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Multipole wave functions for photoelectrons in crystals. III. The role of singular points in the band structure and the tails of the Wannier functions

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Properties of multipole wave functions and of Wannier functions are studied jointly, because both are generated by unitary transformations of Bloch waves and because their symmetry and localization depend on the analytic behavior and phase normalization of Bloch waves. Fourier theory relates the amplitude and convergence of the tails of Wannier functions to the singularities of Bloch waves in $\vec{k}$ space, specifically to the contribution of singularities to integrals over $\vec{k}$. These singularities may include branch cut surfaces bounded by curves of degeneracy. We discuss the convergence of the coefficients of a linear-combination-of-atomic-orbitals expansion in orbitals introduced recently by Kohn, which are Fourier coefficients of the eigenvectors $\vec{U}^{(\omega)}(\vec{k})$ of the Hamiltonian in Kohn's basis. The phases of Bloch waves are fixed by a constraint on the Wannier functions. The symmetry of Bloch waves determines then both the species and the center of symmetry of the Wannier functions. An application to the conduction band of copper is presented. Contributions of neighborhoods of loci of degeneracy in the Brillouin zone to the multipole wave functions are singled out and the rate of convergence of their Wannier series is examined. The series converges faster than the corresponding Wannier series of Bloch waves.

I. INTRODUCTION

The work reported in the present paper originates from a program to construct crystal wave functions adapted to the point-group symmetry about an isolated impurity. The purposes and approach of the program are outlined in the Introduction to the companion paper.[1] Here, however, we deal with broader questions of band theory that had to be settled in order to proceed with that program.

In the physics of crystalline matter one faces the task of separating local properties, which depend on the chemical bonding, from long-range properties. In the one-electron-band approximation, this dichotomy can be discussed in terms of the localization properties of the two generally employed basis sets of functions:

(i) The Bloch waves $\varphi_\mu(\vec{r};\vec{k})$ are characterized by moduli with the full translational symmetry of the crystal. Their analytic dependence on the wave vector $\vec{k}$ has singularities which relate to long-range order and which will be discussed extensively in this paper.

(ii) The Wannier functions $a_\mu(\vec{r}-\vec{n})$ are localized about individual lattice sites $\vec{n}$. This basis is thus suitable to describe local effects, but each of its elements has also a long-range tail which is associated to the singularities of the $\varphi_\mu(\vec{r};\vec{k})$, as we shall see.

The two sets of functions are related by the unitary Fourier transformation

$$a_\mu(\vec{r}-\vec{n}) = \frac{1}{\sqrt{\Omega}} \int_\Omega d\vec{k}\, \varphi_\mu(\vec{r};\vec{k}) e^{-i\vec{k}\cdot\vec{n}}, \qquad (1.1)$$

where Ω stands both for the Brillouin zone and for its volume. Bloch functions have served as the basis set for solving the majority of problems in the physics of crystalline media. This is because one was mainly interested in physical effects characterized by momenta $\vec{k}$ belonging only to *small portions* of the Brillouin zone. Limited efforts have thus been directed to the calculation of Wannier functions. This paper will study in particular the contrasting properties of the Bloch and the Wannier functions on an equal footing, interconnecting them by the theory of Fourier analysis.

This study appears particularly desirable at this time owing to two new developments. One development stems from Kohn's[2] proposal to construct the Wannier functions as superpositions of exponentially localized atomiclike orbitals, i.e., in chemical language, by LCAO. These orbitals and the Wannier functions are calculated variationally, without advance knowledge of the Bloch waves. The other development is our own program, mentioned above,[1,3,4] which made it necessary to identify the effects of the nonanalyticity of the Bloch waves about the loci of degeneracy. Points of degeneracy in the Brillouin zone are an analog of the level crossings of independent electron orbitals in molecules. As for molecules, the degeneracies will be lifted by the interactions among electrons and phonons, but nonanalytical singularities will remain nearby in the complex domain of $\vec{k}$ vectors. This paper intends to bring out combined implications of these developments. We note at the outset that degeneracies in condensed matter are known to be related to long-range order,[5] even though we do not attain yet a

full interpretation of this connection.

More specifically, our apprach starts from breaking the matrix elements of the unitary transformation (1.1) between Bloch waves and Wannier functions into contributions from the various symmetry species Γi,[4]

$$e^{i\vec{n}\cdot\vec{k}} = \sum_{\Gamma i}\sum_{Lq} \langle \vec{n}|\Gamma i L q\rangle_{E_\mu} P_{Lq}^{(\Gamma i)}(\vec{k};E_\mu)\,, \qquad (1.2)$$

where

$$\langle \vec{n}|\Gamma i L q\rangle_{E_\mu} = \frac{1}{\Omega}\oint_{E_\mu(\vec{k})=E} \frac{dS_{E_\mu}}{|\vec{\nabla}_{\vec{k}} E_\mu(\vec{k})|} \times P_{Lq}^{(\Gamma i)}(\vec{k};E_\mu) e^{i\vec{k}\cdot\vec{n}}\,. \qquad (1.3)$$

Equation (1.2) extends to nonspherical symmetries the partial wave expansion of a plane wave. The vector $\vec{k}$ ranges here over the constant-energy surface $E_\mu(\vec{k})=E$, whose harmonics are the polynomials $P_{Lq}^{(\Gamma i)}(\vec{k};E_\mu)$.[1] The relevance of the decomposition (1.2) results from two considerations:

(a) All symmetries of the system, i.e., translational, point group, and time reversal, will be taken into account consistently by specifying details of the integration process in Eq. (1.1) which defines the Wannier functions. Specifically, we shall have to define properly the relative phases of the Bloch waves with different momenta $\vec{k}$, a goal whose desirability has been stressed repeatedly but never attained in the literature.[2] The analysis of the Fourier transformation in terms of symmetry species will provide the framework for attaining this goal, much as the Lie algebra of angular momenta does for the phases of spherical harmonics and of more general atomic wave functions.

(b) Following Lighthill's approach to Fourier analysis,[6] we shall investigate separately the Bloch waves near their singularities which contribute long tails to the Wannier functions. In fact, these tails cannot be neglected if one wants to reproduce the Bloch functions *everywhere* in the Brillouin zone. By contrast, the multipole wave functions are obtained by *integrating* over all Bloch waves of given energy, $E_\mu(k)=E$. Contributions from small neighborhoods of the points of discontinuity can, therefore, be neglected for many practical purposes. Note particularly that when a Fourier series is slowly convergent or even not convergent at all, its term-by-term integration yields a series which converges faster and irrespective of the convergence of the original series.[7] This property, and many others, are well established only for functions of a single variable; their extension to functions of three variables, such as the components of $\vec{k}$, is still under development.

In the course of this work I have encountered many problems that had been raised previously. The framework which underlies this paper seems to have helped in removing obstacles. Thus we note that the points of degeneracy in the Brillouin zone are responsible for the long-range order and for the characteristics of the tails of the Wannier functions; by contrast the bulk of the Brillouin zone appears to contribute only local properties. Further, the study of particular examples suggests that the successive bands of a crystal may be classified by the symmetry properties of their Wannier functions. These properties depend essentially on the treatment of degeneracy points and curves. They include the identification of centers of symmetry for the various Wannier functions which may belong to different Bravais lattices, displaced one with respect to another.

