\mathbf{r}|P|\mathbf{r}'\rangle. \tag{9}$$

In connection with the analyticity properties of $P(\mathbf{K})$, it was proved also that the matrix elements $\langle\mathbf{r}|P|\mathbf{r}'\rangle$ decrease exponentially with the distance $|\mathbf{r}-\mathbf{r}'|$. More explicitly, we may write $(0<\epsilon<1)$

$$\lim_{t\to\infty} e^{\epsilon At}\langle\mathbf{r}+\mathbf{t}|P|\mathbf{r}'\rangle = 0. \tag{10}$$

This result is used in Sec. IIIC.

III. WANNIER FUNCTIONS FOR SIMPLE BANDS IN AN INFINITE CRYSTAL

A. Wannier Functions and Bloch Waves

When a band $\mathcal{B}$ consists of one sheet only ($d=1$), its analyticity properties are simple, and the definition of the corresponding Wannier functions are more straightforward than in the general case. For this reason, this section deals only with simple bands and the treatment of this interesting case serves as an illustration of the general method which is described in Sec. IV.

Here, the basic assumptions of paper II concerning the group theoretical properties of Wannier functions are used, but, in the case of simple bands, they are rather trivial. The set of all the space transformations which leave the Hamiltonian H invariant is a group G_H. The Wannier functions are located around sites M. By definition, these sites are generated by applying to an origin M_0 all the elements of G_H; thus, when the band $\mathcal{B}$ is simple, they must form a translation lattice $\mathcal{L}$. On the other hand, when $\mathcal{B}$ is simple, we associate only one Wannier function with each site; it is assumed that this function is the basis of a one-dimensional representation of the subgroup G_M consisting of all the elements of G_H which leave M invariant. Of course, the symmetry properties of the Wannier functions are determined by the characteristics of the band. In the following, we consider the lattice $\mathfrak{L}$ and the representation $\Gamma_{M_0}{}^m$ as given and compatible with the properties of the band $\mathfrak{B}$ which the Wannier functions must span.

In particular, if there is a center of inversion in the crystal, the points M are centers of inversion. This property can be derived as follows. Let I be an inversion belonging to G_H; it transforms any point P of the ordinary space into a point P'; for instance, it transforms the origin M_0 of $\mathfrak{L}$ into M_0' and we have

$$\mathbf{M}_0\mathbf{P}+\mathbf{M}_0'\mathbf{P}'=0. \tag{11}$$

As the points M are obtained by applying all the elements of G_H to M_0, the lattice $\mathfrak{L}$ remains invariant, with respect to I. Therefore M_0' belongs to $\mathfrak{L}$ and $\mathbf{M}_0\mathbf{M}_0'$ is a translation vector of the crystal. Let us now consider the transformation I_0 which is the product of I by a translation of vector $\mathbf{M}_0'\mathbf{M}_0$: it belongs to G_H and transforms P into P''. We have

$$\mathbf{P}'\mathbf{P}''=\mathbf{M}_0'\mathbf{M}_0. \tag{12}$$

By combining Eqs. (11) and (12), we obtain

$$\mathbf{M}_0\mathbf{P}+\mathbf{M}_0\mathbf{P}''=0. \tag{13}$$

Therefore, the transformation I_0 is an inversion with respect to M_0. Thus, if the crystal has a center of inversion, the sites M are also centers of inversions and, the Wannier function which corresponds to a site M must be symmetrical or antisymmetrical with respect to M.

Special attention is paid to the problem of simple bands, for crystals having a center of inversion, because in this case, we can prove directly the existence of Wannier functions decreasing exponentially at infinity. In other cases, (simple bands without centers of inversion, complex bands), a special difficulty prevents giving a really general proof of this possibility. The nature of this difficulty is explained in Sec. IIIC.

The Wannier functions can be defined now in terms of Bloch waves and conversely. By definition, the Wannier functions which are associated with a simple band $\mathfrak{B}$, are given in terms of the Bloch waves belonging to $\mathfrak{B}$ by

$$|M\rangle=\Omega^{-1/2}\int_{B.Z.} d^n\mathbf{K}\exp[-i(\mathbf{K}\cdot\mathbf{M}_0\mathbf{M})]|\varphi(\mathbf{K})\rangle. \tag{14}$$

The domain of integration is the Brillouin zone of volume Ω. The states $|\varphi(\mathbf{K})\rangle$ are normalized [see Eq. (2)]

$$\langle\varphi(\mathbf{K})|\varphi(\mathbf{K}')\rangle=\delta_c(\mathbf{K}-\mathbf{K}'), \tag{15}$$

and, therefore, we have

$$\langle M|M'\rangle=\delta_{MM'}. \tag{16}$$

Conversely, the Bloch states are sums of Wannier functions:

$$|\varphi(\mathbf{K})\rangle=\Omega^{-1/2}\sum_M \exp[i(\mathbf{K}\cdot\mathbf{M}_0\mathbf{M})]|M\rangle. \tag{17}$$

This expansion is a Fourier series with respect to $\mathbf{K}$ because the vectors $\mathbf{M}_0\mathbf{M}$ coincide with the translations $\mathbf{t}$ of the crystal. This expression can be written in a slightly different way. By using Eq. (1) and definition (14), we obtain

$$\langle\mathbf{r}|M\rangle=\langle\mathbf{r}+\mathbf{M}\mathbf{M}_0|M_0\rangle. \tag{18}$$

We can now apply this identity to transform Eq. (17)

$$\langle\mathbf{r}|\varphi(\mathbf{K})\rangle=\Omega^{-1/2}\sum_{\mathbf{t}} e^{i\mathbf{K}\mathbf{t}}\langle\mathbf{r}-\mathbf{t}|M_0\rangle. \tag{19}$$

This equation is convenient to discuss the connection which appears between the analyticity properties of the Bloch waves and the asymptotic properties of the Wannier functions. It is well known that the asymptotic behavior of the coefficients of a Fourier series is directly related to the analytic properties of the sum of the series. Actually, a direct application of a typical theorem (Sec. IIIB of paper II) shows that, if the function $\langle\mathbf{r}|\varphi(\mathbf{K})\rangle$ of the complex vector $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ is analytic in a strip of the complex $\mathbf{K}$ space defined by an equation $|\mathbf{K}''|<A$ (where A is a positive constant), then the Fourier coefficients $\langle\mathbf{r}+\mathbf{t}|M_0\rangle$ satisfy conditions of the form: (with $0<\epsilon<1$ and $\mathbf{r}$ fixed)

$$\lim_{t\to\infty} e^{\epsilon At}\langle\mathbf{r}+\mathbf{t}|M\rangle=0. \tag{20}$$

The converse is also true because the existence of relations of this kind [Eq. (20)] implies the uniform convergence of the series (19) in any compact region contained in the domain $|\mathbf{K}''|<A$.

Our problem is now reduced to the construction of Bloch functions which are analytic with respect to $\mathbf{K}$, in strips centered on the real $\mathbf{K}$ space. If this is possible, there exists always a set of localized Wannier functions.