Sections II–IV of this paper introduce a number of conventions, definitions, and mathematical statements. Sections V and VI contain the essential developments, illustrated by a simple example in Sec. VII. Sections VIII–X deal with the main application to the *s-d* bands of Cu and to the construction of the corresponding multipole wave functions.

II. FOURIER ANALYSIS OF THE BLOCH WAVES

Here, we regard the Bloch waves $\varphi_\mu(\vec{r};\vec{k})$ as functions of the continuous variable $\vec{k}$, while the space coordinate $\vec{r}$ is considered as a parameter. Because crystal momenta $\vec{k}$ differing by vectors of the reciprocal lattice are physically equivalent, the vector $\vec{k}$ is confined to vary within the Brillouin zone (or fundamental domain), Ω. Equivalently, we may set the periodicity condition

$$\varphi_\mu(\vec{r};\vec{k}+\vec{h}) = \varphi_\mu(\vec{r};\vec{k}) \qquad (2.1)$$

for any vector $\vec{h}$ of the reciprocal lattice and for all $\vec{r}$. Here we assume that the "band" index μ labels a well-defined, periodic function of $\vec{k}$, which is an eigenfunction of the one-electron crystal Hamiltonian $\hat{H}_c$. The actual definition of a "band" will be discussed in Sec. III.

The Bloch waves, considered as functions of $\vec{k}$, belong to the class of mathematical functions called *piecewise smooth*, which are generally studied through their Fourier series. In the case of Bloch wave, the series is

$$\varphi_\mu(\vec{r};\vec{k}) = \frac{1}{\sqrt{\Omega}}\sum_{\vec{n}} a_\mu(\vec{r};\vec{n}) e^{i\vec{n}\cdot\vec{k}}\,, \qquad (2.2)$$

where $\vec{n}$ is a vector of the physical lattice. The translational invariance of the crystal requires the Fourier coefficients to satisfy

$$a_\mu(\vec{r};\vec{n}) = a_\mu(\vec{r}-\vec{n})\,. \qquad (2.3)$$

The Fourier coefficients (or Wannier functions) $a_\mu(\vec{r}-\vec{n})$ are then obtained by the inversion formula, Eq. (1.1).

Whereas Fourier series of piecewise smooth functions of one variable have been investigated extensively,[8] the same does not hold for functions of several variables. I am indebted to Professor R. Fefferman for bringing several results to my attention. Apart from convergence properties to be discussed in Sec. V and of term-by-term integration discussed in Sec. IX, the following general properties are relevant:

(i) First of all, the summation over the three-dimensional net of points in Eq. (2.2) acquires a definite meaning only after we specify the procedure for performing the sum. We choose to sum first over each "shell" of lattice vectors, the nth shell being defined as the set of lattice nodes having equal distance $n=|\vec{n}|$ from a fixed node of the Bravais lattice taken as the origin. (Lattice nodes belonging to the same shell can be grouped into "stars" of nodes related to each other by operations of the point group of the Bravais lattice.) The subsequent summation over $|\vec{n}|$ is then one dimensional. The equality sign in Eq. (2.2) must be thus understood as the limit of finite sums, over $|\vec{n}|\leq N$, when $N\to\infty$. That is, we set

$$\sum_{\vec{n}} \equiv \lim_{N\to\infty} \sum_{n=0}^{N} \sum_{|\vec{n}|=n} . \tag{2.4}$$

Any truncation of the infinite sum constitutes an *analytic approximation* to the Bloch wave $\varphi_\mu(\vec{r};\vec{k})$, whose nonanalytic behavior about the loci of degeneracy manifests itself in slow convergence of the series. Moreover, we stress that the choice of *spherical partial sums ensures uniform convergence* of the Fourier series (2.2) in every subdomain of the Brillouin zone where the Bloch function is continuous.

(ii) The Fourier coefficients of any piecewise smooth function have the property

$$\lim_{|\vec{n}|\to\infty} |a_\mu(\vec{r};\vec{n})| = 0 . \tag{2.5}$$

This equation holds regardless of the direction of $\vec{n}$. Equation (2.5) ensures that the tails of the Wannier functions $a_\mu(\vec{r}-\vec{n})$ will fall off for $|\vec{r}-\vec{n}|\to\infty$. The rate of the falloff is determined, as we shall see, by the nature of the singularities of the Bloch waves about loci of degeneracy.

(iii) The expansion of a function in Fourier series tends to emphasize the behavior of the function *in the large*, i.e., over the whole fundamental domain. For instance, the zero-th Fourier coefficient represents the average value of the function. In contrast with the coefficients of a local Taylor expansion, which are obtained by differentiation, the Fourier coefficients are, in fact, obtained by integration. Conversely, a *single point* $\vec{k}_0$ of nonanalyticity of the Bloch wave $\varphi_\mu(\vec{r};\vec{k})$ affects the convergence of the Fourier series (2.2) *everywhere* in the Brillouin zone. This is a well-known problem with any Fourier series, which makes it impractical in many cases.

(iv) Among the methods which can be used to improve the convergence of a Fourier series are: (a) "adjusting" the function in a neighborhood of small measure of the loci of discontinuity so that the high Fourier coefficients of the "adjusted" function will converge to zero at any desired rate. In this way, one gains uniform and rapid convergence at the price of reproducing the original function everywhere *except* in the neighborhood of the loci of discontinuity; and (b) integrating the function represented by the series causes the series of integrals to converge uniformly as noted in Sec. I. Furthermore, integration will improve the rate of convergence of the series by smoothing its singularities.

As we recalled in Sec. I, our main goal is to construct multipole wave function, which are obtained by integrating over all Bloch waves of given energy $E_\mu(\vec{k})=E$. We can thus use the *smoothing effect of the integration* to improve the convergence of the Fourier (Wannier) series of the Bloch waves, Eq. (2.2). To do this, we follow Lighthill's approach[6] and split any Bloch function $\varphi_\mu(\vec{r};\vec{k})$ into the sum of a smooth well-behaved function $\bar{\varphi}_\mu(\vec{r};\vec{k})$, whose Fourier coefficients $\bar{a}_\mu(\vec{r}-\vec{n})$ converge to zero for large $|\vec{n}|$ at any desired rate, and of a remainder $\Phi_\mu(\vec{r};\vec{k})$, which is appreciably different from zero only in a neighborhood of small measure of the loci of nonanalyticity of the original function, $\varphi_\mu(\vec{r};\vec{k})$:

$$\varphi_\mu(\vec{r};\vec{k}) = \bar{\varphi}_\mu(\vec{r};\vec{k}) + \Phi_\mu(\vec{r};\vec{k}) , \tag{2.6}$$

$$a_\mu(\vec{r}) = \bar{a}_\mu(\vec{r}) + \alpha_\mu(\vec{r}) . \tag{2.7}$$

By construction, $\varphi_\mu(\vec{r};\vec{k})$ and $\Phi_\mu(\vec{r};\vec{k})$ have the same singularities, so that their Fourier coefficients, $a_\mu(\vec{r})$ and $\alpha_\mu(\vec{r})$ will coincide as $|\vec{r}|\to\infty$.

The decomposition in (2.6) is, of course, not unique. It will, in fact, depend on the degree of accuracy one wants to achieve by summing over a given number of shells. In any specific case, the contribution of the remainder $\Phi_\mu(\vec{r};\vec{k})$ to the multipole wave functions depends on the constant energy surface, $E_\mu(\vec{k})=E$, under consideration, and can be estimated. This contribution can presumably be neglected for many purposes. We thus conclude that, while the Fourier (Wannier) series might be impractical for representing

Bloch functions for a band with points of degeneracy, it can nevertheless serve well for expressing the set of multipole wave functions.

III. KOHN METHOD AND THE ANALYTICITY OF BLOCH FUNCTIONS

We shall use here the Kohn representation[2] as a framework to study the analyticity of Bloch functions and, first of all, to specify a meaning of the "band" index μ. This representation enables us to locate more precisely the origin of the singularities of Bloch functions and then to evaluate the magnitude of the tails of Wannier functions.

The method proposed by Kohn consists of an *ab initio* variational calculation which generates a set of atomiclike orbitals, $\{a_{\Gamma i,\gamma}(\vec{r})\}$, from which an optimized band structure can, in turn, be obtained. By construction, the orbitals $a_{\Gamma i,\gamma}(\vec{r})$ are orthonormal over different lattice sites and exponentially localized; the tail of Wannier functions results from superposition of orbitals centered at different sites.

One starts by selecting a set of $\mathfrak{N}$ bands. For the sake of definiteness, we will restrict the discussion to the s-d bands of metallic copper. Nine orbitals are needed to describe these bands with $\Gamma \equiv \{A_{1g}, E_g, T_{2g}, T_{1u}\}$. Here, Γ stands for an irreducible representation of the point group of the crystal (O_h for Cu) and i for one of its rows. That is,

$$a_{\Gamma i,\gamma}(R\vec{r}) = \sum_{j=1}^{\dim(\Gamma)} a_{\Gamma j,\gamma}(\vec{r}) D^{(\Gamma)}_{ji}(R^{-1}), \tag{3.1}$$

where $\dim(\Gamma)$ means "dimension of the irreducible representation Γ," for any operation R of the point group. The index γ, which distinguishes different orbitals belonging to the same row of the same irreducible representation, is superfluous for the s-d bands of Cu, but we will keep it in the course of the formal discussion.

Then, one constructs $\mathfrak{N}$ Bloch sums at each $\vec{k}$,

$$S_{\Gamma i,\gamma}(\vec{r};\vec{k}) \equiv \frac{1}{\sqrt{\Omega}} \sum_{\vec{n}} a_{\Gamma i,\gamma}(\vec{r}-\vec{n}) e^{i\vec{n}\cdot\vec{k}}, \tag{3.2}$$

and represents the Bloch waves $\varphi_\mu(\vec{r};\vec{k})$ as

$$\varphi_\mu(\vec{r};\vec{k}) = \sum_{\{\Gamma i,\gamma\}} S_{\Gamma i,\gamma}(\vec{r};\vec{k}) U^{(\mu)}_{\Gamma i,\gamma}(\vec{k}). \tag{3.3}$$

The fact that the $\varphi_\mu(\vec{r};\vec{k})$ are eigenfunctions of the crystal Hamiltonian $\hat{H}_c$ implies that the coefficients $\vec{U}^{(\mu)}(\vec{k})$ are the eigenvectors of the Hamiltonian matrix

$$\langle \Gamma i,\gamma | \mathcal{E}(\vec{k}) | \Gamma' i',\gamma' \rangle \equiv \sum_{\vec{n}} \langle a_{\Gamma i,\gamma}(\vec{r}) | \hat{H}_c | a_{\Gamma' i',\gamma'}(\vec{r}-\vec{n}) \rangle e^{i\vec{n}\cdot\vec{k}}, \tag{3.4}$$

corresponding to the band eigenvalues $E_\mu(\vec{k})$. Note that:

(i) The number of Bloch sums to be included in the expansion (3.3) should, of course, increase as the energy range of interest increases or as higher accuracy is sought, as one does in quantum chemistry.

(ii) Equations (3.2)–(3.4) resemble a tight-binding method, but the $\{a_{\Gamma i,\gamma}(\vec{r})\}$ are *not* free-atom orbitals. They are obtained by a first principle variational procedure so that the eigenvalues $E_\mu(\vec{k})$ of the matrix (3.4) are optimized band eigenvalues.

(iii) Owing to the exponential localization of the orbitals $\{a_{\Gamma i,\gamma}(\vec{r})\}$, the Bloch sums (3.2) and the matrix elements (3.4) are analytic functions of $\vec{k}$.[9,10] Singularities of the Bloch waves, $\varphi_\mu(\vec{r};\vec{k})$, as functions of $\vec{k}$, are thus traced to *singularities in the eigenvectors* $\vec{U}^{(\mu)}(\vec{k})$.

The band index μ will be labeled in order of increasing energy at each $\vec{k}$, i.e., according to the customary "ordered labeling." This choice is, however, not altogether trivial. A different device is made in diatomic molecules, whose Hamiltonian depends on a single parameter[11]; the molecular argument has also led to departures from the usual practice in crystals,[12] even though the relevant Hamiltonian matrix depends on the three components of $\vec{k}$. We base the choice of ordered labeling on analytic continuation of $E_\mu(\vec{k})$ starting from a nondegenerate reference point $\vec{k}_i$. Analytic continuation is possible and appropriate because both $E_\mu(\vec{k})$ and the Bloch functions $\varphi_\mu(\vec{r};\vec{k})$ are analytic throughout the Brillouin zone except at points of degeneracy.[13] As $\vec{k}$ approaches any point of degeneracy, analytic continuation must follow a path that bypasses that point and one verifies that ordered labeling is preserved along the path.[14] The characteristic behavior of the eigenvalues, $E_\mu(\vec{k})$, and the eigenvectors, $\vec{U}^{(\mu)}(\vec{k})$, about the loci of degeneracy will be discussed in Sec. V.

IV. WANNIER FUNCTIONS AND KOHN'S ORBITALS

As in Sec. II, we consider a Wannier function $a_\mu(\vec{r}-\vec{n})$ as a Fourier coefficient of the expansion of the Bloch wave $\varphi_\mu(\vec{r};\vec{k})$ as function of $\vec{k}$ and for a particular band. In Sec. III we have defined the bands through a process of analytic continuation covering the whole Brillouin zone. In this section we will express the set of Wannier functions $\{a_\mu(\vec{r}-\vec{l})\}$ in terms of the set of Kohn's orbitals, $\{a_{\Gamma i,\gamma}(\vec{r}-\vec{n})\}$, associated with a chosen set of $\mathfrak{N}$ bands. We shall express the Wannier functions thus defined as combinations of orthogonalized atomic orbitals with LCAO coefficients, in a form that permits the identification and estimation of

their long tails.