B. Construction and Analyticity of the Bloch Waves

The operator of projection $P(\mathbf{K})$ on the Bloch state of wave number $\mathbf{K}$, belonging to a simple band $\mathfrak{B}$, can be defined directly by its matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$

$$\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle=\langle\mathbf{r}|\varphi(\mathbf{K})\rangle\langle\varphi(\mathbf{K})|\mathbf{r}'\rangle. \tag{21}$$

This definition is valid for real values of $\mathbf{K}$ only, but can be generalized without difficulty for complex values of $\mathbf{K}$. In paper II, it was shown that the matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$ are analytic functions of $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ in a domain defined by a condition of the form $|\mathbf{K}''|<A$, where A is a positive constant independent of $\mathbf{K}'$, $\mathbf{r}$, and $\mathbf{r}'$. This property of the matrix elements of $P(\mathbf{K})$ is used to build analytic Bloch waves.

The matrix elements $\langle \mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$ are invariant with respect to phase transformations of the wave function $\langle \mathbf{r}|\varphi(\mathbf{K})\rangle$. Therefore, in order to construct explicitly this function, we have to find a means of fixing its phase. We note that according to Eqs. (21), (17), and (16), we have

$$|\varphi(\mathbf{K})\rangle=\Omega^{1/2}P(\mathbf{K})|M_0\rangle. \quad (22)$$

Therefore, it seems natural to introduce a trial Wannier function $\langle \mathbf{r}|\bar{M}_0\rangle$ which is an arbitrary normalizable function and to define the Bloch waves by putting

$$|\varphi(\mathbf{K})\rangle=[G(\mathbf{K})]^{-1/2}P(\mathbf{K})|\bar{M}_0\rangle, \quad (23)$$

$$G(\mathbf{K})=\langle\bar{M}_0|P(\mathbf{K})|\bar{M}_0\rangle. \quad (24)$$

This Bloch function is obtained by projection of the trial Wannier function on the subspace which contains $|\varphi(\mathbf{K})\rangle$. This subspace is determined by $P(\mathbf{K})$. More precisely, we define $\langle \mathbf{r}|\varphi(\mathbf{K})\rangle$ by the following equations:

$$\langle \mathbf{r}|\varphi(\mathbf{K})\rangle=[G(\mathbf{K})]^{-1/2}\langle \mathbf{r}|\psi(\mathbf{K})\rangle, \quad (25)$$

$$\langle \mathbf{r}|\psi(\mathbf{K})\rangle=\int d^n\mathbf{r}'\langle \mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle\langle \mathbf{r}'|\bar{M}_0\rangle, \quad (26)$$

$$G(\mathbf{K})=\int d^n\mathbf{r}\int d^nr'\langle\bar{M}_0|\mathbf{r}\rangle\langle \mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle\langle \mathbf{r}'|\bar{M}_0\rangle. \quad (27)$$

Here $\langle \mathbf{r}|\psi(\mathbf{K})\rangle$ is not a normalized function and $[G(\mathbf{K})]^{-1/2}$ is the normalization factor. By definition, when $\mathbf{K}$ is real, $G(\mathbf{K})$ is non-negative but difficulties may arise if $G(\mathbf{K})$ vanishes for a real value of $\mathbf{K}$. For this reason, we choose trial functions $\langle \mathbf{r}|\bar{M}_0\rangle$ which have always the same symmetry properties as the true Wannier functions $\langle \mathbf{r}|M_0\rangle$. These symmetry requirements are determined by the structure of the band. (See paper I.)

The preceding formulas can be used for complex values of $\mathbf{K}$. The operator $P(\mathbf{K})$ is defined and analytic in the domain $|\mathbf{K}''|<A$ and Eq. (5) shows that for $|\mathbf{K}''|\leqslant B<A$, we have

$$|\langle \mathbf{r}|P(\mathbf{K})|\mathbf{r}'+\mathbf{t}\rangle|\leqslant e^{Bt}|\langle \mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle|. \quad (28)$$

In order to insure a uniform convergence of the integrals of Eq. (26) and (27), in any closed domain defined by an inequality of the form $|\mathbf{K}''|\leqslant B$, we choose a trial Wannier function which satisfies the condition

$$e^{Ar}|\langle \mathbf{r}|\bar{M}_0\rangle|<\infty. \quad (29)$$

For instance, we may choose a trial Wannier function with a cutoff ($\langle \mathbf{r}|M_0\rangle=0$ for $|\mathbf{r}|>R$). As the integrals converge uniformly the functions $\langle \mathbf{r}|\psi(\mathbf{K})\rangle$ and $G(\mathbf{K})$ are analytic with respect to $\mathbf{K}$, for $|\mathbf{K}''|<A$. On the other hand, by definition, for $\mathbf{K}$ real $G(\mathbf{K})$ is always finite, real, and non-negative. If $G(\mathbf{K})$ is strictly positive for real values of $\mathbf{K}$, the inequality $|G(\mathbf{K})|>0$ remains true in a domain defined by an equation of the form $|\mathbf{K}''|<A_0\leqslant A$ where A_0 is a positive constant. In this case, $[G(\mathbf{K})]^{-1/2}$ is analytic in the same domain. Consequently, $\langle \mathbf{r}|\varphi(\mathbf{K})\rangle$ is also an analytic function of $\mathbf{K}$, in the domain defined by $|\mathbf{K}''|<A_0$. The corresponding Wannier function decreases exponentially at infinity[5] as was predicted in Sec. IIIA.

Unfortunately, $G(\mathbf{K})$ may vanish for real values of $\mathbf{K}$. This fact introduces difficulties which are discussed in the next section.

C. Analyticity of $[G(K)]^{-1/2}$ and Existence of Localized Wannier Functions

The analyticity of the wave function $\langle \mathbf{r}|\varphi(\mathbf{K})\rangle$ depends essentially on the analyticity of the operator $[G(\mathbf{K})]^{1/2}$. Unfortunately, we do not know whether, by a proper choice of the trial Wannier function, it is always possible or not, to obtain functions $G(\mathbf{K})$ which do not vanish or real values for $\mathbf{K}$; actually this problem is of topological nature and may be difficult to solve directly. For this reason, in this section, we present only a discussion of the difficulties which are introduced by the fact that $G(\mathbf{K})$ may vanish for real values of $\mathbf{K}$.

We prove the possibility of building localized Wannier functions (with exponential tails) in the following cases. (1) The atoms are far apart. This is the strong binding limit. (2) The crystal is linear. The result is not new because the problem has been treated by Kohn.[3] (3) The crystal has a center of inversion. (4) The Hamiltonian of the problem depends on a real parameter and the property can be derived by continuation.

In the strong binding limit, when the atoms of the crystal are far apart, we can choose the atomic orbitals (with a cutoff) as trial functions. In the vicinity of the atom centered at the origin M_0, the Bloch function looks very much like the atomic orbital and therefore it can never be orthogonal to the trial Wannier function, which we are using. In this case, for real values of $\mathbf{K}$, $G(\mathbf{K})$ remains always positive.