Because the matrix elements (3.4) are periodic in $\vec{k}$, with the periodicity of the reciprocal lattice, its eigenvectors can also be taken as periodic,

$$\vec{U}^{(\mu)}(\vec{k}+\vec{h}) = \vec{U}^{(\mu)}(\vec{k}) , \tag{4.1}$$

and can be expanded in Fourier series:

$$\vec{U}^{(\mu)}(\vec{k}) = \sum_{\vec{m}} \vec{u}^{(\mu)}(\vec{m}) e^{i\vec{m}\cdot\vec{k}} . \tag{4.2}$$

The Fourier coefficients $\vec{u}^{(\mu)}(\vec{m})$ are determined by the inversion formula

$$\vec{u}^{(\mu)}(\vec{m}) = \frac{1}{\Omega} \int_{\Omega} d\vec{k}\, \vec{U}^{(\mu)}(\vec{k}) e^{-i\vec{k}\cdot\vec{m}} . \tag{4.3}$$

Here again, Ω stands both for the Brillouin zone and for its volume. Insertion of Eq. (4.2) into the expansion (3.3) gives

$$\varphi_{\mu}(\vec{r};\vec{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\vec{l}} \left(\sum_{\vec{n}} \sum_{\{\Gamma i,\gamma\}} a_{\Gamma i,\gamma}(\vec{r}-\vec{n}) u^{(\mu)}_{\Gamma i,\gamma}(\vec{l}-\vec{n}) \right) \times e^{i\vec{l}\cdot\vec{k}} . \tag{4.4}$$

Comparing this result with the Fourier series (2.2), we get the desired relationship

$$a_{\mu}(\vec{r}-\vec{l}) = \sum_{\vec{n}} \sum_{\{\Gamma i,\gamma\}} a_{\Gamma i,\gamma}(\vec{r}-\vec{n}) u^{(\mu)}_{\Gamma i,\gamma}(\vec{l}-\vec{n}) , \tag{4.5}$$

which expresses the Wannier function $a_{\mu}(\vec{r}-\vec{l})$ centered at the lattice site $\vec{l}$, as a linear superposition of the Kohn's orbitals $\{a_{\Gamma i,\gamma}(\vec{r}-\vec{n})\}$ centered at all surrounding sites.

The functions

$$u^{(\mu)}_{\Gamma i,\gamma}(\vec{l}-\vec{n}) = u^{(\mu)}_{\Gamma i,\gamma}(\vec{l};\vec{n}) \equiv \langle \Gamma i,\gamma;\vec{n}|\mu;\vec{l}\rangle , \tag{4.6}$$

constitute the matrix elements of the *unitary transformation* between the sets $\{a_{\Gamma i,\gamma}(\vec{r}-\vec{n})\}$ and $\{a_{\mu}(\vec{r}-\vec{l})\}$. In particular, the moduli of these matrix elements obey the "sum rule"

$$\sum_{\vec{n}} \vec{u}^{(\mu)}(\vec{n})^* \cdot \vec{u}^{(\mu)}(\vec{n}) = 1 , \tag{4.7}$$

where the scalar product of vectors $\vec{u}^{(\mu)}(\vec{n})$ implies a sum over their component indices $\{\Gamma i,\gamma\}$. As in Sec. II, the equality sign must be understood as the limit of a sequence of partial sums over an increasing number of shells of lattice vectors. Equation (4.7) thus specifies how many shells must be included for the sum to become arbitrarily close to unity.

Section V will study the convergence of the Fourier series (4.2) in some cases of interest. Owing to the exponential localization of the orbitals $\{a_{\Gamma i,\gamma}(\vec{r}-\vec{n})\}$, the *falloff of the envelope of the tails* of the Wannier function $a_{\mu}(\vec{r})$ is determined by the rate of *convergence of the Fourier coefficients* $\vec{u}^{(\mu)}(\vec{n})$ for $|\vec{n}| \to \infty$. The magnitude of the tails will depend on the contribution of large $|\vec{n}|$ terms to the normalization sum (4.7).

V. AYMPTOTIC BEHAVIOR OF THE WANNIER FUNCTIONS AND THE SINGULARITIES OF $\vec{U}^{(\mu)}(\vec{k})$

According to Sec. III both $E_{\mu}(\vec{k})$ and the eigenvectors $\vec{U}^{(\mu)}(\vec{k})$ of Eq. (3.3) are defined by analytic continuation and have singularities at the loci of degeneracy. However, the eigenvectors have stronger singularities owing to their orthonormalization condition

$$\vec{U}^{(\mu)}(\vec{k})^* \cdot \vec{U}^{(\mu')}(\vec{k}) = \delta_{\mu\mu'} . \tag{5.1}$$

We describe here examples concerning the s-d bands of Cu.

We start by splitting $\vec{U}^{(\mu)}(\vec{k})$ in analogy to Eq. (2.6),

$$\vec{U}^{(\mu)}(\vec{k}) = \vec{V}^{(\mu)}(\vec{k}) + \vec{W}^{(\mu)}(\vec{k}) , \tag{5.2}$$

where $\vec{V}^{(\mu)}(\vec{k})$ is analytic in the whole Brillouin zone and $\vec{W}^{(\mu)}(\vec{k})$ differs from zero appreciably only in a neighborhood of small measure of the loci of discontinuity. The Fourier coefficients (4.3) are similarly split as

$$\vec{u}^{(\mu)}(\vec{m}) = \vec{v}^{(\mu)}(\vec{m}) + \vec{w}^{(\mu)}(\vec{m}) , \tag{5.3}$$

where $\vec{v}^{(\mu)}(\vec{m})$ decays exponentially for large $|\vec{m}|$, whereas $\vec{w}^{(\mu)}(\vec{m})$ is responsible for the long tails of the Wannier functions.

Degeneracy in the s-d bands of Cu occurs either along lines of symmetry in the Brillouin zone (essential degeneracy) or along curves in symmetry planes (accidental degeneracy between inequivalent representations). Moreover, the inversion symmetry of the crystal allows curves of degeneracy to occur also at general points (accidental degeneracy between equivalent representations).[15] We discuss in detail the examples of the essential degeneracy at the line Δ (A) and the accidental degeneracy along a curve through the point W (B).

Example A. The threefold degenerate irreducible representation Γ'_{25} decomposes into the singly degenerate Δ'_2 and the twofold degenerate Δ_5, so that two bands stick together along the symmetry line $\Delta \equiv (0, k_y, 0)$. To find the behavior of the eigenvectors $\vec{U}^{(\mu)}(\vec{k})$ about Δ, we need to diagonalize only the submatrix of the Hamiltonian matrix (3.4) in the space of the two Bloch sums which are degenerate along Δ. These sums are constructed from orbitals $\Gamma i \equiv (d_{yz}, d_{yx})$ and we call them $S_{yz}(\vec{r};\vec{k})$ and $S_{yx}(\vec{r};\vec{k})$. Expanding Eq. (3.4) for small values of the coordinates k_z and k_x in a plane orthogonal to Δ up to second order, one may show that

$$\langle yz|\mathcal{E}(\vec{k})|yz\rangle \simeq \alpha - \beta k_z^2 - \gamma k_x^2,$$
$$\langle yz|\mathcal{E}(\vec{k})|yx\rangle \simeq \delta k_z k_x, \tag{5.4}$$
$$\langle yx|\mathcal{E}(\vec{k})|yx\rangle \simeq \alpha - \gamma k_z^2 - \beta k_x^2.$$

The parameters α, β, γ, and δ are analytic functions of the coordinate k_y along Δ. Introducing cylindrical coordinates (ρ, ϕ, ζ) about the Δ line, we find that for small values of ρ (i) the matrix elements (5.4) depend on 2ϕ; (ii) the two eigenvalues can be expressed in the form

$$E_{(\pm)}(\rho, \phi, \zeta) = \alpha + \rho^2 f_{(\pm)}(\phi, \zeta); \tag{5.5}$$

(iii) the eigenvectors $\vec{U}^{(\pm)}(\rho, \phi, \zeta)$ are independent of ρ, single valued in ϕ, and analytic in ζ. Therefore, they have a jump discontinuity across the Δ line. The nonanalytic part can then be expressed as

$$\vec{W}^{(\pm)}(\rho, \phi, \zeta) = e^{-\rho/\lambda}\vec{Z}^{(\pm)}(\phi, \zeta). \tag{5.6}$$

Here λ is a linear measure of the neighborhood of the line Δ where $\vec{W}^{(\pm)}$ is appreciably different from zero. The analytic part $\vec{V}^{(\pm)}$ vanishes instead at $\rho = 0$ without any discontinuity.

The Fourier coefficients $\vec{w}^{(\mu)}(\vec{m})$ are obtained by entering the expression (5.6) in the integral of Eq. (4.3). They decay exponentially for $|\vec{m}| \to \infty$ in the ζ direction and fall off as $|\vec{m}|^{-2}$ as $|\vec{m}| \to \infty$ in any direction orthogonal to ζ.

Example B. At the point $W \equiv (\pi/a)(1, 2, 0)$ on the boundary of the Brillouin zone we deal with two Bloch sums $S_{xy}(\vec{r}; \vec{k})$ and $S_{xz}(\vec{r}; \vec{k})$ which are degenerate by symmetry. In a neighborhood of W the Hamiltonian submatrix analogous to (5.4) is

$$\langle xy|\mathcal{E}(\vec{q})|xy\rangle \simeq \alpha - \beta q_x + \gamma q_y^2 + \delta q_z^2,$$
$$\langle xy|\mathcal{E}(\vec{q})|xz\rangle \simeq \eta q_y q_z, \tag{5.7}$$
$$\langle xz|\mathcal{E}(\vec{q})|xz\rangle \simeq \alpha + \beta q_x + \delta q_y^2 + \gamma q_z^2,$$

where $\vec{q} \equiv \vec{k} - \vec{k}_W$ and the parameters α, β, γ, δ, and η are constant. From the structure of this matrix we see that its two eigenvalues vary quadratically with $|\vec{q}|$ along the Q line ($q_x = 0$ and $q_y + q_z = 0$) but linearly along the Z line ($q_y = q_z = 0$), and that $\vec{\nabla}_{\vec{q}} E_{(\pm)}(\vec{q})$ vanishes at W along $\hat{q}_y$ and $\hat{q}_z$ while it is discontinuous along $\hat{q}_x$. (W is a singular critical point.[16]) Moreover, the degeneracy persists along a curve in the symmetry plane $k_z = 0$. This curve is tangent to the q_y axis at W; it is also seen to cross the line Σ at about $\frac{2}{3}$ of the distance ΓK by inspection of Fig. 3 of Ref. 17.

Let us now consider the behavior of the eigenvectors of the matrix (5.7) around a loop which encloses the curve of degeneracy. Specifically, we consider a small circle in the plane $-q_y = q_{y_0} \ll \pi/a$ with radius $\rho = (q_x^2 + q_z^2)^{1/2}$ and center at $q_x = q_z = 0$. On this circle the matrix (5.7) reduces to

$$\langle xy|\mathcal{E}(\vec{q})|xy\rangle \simeq \alpha - \beta q_x,$$
$$\langle xy|\mathcal{E}(\vec{q})|xz\rangle \simeq B q_z, \tag{5.8}$$
$$\langle xz|\mathcal{E}(\vec{q})|xz\rangle \simeq \alpha + \beta q_x,$$

to lowest order in q_x and q_z, and where $B = \eta q_{y_0}$. Introducing cylindrical coordinates (ρ, ϕ, ζ) about the q_y axis, we find that for small values of ρ (i) the matrix elements (5.8) depend on ϕ in contrast to their 2ϕ dependence in example A; (ii) the eigenvalues can be expressed in the form

$$E_{(\pm)}(\rho, \phi, \zeta) = \alpha + \rho g_{(\pm)}(\phi, \zeta); \tag{5.9}$$

(iii) the eigenvectors $\vec{U}^{(\pm)}(\rho, \phi, \zeta)$ are independent of ρ, single valued in $\frac{1}{2}\phi$, and analytic in ζ.

As we analytically continue the eigenvectors $\vec{U}^{(\pm)}$ around any loop which encloses the curve of accidental degeneracy, the eigenvectors are now seen to change sign when ϕ increases by 2π. A *branch cut* is thus required. This surface of discontinuity might be placed anywhere about the curve of degeneracy. However, we shall see that the Wannier function can be symmetry adapted to the point group of the crystal only if the surface of discontinuity is placed *in the plane of symmetry* on one side of the curve of degeneracy.

Proceeding as in example A one finds the Fourier coefficients, $\vec{w}^{(\pm)}(\vec{m})$, to fall off as $|\vec{m}|^{-1}$ for $|\vec{m}| \to \infty$ in the direction orthogonal to the plane surface of discontinuity. The behavior for $|\vec{m}| \to \infty$ parallel to the surface of discontinuity is more involved because it depends, in general, on the shape of the curve of degeneracy. In any case, the falloff will not be slower than $|m_i|^{-1}$ in any direction.

This discussion of the singular functions $\vec{W}^{(\mu)}(\vec{k})$ and of their Fourier coefficients $\vec{w}^{(\mu)}(\vec{m})$ enables one to estimate the magnitude of the tails of the Wannier functions as represented by the functions $\alpha_\mu(\vec{r})$ of Eq. (2.7). The contribution of $\alpha_\mu(\vec{r})$ to the normalization integral of the Wannier functions reflects the contribution of $\vec{W}^{(\mu)}(\vec{k})$ to the integral

$$\Omega^{-1}\int_\Omega d\vec{k}\, \vec{U}^{(\mu)}(\vec{k})^* \cdot \vec{U}^{(\mu)}(\vec{k}) = 1.$$

One can thus show that

$$\int d\vec{r}\{|\alpha_\mu(\vec{r})|^2 + 2\,\mathrm{Re}[\alpha_\mu(\vec{r})\bar{\alpha}_\mu(\vec{r})]\} \leq C_p\left(\frac{\lambda}{d}\right)^p, \tag{5.10}$$

where C_p is a numerical constant of order unity, λ is a linear measure of the smoothing range near a singularity—as in Eq. (5.6)—and d is a linear dimension of the Brillouin zone; the exponent p equals 2 in example A of a line singularity, it equals 1 in example B of a plane surface and it

would equal 3 for a point singularity.