Linear crystals can be treated also in a very simple way. Let us show that the vanishing of $G(K)$ for a value $K=K_0$, does not prevent us from building Bloch waves which are analytic for $K=K_0$. As $G(K)$ is analytic, it can be expanded in convergent series, in the vicinity of $K=K_0$, and, as it is non-negative for real values of K, this expansion can be written

$$G(K)=a^2(K-K_0)^{2p}[1+\epsilon(K-K_0)]. \quad (30)$$

Here a is a positive constant, p an integer and $\epsilon(K-K_0)$ an analytic function of K, which has a zero for $K=K_0$. Thus we have

$$[G(K)]^{1/2}=\pm a(K-K_0)^p[1+\epsilon(K-K_0)]^{1/2}. \quad (31)$$

We can choose a determination of $[G(K)]^{1/2}$ which is perfectly analytic for $K=K_0$. On the other hand, if

[5] Conversely, if there exist really localized Wannier functions, it is always possible to build functions $G(\mathbf{K})$ which never vanish for real values of $\mathbf{K}$; in fact, we may choose as trial Wannier functions, the true localized Wannier functions since we know that these functions have exponential tails.

$G(K)$ has a zero for $K=K_0$, it has a zero of the same order for $K=-K_0$. This is a consequence of Kramers degeneracy. Now we may always assume that $G(0)\neq 0$ and $G(\pi/L)\neq 0$ (L is the length of a cell). In this case, we see immediately that the determinations of $[G(K)]^{1/2}$ which are analytic are also periodic with the same period as $G(K)$. Therefore, these functions can be used to build Bloch waves. The function $[G(K)]^{-1/2}$ which appears in Eq. (25) has poles on the real axis but no branch points. However, for real values of K, the function $\langle r|\varphi(K)\rangle$ cannot have any pole; otherwise, it would not be normalized. This result is easy to understand. For $K=K_0$, the states $|\varphi(K)\rangle$ and $|\bar{M}_0\rangle$ are orthogonal to each other, and therefore for $K=K_0$, the function $\langle r|\psi(K)\rangle$ of Eqs. (25) and (26) vanishes. The zero of $\langle r|\psi(K)\rangle$ cancels the pole of $[G(K)]^{-1/2}$ and thus $\langle r|\varphi(K)\rangle$ has a finite limit when K approaches K_0. In brief, $\langle r|\varphi(K)\rangle$ is analytic everywhere on the real axis. The corresponding Wannier functions decrease exponentially and we find in this way the same result as Kohn.

In n-dimensional crystals, more serious difficulties appear. If $G(\mathbf{K}_0)=0$, the function $[G(\mathbf{K})]^{1/2}$ has a singularity for $\mathbf{K}=\mathbf{K}_0$ (for instance, an acnode) and often the effect of this singularity cannot be eliminated. This fact can be demonstrated as follows: By using another trial Wannier function $|\bar{M}_0'\rangle$, we can build a Bloch wave $\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle$ which is analytic in the vicinity of the value $\mathbf{K}=\mathbf{K}_0$. We have

$$P(\mathbf{K})=|\varphi'(\mathbf{K})\rangle\langle\varphi'(\mathbf{K})|\,. \tag{32}$$

Now, we can separate the real and the imaginary parts of $\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle$,

$$\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle=\langle\mathbf{r}|R(\mathbf{K})\rangle+i\langle\mathbf{r}|I(\mathbf{K})\rangle. \tag{33}$$

Thus, $P(\mathbf{K})$ can be written

$$P(\mathbf{K})=(|R(\mathbf{K})\rangle\langle R(\mathbf{K})|+|I(\mathbf{K})\rangle\langle I(\mathbf{K})|) -i(|R(\mathbf{K})\rangle\langle I(\mathbf{K})|-|I(\mathbf{K})\rangle\langle R(\mathbf{K})|)\,. \tag{34}$$

The Hamiltonian is real and therefore the Wannier functions can always be real; in the same way, the trial Wannier functions are always real. Thus, $G(\mathbf{K})$ is given by

$$G(\mathbf{K})=(\langle R(\mathbf{K})|\bar{M}_0\rangle)^2+(\langle I(\mathbf{K})|\bar{M}_0\rangle)^2. \tag{35}$$

Therefore, $G(\mathbf{K})$ has a zero if, for $\mathbf{K}-\mathbf{K}_0$

$$\langle R(\mathbf{K})|\bar{M}_0\rangle=0\,, \tag{36}$$

$$\langle I(\mathbf{K})|\bar{M}_0\rangle=0. \tag{37}$$

In general, these equations are independent of each other. Let us expand $\langle R(\mathbf{K})|\bar{M}_0\rangle$ and $\langle I(\mathbf{K})|\bar{M}_0\rangle$ in terms of the components of $(\mathbf{K}-\mathbf{K}_0)$. $G(\mathbf{K})$ is equivalent to a quadratic form, which, in general, is not the square of a linear form. For instance, for a two-dimensional crystal, we may write

$$G(\mathbf{K})\sim aK_x^2+2bK_xK_y+cK_y^2\,, \tag{38}$$

with

$$a>0 \quad c>0 \quad ac\geqslant b^2.$$

Since, in general, $ac>b^2$, the quadratic form is nondegenerate $[G(\mathbf{K})]^{1/2}$ remains positive and well defined in the vicinity of $K=K_0$, but retains a singularity at this point and cannot be used to build analytic Bloch waves. In this case, the Eqs. (36) and (37) define the singularities of $[G(\mathbf{K})]^{1/2}$; for $n=2$ we have isolated points (acnodes), for $n=3$ we have lines of singularities.

However, this situation does not occur when there is a center of inversion in the crystal. In this case, M_0 is also a center of inversion and the trial Wannier function $\langle\mathbf{r}|\bar{M}_0\rangle$ is symmetric or antisymmetric with respect to this point. Moreover, the Bloch function $\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle$ can be written in the form

$$\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle=\langle\mathbf{r}|S(\mathbf{K})\rangle+i\langle\mathbf{r}|A(\mathbf{K})\rangle\,, \tag{39}$$

where the functions $\langle\mathbf{r}|S(\mathbf{K})\rangle$ and $\langle\mathbf{r}|A(\mathbf{K})\rangle$ are real and respectively symmetric and antisymmetric (for instance, this fact can be proved by remarking that the function $[\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle+(\langle-\mathbf{r}|\varphi'(\mathbf{K})\rangle)^*]$ is a Bloch wave of wave vector $\mathbf{K}$, if it does not vanish identically). We see immediately that we have

$$G(\mathbf{K})=(\langle S(\mathbf{K})|\bar{M}_0\rangle)^2,\ \text{if}\ \langle r|M_0\rangle\ \text{is symmetric}, \tag{40}$$

$$G(\mathbf{K})=(\langle A(\mathbf{K})|\bar{M}_0\rangle)^2,\ \text{if}\ \langle r|M_0\rangle\ \text{is antisymmetric}. \tag{41}$$

In this case, $[G(\mathbf{K})]^{1/2}$ is analytic and real: as the signs are irrelevant here, we put simply

$$[G(\mathbf{K})]^{1/2}=\langle\varphi'(\mathbf{K})|\bar{M}_0\rangle. \tag{42}$$

Finally Eqs. (23) and (32) show that we have

$$\langle\mathbf{r}|\varphi(\mathbf{K})\rangle=\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle. \tag{43}$$

This equation gives several pieces of information: (1) As $\langle\mathbf{r}|\varphi'(\mathbf{K})\rangle$ is analytic for $\mathbf{K}=\mathbf{K}_0$, the function $\langle\mathbf{r}|\varphi(\mathbf{K})\rangle$ is also analytic for $\mathbf{K}=\mathbf{K}_0$ in spite of the fact that we have $G(\mathbf{K}_0)=0$. (2) Equation (43) shows also that our method leads always to the same result which is independent of the initial choice of $\langle\mathbf{r}|\bar{M}_0\rangle$. (3) As the reasoning is valid also for complex values of $\mathbf{K}$, we see that the functions $\langle\mathbf{r}|\varphi(\mathbf{K})\rangle$ have in the $\mathbf{K}$ space the same singularities as the matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$.