The parameter λ, which characterizes the effective range of the singularity associated with a degeneracy, will presumably be reflected in the long-range order properties of crystals, which are known to be connected with degeneracies.[5] Examples of this connection can be found in the works of Ashkin and Lamb[18] and of Zunger.[19] Ashkin and Lamb proved that for a binary alloy the existence of long-range order implies degeneracy in the spectrum of a characteristic matrix concerned with atomic correlation. Zunger's work concerns the electronic spectrum of a two-dimensional hexagonal crystal. (I am indebted to Dr. A. Zunger for bringing this subject to my attention.) By treating the crystal as a macromolecule and calculating the electronic levels by LCAO method, Zunger showed that the band gap, i.e., the difference between the highest occupied and the lowest vacant molecular orbitals, vanishes only in the limit of an infinite macromolecule. On the other hand, by imposing cyclic conditions from the beginning and using a tight-binding scheme, he showed that the band gap is identically zero even in the nearest-neighbor approximation.

VI. PHASES OF BLOCH WAVES AND THE SYMMETRY OF WANNIER FUNCTIONS

As noted in Sec. I, our main goal is to construct a set of multipole wave functions by superposition of all Bloch waves of given energy, $E_\mu(\vec{k})=E$.[1] Each function of this set should be *symmetry adapted* to the point group of operations acting at the "central cell" node of the Bravais lattice which serves as the origin of $\vec{r}$ and $\vec{n}$. This condition puts restrictions on the phase normalization of the Bloch waves and of the coefficients in the superposition. We choose to satisfy these restrictions by establishing first of all a phase normalization of the Bloch waves which will symmetry adapt their Fourier coefficients, $a_\mu(\vec{r})$. We shall see here how this constraint all but determines the phases of Bloch waves, much as rotational symmetries do for atomic wave functions.

We confine ourselves in this paper to crystals with a single atom per unit cell and with the atom at the cell's center, such as fcc copper and other metals. In this case, the isogonal point group of the crystal coincides with the (holosymmetric) point group of the Bravais lattice and constitutes itself a symmetry subgroup of the Hamiltonian. More general cases require additional considerations to be developed elsewhere.

A. Phase normalization

The symmetry adaptation relies on the contragradience of the point-group transformations on the dual spaces $\vec{r}$ and $\vec{k}$. We deal with point group operations R which leave invariant the center Γ of the Brillouin zone and with the corresponding R^{-1} which leave invariant the "central" cell node at $\vec{r}=\vec{n}=0$. Application of this operation to Eq. (1.1) for $\vec{n}=0$ gives initially

$$a_\mu(R^{-1}\vec{r})=\frac{1}{\sqrt{\Omega}}\int_\Omega d\vec{k}\,\varphi_\mu(R^{-1}\vec{r};\vec{k}). \tag{6.1}$$

The implications of Eq. (6.1) will be drawn by relating first $\varphi_\mu(R^{-1}\vec{r};\vec{k})$ to $\varphi_\mu(\vec{r};R\vec{k})$. For any nondegenerate $\vec{k}$, the $\varphi_\mu(R^{-1}\vec{r};\vec{k})$ (a) is a Bloch wave with wave vector $R\vec{k}$; and (b) corresponds to the same energy, $E_\mu(\vec{k})$. Therefore, it differs from $\varphi_\mu(\vec{r};R\vec{k})$ only by a phase factor. We set in general

$$\varphi_\mu(R^{-1}\vec{r};\vec{k})=\varphi_\mu(\vec{r};R\vec{k})\exp[i\tau_\mu^{(R)}(R\vec{k})]. \tag{6.2}$$

[We need not deal with degenerate $\vec{k}$, because they form a set of measure zero which does not contribute to the integral in Eq. (6.1).] The function $\exp[i\tau_\mu^{(R)}(\vec{k})]$ may be arbitrary at general $\vec{k}$ vectors, but it must reduce to a character of a "small" representation of the group of wave vectors when $\vec{k}$ belongs to symmetry planes and for operations R such that $R\vec{k}\equiv\vec{k}$ (up to equivalence).

Upon substitution of Eq. (6.2) into (6.1) we note that $a_\mu(R^{-1}\vec{r})$ is the $\vec{n}=0$ Fourier coefficient of the product of the two functions of $\vec{k}$ on the right of Eq. (6.2). It can therefore be expressed as[20]

$$a_\mu(R^{-1}\vec{r})=\sum_{\vec{n}}a_\mu(\vec{r}-\vec{n})\frac{1}{\Omega}\times\int_\Omega d\vec{k}\exp\{i[\tau_\mu^{(R)}(\vec{k})+\vec{k}\cdot\vec{n}]\}. \tag{6.3}$$

According to this formula the operation R would transform the Wannier function at $\vec{n}=0$ into a superposition of functions at all different sites for an arbitrary choice of the phase $\tau_\mu^{(R)}(\vec{k})$. We restrict this choice by requiring the coefficient of $a_\mu(\vec{r}-\vec{n})$ in Eq. (6.3) to vanish for all but *a single* $\vec{n}$. This $\vec{n}$ equals zero if the Wannier function $a_\mu(\vec{r})$ is centered on the node of the Bravais lattice of the "central" cell. However $a_\mu(\vec{r})$ could be centered at some *interstitial* position $\vec{t}_\mu$ within the central cell, if any, which must be itself a *point of full symmetry* of the Bravais lattice. Such an interstitial position would yield

$$-\vec{n}=\vec{l}_{\mu R}\equiv\vec{t}_\mu-R\vec{t}_\mu, \tag{6.4}$$

a formula that reduces to $\vec{n}=0$ for $\vec{t}_\mu=0$. In the example of fcc copper, with a single atom per unit cell, there are two possible positions for the center of symmetry of $a_\mu(\vec{r})$, $\vec{t}_\mu=0$, and $\vec{t}_\mu\equiv\frac{1}{2}a(1,1,1)$.

Thus we set in Eq. (6.3)

$$\frac{1}{\Omega}\int_{\Omega} d\vec{k}\exp\{i[\tau_{\mu}^{(R)}(\vec{k})+\vec{k}\cdot\vec{n}]\} = \chi^{[\Gamma(\mu)]}(R)\delta(-\vec{n};\vec{l}_{\mu R}), \quad (6.5)$$

where the symbol $\chi^{[\Gamma(\mu)]}(R)$—discussed below—has the values ± 1. The uniqueness of Fourier coefficients shows that

$$\exp[i\tau_{\mu}^{(R)}(\vec{k})] = \chi^{[\Gamma(\mu)]}(R)\exp(i\vec{k}\cdot\vec{l}_{\mu R}), \quad (6.6)$$

except possibly for a set of $\vec{k}$ of measure zero. Substitution of Eq. (6.6) into (6.3) shows now that the Wannier function $a_{\mu}(\vec{r})$ belongs to a *one-dimensional* irreducible representation of the point group of the Bravais lattice with center of symmetry at $\vec{t}_{\mu}$. This representation is identified by the values of the coefficient $\chi^{[\Gamma(\mu)]}(R)$ in Eq. (6.5) for the alternative operations R; for this reason we have used the symbol $\chi^{[\Gamma(\mu)]}(R)$ which serves normally to label the characters of a representation $\Gamma(\mu)$. It remains to be shown how $\chi^{[\Gamma(\mu)]}(R)$ and $\vec{t}_{\mu}$ are determined.

That any Wannier function belongs to a one-dimensional representation of the point group has been suggested by Koster[21] on grounds of the group invariance of the energy $E_{\mu}(\vec{k})$. Dr. B. Reiser has remarked (private communication) that this property of $a_{\mu}(\vec{r})$ is sufficient but not necessary for the invariance of $E_{\mu}(\vec{k})$. Here the same property has been used to phase normalize the Bloch functions. Our criterion for the transformation of $a_{\mu}(\vec{r})$ coincides with that adopted previously by Callaway and Hughes,[12] but these authors did not press the analysis of its implications; difficulties of Ref. 12 arise, at least in part, from a definition of band indices which prevented the control of analyticity of $\varphi_{\mu}(\vec{r};\vec{k})$, and which proves inconsistent at the boundary of the Brillouin zone for many lattices. That the symmetry adaptation of $a_{\mu}(\vec{r})$ may be achieved for a single one among the alternative centers of full symmetry which may exist within the "central cell," $\vec{n}=0$, has been noticed by Kohn in his study of one-dimensional lattices.[9] The physical interpretation of the shift to an interstitial position remains an open question.

B. Symmetry of Wannier functions

The determination of the coefficients $\chi^{[\Gamma(\mu)]}(R)$ and of $\vec{t}_{\mu}$ in Eq. (6.5) will now be achieved by studying the symmetry of the Bloch functions for special momenta $\vec{k}$ on the *planes delimiting a basic domain* of the Brillouin zone, where $R\vec{k}\equiv\vec{k}$ for one particular R in Eq. (6.2). These special momenta will be further confined to portions of these planes that are *free from the branch cut discontinuities* introduced by curves of degeneracy and discussed in Sec. V. As anticipated in Sec. V, our symmetry equation (6.6) requires these discontinuities to lie *on portions of the symmetry planes*. In our applications the surfaces of discontinuity have been placed in the interior of the closed curves of degeneracy, so as to have a simply connected domain.

Two distinct situations must be considered:

(a) When $\vec{k}$ lies on a symmetry plane in the *interior* of the Brillouin zone, the operation R for which $R\vec{k}=\vec{k}$ is a reflection through the plane. For this R we have

$$R\vec{k}\circ\vec{l}_{\mu R} = R\vec{k}\cdot\vec{t}_{\mu}-\vec{k}\cdot\vec{t}_{\mu}=0, \quad (6.7)$$

and the value of $\chi^{[\Gamma(\mu)]}(R)$ is given by the character of $\varphi_{\mu}(\vec{r};\vec{k})$ under reflection of $\vec{r}$ through the plane,

$$\varphi_{\mu}(R^{-1}\vec{r};\vec{k}) = \chi^{[\Gamma(\mu)]}(R)\varphi_{\mu}(\vec{r};\vec{k}). \quad (6.8)$$

This procedure is to be applied to each symmetry plane delimiting the basic domain. Note at this point that reflection on a boundary face of a basic domain—whether in $\vec{r}$ or $\vec{k}$ space—shifts the domain into an adjacent one. Successive application of such reflections on all faces fills the whole space and thus yields the values of $\chi^{[\Gamma(\mu)]}(R)$ *for all operations R of the point group*. It is indeed apparent from the examination of character tables that the characters of reflection operations on the boundaries of a basic domain in $\vec{r}$ space suffice to distinguish any single *one-dimensional representation* from the others. This property is understood from the genealogy of group representations from the representations of subgroups according to Altmann[22]; alternative one-dimensional representations of the holosymmetric point groups differ by parities under subgroups C_s consisting of the identity and a reflection (or, equivalently, by $C_2\times C_i$).

(b) When $\vec{k}$ extends to an *external boundary* face of the basic domain, we consider the operation R for which $R\vec{k}=\vec{k}+\vec{h}_R$, where $\vec{h}_R$ is a vector of the reciprocal lattice. For this R we have

$$R\vec{k}\cdot\vec{l}_{\mu R} = (\vec{k}+\vec{h}_R)\cdot(\vec{t}_{\mu}-R\vec{t}_{\mu}) = \vec{h}_R\cdot\vec{t}_{\mu}, \quad (6.9)$$

so that

$$\varphi_{\mu}(R^{-1}\vec{r};\vec{k}) = \chi^{[\Gamma(\mu)]}(R)\exp(i\vec{h}_R\cdot\vec{t}_{\mu})\varphi_{\mu}(\vec{r};\vec{k}); \quad (6.10)$$

on the right-hand side we have replaced $\varphi_{\mu}(\vec{r};\vec{k}+\vec{h}_R)$ by $\varphi_{\mu}(\vec{r};\vec{k})$ owing to the periodicity of $\varphi_{\mu}(\vec{r};\vec{k})$. The phase factor $\exp(i\vec{h}_R\cdot\vec{t}_{\mu})$ equals ± 1 because $2\vec{t}_{\mu}$ belongs to the Bravais lattice. The character of $\varphi_{\mu}(\vec{r};\vec{k})$ under this operation R determines the eigenvalue of Eq. (6.10), as it did for a different R in Eq. (6.8). Since $\chi^{[\Gamma(\mu)]}(R)$ is already known from procedure (a), we have thus determined $\exp(i\vec{h}_R\cdot\vec{t}_{\mu})$. A value $+1$ of this phase factor implies that either $\vec{t}_{\mu}=0$ or $\vec{h}_R\cdot\vec{t}_{\mu}$ is a multiple of 2π, while

$\vec{t}_\mu \neq 0$ for $\exp(i\vec{k}_R \cdot \vec{t}_\mu) = -1$. Examples in Secs. VII and VIII will verify that application of Eq. (6.10) to different external faces of the basic domain identifies $\vec{t}_\mu$ consistently.

Thus we have found that the reflection symmetries of the Bloch functions for $\vec{k}$ on the faces of a basic domain identify the two phase factors on the right of Eq. (6.6). These factors identify the one-dimensional representation of the Wannier function $a_\mu(\vec{r})$ and its center of symmetry $\vec{t}_\mu$ within the central cell, respectively. The classification of each band thus obtained in terms of the properties of Wannier functions is substantially equivalent to the familiar classification in terms of the reflection symmetries of Bloch functions outside their loci of discontinuity, as introduced by Bouckaert *et al.*[23] In a calculation of Wannier functions by the method of Kohn (Secs. III and IV) the symmetry of both the Wannier and Bloch functions is embodied in the eigenvectors $\vec{U}^{(\mu)}(\vec{k})$ of the Hamiltonian (3.4).

C. Reality of Wannier functions

There seems to remain, for the Bloch functions, a residual phase arbitrariness represented by a renormalization

$$\psi_\mu(\vec{r};\vec{k}) \equiv \varphi_\mu(\vec{r};\vec{k}) \exp[i\lambda_\mu(\vec{k})], \tag{6.11}$$

where $\lambda_\mu(\vec{k})$ is any analytic function of $\vec{k}$ with the *full symmetry* of the Brillouin zone. These requirements on $\lambda_\mu(\vec{k})$ ensure that $\psi_\mu(\vec{r};\vec{k})$ and $\varphi_\mu(\vec{r};\vec{k})$ have identical singularities and generate Wannier functions with the same transformation properties. This arbitrariness of $\lambda_\mu(\vec{k})$ is, however, all but eliminated if we require the Wannier functions to be real. To this end the Bloch waves conjugate under time reversal must be complex conjugate, at any nondegenerate $\vec{k}$,

$$\varphi_\mu^*(\vec{r};\vec{k}) = \varphi_\mu(\vec{r};-\vec{k}). \tag{6.12}$$

To preserve this property under the phase renormalization (6.11) we must have

$$\lambda_\mu(-\vec{k}) = -\lambda_\mu(\vec{k}) + 2\pi(\text{integer}). \tag{6.13}$$

Since the full symmetry of $\lambda_\mu(\vec{k})$ includes invariance under inversion operation, it follows that

$$\lambda_\mu(\vec{k}) = \pi(\text{integer}). \tag{6.14}$$

That is, the arbitrariness of $\varphi_\mu(\vec{r};\vec{k})$ is reduced to a common factor ± 1 over the entire Brillouin zone.