When the crystal has no center of inversion, it is difficult to prove directly the existence of localized Wannier functions but sometimes this property can be established indirectly. Such a situation will be described now. Our assumptions are the following. (1) The Hamiltonian $H\{\lambda\}$ is a good continuous function of a real parameter λ; for instance, we may have $H=H_0+\lambda V$. (2) For $\lambda=\lambda_0$, there exists a band $\mathcal{B}\{\lambda_0\}$ which can be described in terms of localized Wannier functions. (3) When λ belongs to a compact neighborhood Λ of λ_0, the band $\mathcal{B}\{\lambda\}$ can be traced by continuity and never touches any other band corresponding to the same value of λ. (4) In order to remain consistent with the point of view of paper I, we need also the following symmetry condition: for $\lambda\neq\lambda_0$, the space group $G_H\{\lambda\}$ of invariance of $H\{\lambda\}$ is independent of λ, and we have also $G_H\{\lambda\}\subset G_H\{\lambda_0\}$.

Let us show now that for values of λ belonging to Λ, these conditions imply the possibility of describing the band $\mathcal{B}\{\lambda\}$ in terms of localized Wannier functions. With each band $\mathcal{B}\{\lambda\}$, we can associate the operator $P\{\lambda\}$ of projection on the set of all the eigenfunctions of $H\{\lambda\}$ which belong to $\mathcal{B}\{\lambda\}$. According to Eq. (8) we have

$$P^2\{\lambda\}=P\{\lambda\}\,, \tag{44}$$

and we know also (see Sec. II) that the matrix elements $\langle\mathbf{r}|P\{\lambda\}|\mathbf{r}'\rangle$ decrease exponentially when $|\mathbf{r}-\mathbf{r}'|$ goes to infinity. For each value of λ, there exists a constant $A\{\lambda\}$ which is the largest number for which we have $(0<\epsilon<1)$

$$\lim_{t\to\infty}\exp[\epsilon t A\{\lambda\}]\langle\mathbf{r}+\mathbf{t}|P\{\lambda\}|\mathbf{r}\rangle=0\,. \tag{45}$$

$A\{\lambda\}$ is strictly positive and continuous with respect to λ. As the domain Λ is compact by definition, the lower bound of $A\{\lambda\}$ is also a strictly positive number A and for any value of λ belonging to Λ, we have

$$\lim_{t\to\infty}e^{\epsilon A t}\langle\mathbf{r}+\mathbf{t}|P\{\lambda\}|\mathbf{r}\rangle=0\,. \tag{46}$$

We assume now the existence of the Wannier functions $\langle\mathbf{r}|M\{\lambda_0\}\rangle$ associated with $\mathcal{B}\{\lambda_0\}$ and we want to build Wannier functions $\langle\mathbf{r}|M\{\lambda\}\rangle$ for $\mathcal{B}\{\lambda\}$. We note that we have

$$\langle M'\{\lambda_0\}|M\{\lambda_0\}\rangle=\delta_{MM'}\,, \tag{47}$$

$$|M\{\lambda_0\}\rangle=P\{\lambda_0\}|M\{\lambda_0\}\rangle\,. \tag{48}$$

These equations suggest defining $|M\{\lambda\}\rangle$ by a method of continuous projection, i.e., by the differential equation

$$\partial_\lambda|M\{\lambda\}\rangle=\partial_\lambda P\{\lambda\}|M\{\lambda\}\rangle\,. \tag{49}$$

In order to take the initial condition into account, we may write also in a more explicit way

$$\langle\mathbf{r}|M\{\lambda\}\rangle=\langle\mathbf{r}|M\{\lambda_0\}\rangle+\int_{\lambda_0}^{\lambda}d\lambda\int d^n\mathbf{r}'\langle\mathbf{r}|\partial_\lambda P\{\lambda\}|\mathbf{r}'\rangle\langle\mathbf{r}'|M\{\lambda\}\rangle\,. \tag{50}$$

On the other hand, for $\lambda=\lambda_0$, we may assume

$$\lim_{t\to\infty}e^{\epsilon Bt}\langle\mathbf{r}+\mathbf{t}|M_0\{\lambda\}\rangle=0\quad(0<\epsilon<1)\,. \tag{51}$$

It is clear now, that as a consequence of Eqs. (50) and (45), the same property must be valid also for all the values of λ which belong to Λ.

We have now to verify that the functions $\langle\mathbf{r}|M\{\lambda\}\rangle$ are really Wannier functions. As a result of our assumption (4) and of the invariance properties of the operator $P\{\lambda\}$, the functions $\langle\mathbf{r}|M\{\lambda\}\rangle$ have exactly the required symmetry properties. Therefore, there remains to show that they are orthonormal and that they span the band $\mathcal{B}\{\lambda\}$. These conditions can be written explicitly,

$$P\{\lambda\}|M\{\lambda\}\rangle=|M\{\lambda\}\rangle\,, \tag{52}$$

$$\langle M'\{\lambda\}|M\{\lambda\}\rangle=\delta_{MM'}\,. \tag{53}$$

They can be derived easily by taking into account the fact that $P\{\lambda\}$ is a projection operator. By differentiation of Eq. (44) ,we get:

$$\partial_\lambda P\{\lambda\}P\{\lambda\}+P\{\lambda\}\partial_\lambda P\{\lambda\}=\partial_\lambda P\{\lambda\}\,. \tag{54}$$

By using definition (49) and this equation, we obtain the identity

$$\begin{aligned}\partial_\lambda[P\{\lambda\}|M\{\lambda\}\rangle-|M\{\lambda\}\rangle]&=P\{\lambda\}\partial_\lambda P\{\lambda\}|M\{\lambda\}\rangle\\&=-\partial_\lambda P\{\lambda\}[P\{\lambda\}|M\{\lambda\}\rangle-|M\{\lambda\}\rangle].\end{aligned} \tag{55}$$

Now, we use the initial condition (48). Equation (55) shows that the relation (48) is also valid for any value of λ belonging to Λ. The orthogonality relations can be derived in the same way: we use first the equation of definition (49) and the fact that $P\{\lambda\}$ is Hermitian, then Eq. (50) and last Eq. (49), to obtain the following identities:

$$\begin{aligned}\partial_\lambda\langle M'\{\lambda\}|M\{\lambda\}\rangle&=2\langle M'\{\lambda\}|\partial_\lambda P\{\lambda\}|M\{\lambda\}\rangle\\&=\langle M'\{\lambda\}|(P\{\lambda\}\partial_\lambda P\{\lambda\}+\partial_\lambda P\{\lambda\}P\{\lambda\})|M\{\lambda\}\rangle\\&=\langle M'\{\lambda\}|\partial_\lambda P\{\lambda\}|M\{\lambda\}\rangle.\end{aligned} \tag{56}$$

Finally, we get, by comparison of these equalities,

$$\partial_\lambda\langle M'\{\lambda\}|M\{\lambda\}\rangle=0\,. \tag{57}$$

The orthogonality condition (53) is a direct consequence of this relation and of the initial condition (47).

IV. WANNIER FUNCTIONS FOR COMPLEX BANDS IN AN INFINITE CRYSTAL

A. Wannier Functions and Symmetry Properties of the Crystal

A definition of generalized Wannier functions for complex bands and a description of their symmetry properties has been given by the author in paper I, where a group theoretical point of view was adopted. On the contrary, we want to show here how to build explicitly, really localized Wannier functions and therefore, we are mainly concerned with analyticity properties. However, in order to introduce proper notations, it is useful to summarize the general properties of our Wannier functions, in agreement with the point of view expressed in I.

The one-electron Hamiltonian H is assumed to be invariant with respect to the transformations of a space group G_H which contains as a subgroup, the group T of translations of the crystal. The Wannier functions are associated with the sites M of a lattice which is generated by applying all the elements of G_H to an arbitrary point M_0. Therefore, $\mathcal{L}$ is also invariant with respect to

G_H. In general, $\mathfrak{L}$ is not a Bravais lattice (translation lattice) but can be split into J Bravais lattices $\mathfrak{L}_j$ $[j=0\cdots(J-1)]$. They are generated by applying the elements of T to J points M_j of $\mathfrak{L}$. These points M_j, by definition, are the origins of the sublattices $\mathfrak{L}_j$ and cannot be obtained from each other by translations belonging to T.

The elements of G_H which leave a site M invariant define a subgroup G_H. The Wannier functions which are associated with M_0 form a basis of an irreducible representation $\Gamma_{M_0}{}^m$ of G_{M_0}. They are denoted by the symbol $\langle \mathbf{r}|M_0(m,\mu)\rangle$ where μ is an index which is used to label the different basic vectors of the representation. The index m is considered as fixed but μ may take all possible values. On the other hand, with each site M, we associate one element S_{MM_0} of G_H, which has the property of transforming M_0 into M. An isomorphism of G_M and G_{M_0} is introduced by establishing a correspondence between the elements R_M of G_M and R_{M_0} of G_{M_0}

$$R_M=S_{MM_0}R_{M_0}S_{MM_0}{}^{-1}. \tag{58}$$

The Wannier functions corresponding to a site M are conveniently defined in terms of the Wannier function attached to the origin M_0 of the lattice, by putting

$$|M(m,\mu)\rangle=S_{MM_0}|M_0(m,\mu)\rangle. \tag{59}$$

The functions $\langle \mathbf{r}|M(m,\mu)\rangle$ form a basis of an irreducible representation $\Gamma_M{}^m$ of G_M, isomorphic to $\Gamma_{M_0}{}^m$. More explicitly, we may write

$$R_M|M(m,\mu)\rangle=\sum_\nu |M(m,\nu)\rangle\langle\nu|{}^mR_M|\mu\rangle. \tag{60}$$

The matrix ${}^mR_M$ is a representation of R_M which belongs to $\Gamma_M{}^m$ and we have according to Eqs. (58) and (59)

$$\langle\nu|{}^mR_M|\mu\rangle\equiv\langle\nu|{}^mR_{M_0}|\mu\rangle. \tag{61}$$

For reasons of simplicity, the set of elements S_{MM_0} is chosen as follows. First, we pick in G_M, J elements $S_{M_jM_0}$ transforming M_0 into M_j, respectively; in particular, $S_{M_0M_0}$ is identified with the unit element of G_H. On the other hand, any point M of $\mathfrak{L}$ belongs to one sublattice $\mathfrak{L}_j$ (more exactly $\mathfrak{L}_{j(M)}$) and the translation T_{MM_j} which transforms M_j into M is an element of G_H. Therefore, S_{MM_0} can be defined in a general way, by putting

$$S_{MM_0}=T_{MM_j}S_{M_jM_0}\quad (M\in\mathfrak{L}_j). \tag{62}$$

When a set of Wannier functions can be used to describe a band $\mathfrak{B}$, these functions can be expressed linearly in terms of the Bloch waves belonging to $\mathfrak{B}$ and conversely. Moreover, the Wannier functions are orthornormal,

$$\langle M'(m,\mu')|M(m,\mu)\rangle=\delta_{MM'}\delta_{\mu\mu'}. \tag{63}$$

The structure of the band determines the lattice $\mathfrak{L}$ and the representation $\Gamma_{M_0}{}^m$. For instance, let d be the number of independent Bloch waves which, for each value of $\mathbf{K}$, belong to $\mathfrak{B}$ and let d^m be the dimensionality of $\Gamma_{M_0}{}^m$. As the Wannier functions must span exactly the space defined by the Bloch waves of $\mathfrak{B}$, we must have

$$d=Jd^m. \tag{64}$$

Other symmetry requirements must also be fulfilled, but in the following, it is assumed that the structure of $\mathfrak{B}$ is compatible with a given type of Wannier function; this type is determined by $\mathfrak{L}$ and $\Gamma_{M_0}{}^m$.

B. Definition of Quasi Bloch Waves in Terms of Wannier Functions

In this section, we assume the existence of a set of Wannier functions $\langle \mathbf{r}|M(m,\mu)\rangle$. Now for each value of $\mathbf{K}$ we associate with each sublattice $\mathfrak{L}_j$, a quasi Bloch wave $\langle \mathbf{r}|\varphi_j(\mathbf{K},m,\mu)\rangle$ which is defined in analogy with Eq. (17) by

$$|\varphi_j(\mathbf{K},m,\mu)\rangle=\Omega^{-1/2}\sum_{M\epsilon\mathfrak{L}_j}\exp[i(\mathbf{K}\,\mathbf{M}_j\mathbf{M})]|M(m,\mu)\rangle. \tag{65}$$

Ω is the volume of the Brillouin zone. The orthogonality properties of the Wannier functions imply [see Eq. (58)]

$$\langle\varphi j'(\mathbf{K}',m,\mu')|\varphi j(\mathbf{K},m,\mu)\rangle=\delta(\mathbf{K}-\mathbf{K}')\delta_{jj'}\delta_{\mu\mu'}. \tag{66}$$

We remark that according to Eq. (64), for each value of $\mathbf{K}$, the number of quasi Bloch waves is equal to the number d of Bloch waves. This is consistent with the fact that the Wannier functions can be expressed in terms of the quasi Bloch waves. If M belongs to $\mathfrak{L}_j$, $|M(m,\mu)\rangle$ is given by

$$|M(m\,\mu)\rangle=\Omega^{-1/2}\int_{B.Z.}d^n\mathbf{K}\times\exp[-i(\mathbf{K}\,\mathbf{M}_j\mathbf{M})]|\varphi_j(\mathbf{K},m,\mu)\rangle. \tag{67}$$

In complete analogy with the case of simple bands, we can transform Eq. (65), in order to obtain

$$\langle\mathbf{r}|\varphi_j(\mathbf{K},m,\mu)\rangle=\Omega^{-1/2}\sum_{\mathbf{t}}e^{i\mathbf{K}\mathbf{t}}\langle\mathbf{r}-\mathbf{t}|M_j(m,\mu)\rangle. \tag{68}$$

As before, we represent by $\mathbf{t}$ the translation vectors of the crystal.

Again, by applying always the same theorem on Fourier series, we know that if it is possible to build quasi Bloch waves which are analytic with respect to $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ in a domain $|\mathbf{K}''|<A$, then there exists a set of Wannier functions which decrease exponentially at infinity. More precisely, these Wannier functions satisfy the relations

$$\lim_{t\to\infty}e^{\epsilon At}\langle\mathbf{r}+\mathbf{t}|M_j(m,\mu)\rangle=0\quad 0<\epsilon<1. \tag{69}$$

For this reason, in the following, we do not assume *a priori* the existence of a defined set of Wannier functions but we try to build quasi Bloch waves directly by using the operator $P(\mathbf{K})$; this task is performed in the Sec. IIID. Afterwards, it will be possible to introduce

Wannier functions by using Eq. (67). But first, the characteristic properties of the Bloch waves which we want to obtain must be determined.

C. General Properties of the Quasi Bloch Waves

A set of waves $\langle \mathbf{r} | \varphi_j(\mathbf{K},m,\mu)\rangle$ can be considered as a set of quasi Bloch waves, if the functions $\langle \mathbf{r} | M(m,\mu)\rangle$ which are obtained by application of Eq. (67) are really Wannier functions; more precisely, the functions $\langle \mathbf{r} | M(m,\mu)\rangle$ must fulfill the following requirements: (1) They satisfy orthogonality conditions [Eq. (63)]. (2) They span the space defined by the Bloch waves belonging to $\mathcal{B}$. (3) They satisfy symmetry conditions [Eqs. (59) and (60)].

Consequently the waves $\langle \mathbf{r} | \varphi_j(\mathbf{K},m,\mu)\rangle$ must satisfy also a set of three conditions:

(1) They must be orthonormal.

(2) For each real value of $\mathbf{K}$, the states $| \varphi_j(\mathbf{K},m,\mu)\rangle$ span the space $\mathcal{S}(\mathbf{K})$ defined by the Bloch states of wave vector $\mathbf{K}$ belonging to $\mathcal{B}$.

(3) They have symmetry properties which will be examined now.

The reciprocal space vector which is the transform of a wave vector $\mathbf{K}$ by a point group operation corresponding to an element R of the space group G_H is denoted by $R\mathbf{K}$.

The symmetry properties of the Wannier functions are summarized by the Eqs. (59) and (60) and lead to the following relations which are consequences of definition (65):

$$R_{M_0} | \varphi_0(\mathbf{K},m,\mu)\rangle = \sum_\nu | \varphi_0(R_{M_0}\mathbf{K},m,\nu)\rangle\langle \nu | {}^m R_{M_0} | \mu\rangle, \quad (70)$$

$$S_{M_jM_0} | \varphi_0(\mathbf{K},m,\mu)\rangle = | \varphi_j(S_{MM_0}\mathbf{K},m,\mu)\rangle. \quad (71)$$

Conversely, if these symmetry conditions hold for a set of waves $\langle \mathbf{r} | \varphi_j(\mathbf{K},m,\mu)\rangle$, the corresponding Wannier functions satisfy the required symmetry conditions.

D. Direct Construction of Quasi Bloch Waves

When the band $\mathcal{B}$ is complex ($d = 1$), the Bloch waves of wave vector $\mathbf{K}$ belonging to $\mathcal{B}$ form the basis of a subspace $\mathcal{S}(\mathbf{K})$ of dimension d which is also spanned by the quasi Bloch waves which correspond to the same value. Therefore the projection operator $P(\mathbf{K})$ on $\mathcal{S}(\mathbf{K})$ can be written [compare with Eq. (4)]

$$P(\mathbf{K}) = \sum_{j,\mu} | \varphi_j(\mathbf{K},m,\mu)\rangle\langle \varphi_j(\mathbf{K},m,\mu) | . \quad (72)$$

Moreover, we note that according to Eq. (65) we have

$$| \varphi_j(\mathbf{K},m,\mu)\rangle = \Omega^{1/2} P(\mathbf{K}) | M_j(m,\mu)\rangle. \quad (73)$$

In order to build directly quasi Bloch waves, we want to generalize the method of Sec. IIIB and the preceding formula shows clearly how to proceed.

We introduce a set of trial Wannier functions $|\bar{M}(m,\mu)\rangle$ which have the same symmetry properties as the Wannier functions which we are trying to obtain, namely:

$$R_M | \bar{M}(m,\mu)\rangle = \sum_\nu | \bar{M}(m,\nu)\rangle\langle \nu | {}^m R_M | \mu\rangle, \quad (74)$$

$$| \bar{M}(m,\mu)\rangle = S_{MM_0} | \bar{M}_0(m,\mu)\rangle. \quad (75)$$

Thus, these trial functions which correspond to a site M form a basis for the irreducible representation $\Gamma_M{}^m$ of G_M. For reasons of convergence, we choose functions which decrease exponentially (or faster) at infinity. For instance, for $|\mathbf{r}-\mathbf{r}_M| > R$ the functions $\langle \mathbf{r} | M(m,\mu)\rangle$ may be equal to zero, for $|\mathbf{r}-\mathbf{r}_M| \leqslant R$, they may be equal to a polynomial function of the components of $(\mathbf{r}-\mathbf{r}_M)$. As G_M is a subgroup of the full rotation group (with reflections) around M, the symmetry requirements can be fulfilled easily.

Now the unnormalized wave $\langle \mathbf{r} | \psi_j(\mathbf{K},m,\mu)\rangle$ can be defined by putting

$$| \psi_j(\mathbf{K},m,\mu)\rangle = P(\mathbf{K}) | \bar{M}_j(m,\mu)\rangle. \quad (76)$$

In order to transform this wave into a quasi Bloch wave, we introduce a finite orthonormalization matrix $G(\mathbf{K})$ which is defined by its matrix elements

$$\langle j,\mu | G(\mathbf{K}) | j',\mu'\rangle = \langle \bar{M}_j(m,\mu) | P(\mathbf{K}) | \bar{M}_{j'}(m,\mu')\rangle. \quad (77)$$

This matrix is of order d [see Eq. (64)] and, for real values of $\mathbf{K}$, it is Hermitian and non-negative. These properties are trivial consequences of its definition. If $G(\mathbf{K})$ remains positive for real values of $\mathbf{K}$, it is possible to define $G^{1/2}(\mathbf{K})$ as the positive definite matrix of which the square is $G(\mathbf{K})$. Finally, quasi Bloch waves are introduced by putting

$$| \varphi_j(\mathbf{K},m,\mu)\rangle = \sum_{j'\mu'} | \psi_{j'}(\mathbf{K},m,\mu')\rangle\langle j'\mu' | G^{-1/2}(\mathbf{K}) | j\mu\rangle. \quad (78)$$

We must verify that this definition is compatible with the requirements which must be met by the quasi Bloch waves. The introduction of the normalization matrix $G(\mathbf{K})$ insures the validity of orthogonality relations; in fact, by taking Eqs. (78), (76), and (6) into account, we get

$$\begin{aligned}\langle \varphi_j(\mathbf{K},m,\mu) | \varphi_{j'}(\mathbf{K}',m,\mu')\rangle &= \delta_c(\mathbf{K}-\mathbf{K}') \sum_{\substack{j''\mu'' \\ j'''\mu'''}} \langle j\mu | G^{-1/2}(\mathbf{K}) | j''\mu''\rangle \\ &\quad \times \langle M_{j''}(m,\mu'') | P(\mathbf{K}) | M_{j'''}(m,\mu''')\rangle \\ &\quad \times \langle j'''\mu''' | G^{-1/2}(\mathbf{K}) | j'\mu'\rangle \\ &= \delta_c(\mathbf{K}-\mathbf{K}')\delta_{jj'}\delta_{\mu\mu'}. \end{aligned} \quad (79)$$

On the other hand, the states $|\psi_j(\mathbf{K},m,\mu)\rangle$ and $| \varphi_j(\mathbf{K},m,\mu)\rangle$ belong to the subspace $\mathcal{S}(\mathbf{K})$ by definition. As, for each value of $\mathbf{K}$, there are d states $| \varphi_j(\mathbf{K},m,\mu)\rangle$

which are orthogonal to each other, [see Eq. (64)], they span $\mathcal{S}(\mathbf{K})$ completely.

Now, we must check the symmetry properties of the states $|\varphi_j(\mathbf{K},m,\mu)\rangle$. It is clear that, by construction, the states $|\psi_j(\mathbf{K},m,\mu)\rangle$ satisfy symmetry conditions analogous to Eqs. (70) and (71) and, therefore, they have exactly the symmetry properties required for the states $|\varphi_j(\mathbf{K},m,\mu)\rangle$. On the other hand, it is easy to show that the introduction of the normalization matrix does not destroy the symmetry of the problem. For instance, if we replace the origin M_{j_0} of a sublattice $\mathcal{L}_{j_0}$ by another point M_{j_0}' of the same sublattice, the states $|\psi_{j_0}(m,\mu)\rangle$ are multiplied by the phase factor $\exp[i\mathbf{K}\cdot\mathbf{M}_{j_0}'\mathbf{M}_{j_0}]$ whereas the other states $|\psi_j(\mathbf{K},m,\mu)\rangle$ (with $j\neq j_0$) remain invariant. But the replacement of M_{j_0} by M_{j_0}' leads also to a unitary transformation of the Hermitian matrix $G(\mathbf{K})$. As a result of both effects, the quasi Bloch waves $|\varphi_j(\mathbf{K},m,\mu)\rangle$ defined by Eq. (78) undergo the same phase transformation as the states $|\psi_j(\mathbf{K},m,\mu)\rangle$. The validity of the symmetry conditions given by Eqs. (70) and (71) appears, now, as a rather trivial consequence of this remark; a general space transformation introduces a permutation of the sublattices $\mathcal{L}_j$ and also a change in the origins of each sublattice but it is very easy to take care of this fact by suitable phase transformations of all the waves; therefore, the states $|\varphi_j(\mathbf{K},m,\mu)\rangle$ have the same symmetry properties as the states $|\psi_j(\mathbf{K},m,\mu)\rangle$.

Thus, our method of constructing quasi Bloch waves works well when it is possible to give a precise meaning to the definitions (76) and (78) of the states $|\psi_j(\mathbf{K},m,\mu)\rangle$ and $|\varphi_j(\mathbf{K},m,\mu)\rangle$.

E. Analyticity Properties of the Quasi Bloch Waves

In order to define quasi Bloch waves more explicitly, we may use an ordinary space representation for the states and operators. Thus, Eqs. (76), (77), and (78) can be written

$$\langle\mathbf{r}|\psi_j(\mathbf{K},m,\mu)\rangle=\int d^n\mathbf{r}'\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle\langle\mathbf{r}'|\bar{M}_j(m,\mu)\rangle, \quad (80)$$

$$\langle j\mu|G(\mathbf{K})|j'\mu'\rangle=\int d^n\mathbf{r}d^n\mathbf{r}'\langle\bar{M}_j(m,\mu)|\mathbf{r}\rangle \times\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle\langle r'|M_{j'}(m,\mu')\rangle, \quad (81)$$

$$\langle\mathbf{r}|\varphi_j(\mathbf{K},m,\mu)\rangle=\sum_{j'\mu'}\langle\mathbf{r}|\psi_{j'}(\mathbf{K},m,\mu')\rangle \times\langle j'\mu'|[G(\mathbf{K})]^{-1/2}|j\mu\rangle. \quad (82)$$

The fact that $\mathcal{B}$ is now a complex band does not prevent the matrix elements $\langle\mathbf{r}|P(\mathbf{K})|\mathbf{r}'\rangle$ from being analytical with respect to $\mathbf{K}=\mathbf{K}'+i\mathbf{K}''$ in a strip $|\mathbf{K}''|<A$ where A is a positive constant independent of $\mathbf{K}'$, $\mathbf{r}$, and $\mathbf{r}'$. On the other hand, we choose trial Wannier functions which decrease exponentially at infinity as in the case of simple bands; for instance, they may satisfy the conditions

$$\lim_{r\to\infty} e^{Ar}\langle\mathbf{r}|\bar{M}_j(m,\mu)\rangle<\infty\,. \quad (83)$$

Since Eq. (28) remains valid for complex bands, we see immediately that the functions $\langle\mathbf{r}|\psi_j(\mathbf{K},m,\mu)\rangle$ and the finite matrix $G(\mathbf{K})$ are analytic functions of $\mathbf{K}$ in the domain $|\mathbf{K}''|<A$.

On the other hand, by definition, for real values of $\mathbf{K}$, $G(\mathbf{K})$ is an Hermitian non-negative operator and in many cases may be really a strictly positive operator. For real values of $\mathbf{K}$, we can define $[G(\mathbf{K})]^{1/2}$ as the non-negative matrix of which the square is $G(\mathbf{K})$. If $G(\mathbf{K})$ is strictly positive, for real values of $\mathbf{K}$, $[G(\mathbf{K})]^{1/2}$ can be continued analytically in a strip of the complex $\mathbf{K}$ space $|\mathbf{K}''|<C\leqslant A$ where C is a positive constant. In this case, $[G(\mathbf{K})]^{-1/2}$ is also analytic in the same domain and by using Eq. (82), we define a quasi Bloch wave $\langle\mathbf{r}|\varphi(\mathbf{K},m,\mu)\rangle$ which is also analytic in the domain $|\mathbf{K}''|<C$. Accordingly, the corresponding Wannier functions $\langle\mathbf{r}|M(m,\mu)\rangle$ decrease exponentially at infinity. On the contrary, if one or several of the eigenvalues of $G(\mathbf{K})$ vanishes for real values of $\mathbf{K}$, we meet the same kind of difficulty as in the case of simple bands, and, in general, the difficulty does not disappear if the crystal has a center of inversion [for instance, if two eigenvalues of $G(\mathbf{K})$ vanish at the same time].

However, in the tight binding limit, by choosing atomic orbitals (with a cutoff) as trial Wannier functions, it is always possible to build a matrix $G(\mathbf{K})$ which remains strictly positive in the real $\mathbf{K}$ space. [This is case (1) of Sec. IIIC.] On the other hand, this result can be extended a little further by using a perturbation method. [This is case (4) of Sec. IIIC.] We consider a Hamiltonian $H\{\lambda\}$ which is a good continuous function of the real parameter λ and we assume that a band $\mathcal{B}\{\lambda_0\}$ can be spanned by a set of localized Wannier functions. For values of λ belonging to a compact neighborhood Λ of λ_0, the band $\mathcal{B}\{\lambda\}$ can be treated by continuity and remains isolated. Now, we can introduce the Wannier function $\langle\mathbf{r}|M(m,\mu,\lambda)\rangle$ by using the operator $P\{\lambda\}$ which is associated with $\mathcal{B}\{\lambda\}$. By definition, they are solutions of the equation

$$\partial_\lambda|M(m,\mu,\lambda)\rangle=\partial_\lambda P\{\lambda\}|M(m,\mu,\lambda)\rangle. \quad (84)$$

We can take also into account the initial condition by putting

$$|M(m,\mu,\lambda)\rangle=|M(m,\mu,\lambda_0)\rangle+\int_{\lambda_0}^{\lambda} d\lambda\partial_\lambda P\{\lambda\}|M(m,\mu,\lambda)\rangle. \quad (85)$$

The method which is used in Sec. IIIC to prove the validity of this kind of definition can be generalized in a straightforward manner; it can be shown also by applying the same kind of arguments that the functions

$\langle \mathbf{r} | M_j(m,\mu,\lambda) \rangle$ decrease exponentially when $|\mathbf{r}|$ becomes infinite. These results are really independent of all consideration of symmetry. However, if we want to build Wannier functions $\langle \mathbf{r} | M(\dot{m},\mu,\lambda) \rangle$ which satisfy the symmetry requirements listed in Sec. IVA, we must assume also that the Hamiltonians $H\{\lambda\}$ have suitable symmetry properties. For instance, we are safe, if the symmetry properties of $H\{\lambda\}$ are independent of λ.

Thus, when the band $\mathcal{B}$ is complex, it is often possible to build really localized Wannier functions. Unfortunately, our method is not completely satisfactory, because we do not know whether it can be applied with success in any case. Some ambiguities remain also in the definition of the quasi Bloch waves. As the reader will realize, these waves depend to a certain extent of the shape of the trial Wannier functions and we do not know yet what is the best way of selecting these functions.

V. SUMMARY AND CONCLUSION

In an n-dimensional crystal, the energy bands can be simple ($d=1$) or complex ($d>1$) but, by definition, they are always assumed isolated from each other. The space of functions defined by the set of all the Bloch waves which belong to a given band can often be spanned by a set of Wannier functions attached to the sites of a lattice $\mathcal{L}$ (which is not always a translation lattice). In this case, the structure of the band determines the lattice and the symmetry properties of the Wannier functions, as was shown in paper I. However, these symmetry requirements do not indicate how to build properly localized Wannier functions.

On the other hand, the Bloch waves of wave vector $\mathbf{K}$ which belong to a given band $\mathcal{B}$ define a subspace $\mathcal{S}(\mathbf{K})$ of dimension d and the operator $P(\mathbf{K})$ of projection on $\mathcal{S}(\mathbf{K})$ has interesting analyticity properties which have been derived in paper II. Actually, the matrix elements $\langle \mathbf{r} | P(\mathbf{K}) | \mathbf{r}' \rangle$ can be defined for complex values of $\mathbf{K}$ and are analytic with respect to $\mathbf{K} \equiv \mathbf{K}' + i\mathbf{K}''$ in a strip of the complex $\mathbf{K}$ space defined by an equation of the form $|\mathbf{K}''| < A$ where A is a constant independent of $\mathbf{K}$, $\mathbf{r}$ and $\mathbf{r}'$.

Both results are used to build localized Wannier functions. First, we introduce trial Wannier functions which are well localized and have the same symmetry properties as the Wannier functions which we want to obtain. Then, with the help of these trial functions and by using the operator $P(\mathbf{K})$, we build, for each value of $\mathbf{K}$, Bloch waves ($d=1$) or quasi Bloch waves which span the subspace $\mathcal{S}(\mathbf{K})$ and are orthonormal. Afterwards, Wannier functions are obtained directly by integration of these waves with respect to $\mathbf{K}$ in the Brillouin zone. If the waves are analytic with respect to $\mathbf{K} = \mathbf{K}' + i\mathbf{K}''$ in a strip of the complex $\mathbf{K}$ space given by an equation of the form $|\mathbf{K}''| < B$, then the corresponding Wannier functions have exponentially decreasing tails and the converse is also true. As in general the analyticity of the operator $P(\mathbf{K})$ entails the analyticity of the waves which are built by using this operator, we have a means of proving the existence of really localized Wannier functions in n-dimensional crystals.

Unfortunately, the normalization of the waves introduces square roots in our formulas, and this fact creates a difficulty; the analyticity of the waves which are built by our method can be destroyed by the introduction of branch points for real values of $\mathbf{K}$, and we do not know whether, in the general case, this bad situation can always be avoided by a proper choice of the trial Wannier function.

However, when the band is simple, the difficulty mentioned above does not appear (1) if the crystal is linear or (2) if the crystal has a center of inversion. When at least one of these conditions is realized, the Bloch waves have the same domain of analyticity as the matrix elements $\langle \mathbf{r} | P(\mathbf{K}) | \mathbf{r}' \rangle$. Moreover, if the crystal has a center of inversion and if the band is simple, the Wannier functions are determined and independent of the particular shape of the Wannier function which has been used to build the corresponding Bloch waves; in this case they are also symmetric or antisymmetric with respect to the sites around which they are located.

More generally, the difficulty can be often avoided by selecting properly our trial Wannier functions, and for instance in the following cases for which the band can be simple or complex. (a) In the tight binding limit, we can choose atomic orbitals (with a cutoff) as trial functions. (b) The Hamiltonian can be considered sometimes as a continuous function of a real parameter λ. Then if a band $\mathcal{B}\{\lambda\}$ of $H\{\lambda\}$ is well defined and isolated for $\lambda = \lambda_0$, it can be traced by continuity in a neighborhood Λ of λ_0; in this neighborhood Λ, it remains isolated, and if the symmetry properties of $H\{\lambda\}$ are suitable, $\mathcal{B}\{\lambda\}$ retains its general structure. In this case, if $\mathcal{B}\{\lambda_0\}$ can be described in terms of localized Wannier functions, then, for values of λ belonging to Λ, the same property remains valid for $\mathcal{B}\{\lambda\}$.

Thus, the existence of Wannier functions decreasing exponentially at infinity has been established for n-dimensional crystals in many cases. On the other hand, it is very easy to show that the Wannier functions which correspond to a band in a finite crystal are directly related to the Wannier functions of the corresponding infinite crystal, and have very similar properties.