VII. EXAMPLE OF A TWO-DIMENSIONAL SQUARE LATTICE

We now discuss the example of bands whose singularities do not include branch cuts.

TABLE I. Isomorphism between C_{4v} and C'_{4v}.[a]

R	$\{R\|0\}(x,y)$	$\vec{l}_R$
E	(x,y)	$a(0,0)$
C_{2z}	$(\bar{x},\bar{y})$	$a(1,1)$
C_{4z}^+	$(\bar{y},x)$	$a(1,0)$
C_{4z}^-	$(y,\bar{x})$	$a(0,1)$
σ_x	$(\bar{x},y)$	$a(1,0)$
σ_y	$(x,\bar{y})$	$a(0,1)$
σ_{da}	$(\bar{y},\bar{x})$	$a(1,1)$
σ_{db}	(y,x)	$a(0,0)$

[a] We use the notation of C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, England, 1972).

Consider a two-dimensional square lattice. This lattice is invariant under the operations of the point group C_{4v} acting at the lattice points $\vec{n} = a(n_x, n_y)$, where n_x and n_y are integers and a is the lattice constant, but it is also invariant under the operations of the point group C'_{4v} acting at the interstitial points $\vec{n} + \vec{t}$, where $\vec{t} = \frac{1}{2}a(1,1)$. The point groups C_{4v} and C'_{4v} are isomorphic. In Table I we list the set of lattice vectors $\vec{l}_{\mu R}$ defined by Eq. (6.4), for $\vec{t}_\mu = \vec{t} \neq 0$.

The special points (Γ, M, X) and the special lines (Δ, Z, Σ) in the basic domain (or irreducible wedge) of the Brillouin zone are shown in Fig. 1. By labeling a band by the set of characters of the "small" representations corresponding to the symmetry lines, we see that eight possible types of bands exist. Following the prescriptions given by Eqs. (6.8) and (6.10), we list in Table II the symmetry assignment for the Wannier functions corresponding to the eight types of bands, which are thus mapped in a one-to-one correspondence to the eight available one-dimensional representations,

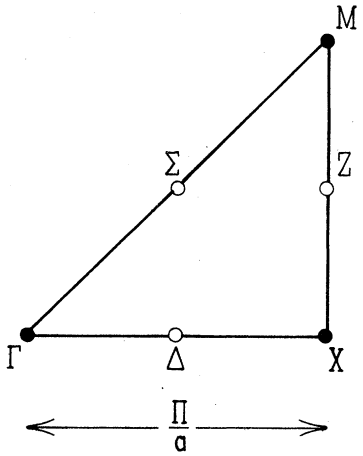

FIG. 1. Basic domain of the Brillouin zone of the square lattice showing special lines and points.

TABLE II. Symmetry assignment for Wannier functions of a two-dimensional square lattice.

Band type	Irreducible representations	Group
$\Delta_+Z_+\Sigma_+$	A_1	C_{4v}
$\Delta_+Z_-\Sigma_+$	A_1	C'_{4v}
$\Delta_-Z_-\Sigma_-$	A_2	C_{4v}
$\Delta_-Z_+\Sigma_-$	A_2	C'_{4v}
$\Delta_+Z_+\Sigma_-$	B_1	C_{4v}
$\Delta_+Z_-\Sigma_-$	B_1	C'_{4v}
$\Delta_-Z_-\Sigma_+$	B_2	C_{4v}
$\Delta_-Z_+\Sigma_+$	B_2	C'_{4v}

four of C_{4v} and four of C'_{4v}.

For this example, the vector $\vec{h}_R$ to be inserted in Eq. (6.10) is $(2\pi/a)(\bar{1}, 0)$, so that $\exp(i\vec{h}_R\cdot\vec{t})$ $=\exp(-i\pi)=-1$. One then sees that the characters of the "small" representations *in the interior* of the Brillouin zone (i.e., on Δ and Σ) uniquely determine the one-dimensional irreducible representation of the Wannier function, whereas those *on the boundary* of the Brillouin zone (i.e., on Z) determine whether the Wannier function is symmetry adapted to C_{4v} or to C'_{4v}.

We now consider the pair of bands that arise from a single pair of orbitals $a_x(\vec{r})$ and $a_y(\vec{r})$ following Sec. III, including only the interaction integrals $E_{ij}(n_x n_y)\equiv\langle a_i(\vec{r})|\hat{H}_c|a_j(\vec{r}-\vec{n})\rangle$ up to the second-nearest neighbors with $i,j\in\{x,y\}$. The matrix elements of the Hamiltonian in the basis of the Bloch sums $S_x(\vec{r};\vec{k})$ and $S_y(\vec{r};\vec{k})$ of Eq. (3.2) are then

$$\begin{aligned}
\langle x|\mathcal{E}(\vec{k})|x\rangle &= E_{xx}(00)+2E_{xx}(10)\cos\xi \\
&\quad +2E_{yy}(10)\cos\eta+4E_{xx}(11)\cos\xi\cos\eta\,, \\
\langle x|\mathcal{E}(\vec{k})|y\rangle &= -4E_{xy}(11)\sin\xi\sin\eta\,, \qquad (7.1)\\
\langle y|\mathcal{E}(\vec{k})|y\rangle &= E_{xx}(00)+2E_{yy}(10)\cos\xi+2E_{xx}(10)\cos\eta \\
&\quad +4E_{xx}(11)\cos\xi\cos\eta\,,
\end{aligned}$$

where $(\xi,\eta)\equiv a(k_x,k_y)$. In Table III we list the four sets of symmetry labels for the upper and the lower band as determined by the values of the interaction integrals. By comparing with Table II we conclude that the Wannier function corresponding to each of the two bands can be symmetry adapted to one of the four one-dimensional irreducible representations of the point group C'_{4v}, whose node is at $\vec{t}=\frac{1}{2}a(1,1)$ rather than at the center of the "central" cell. Note that $a_\mu(\vec{r})$ could be symmetry adapted about $\vec{n}=0$, but only by forcing the Bloch function $\varphi_\mu(\vec{r};\vec{k})$ to be discontinuous at the boundary of the Brillouin zone, and thus causing a wider spread of the tail of $a_\mu(\vec{r})$.

We finally determine the rate of falloff of the tail of the Wannier functions corresponding to the

TABLE III. Four types of upper and lower bands arising from $a_x(\vec{r})$ and $a_y(\vec{r})$ orbitals in a two-dimensional square lattice.

		Upper band	Lower band
$E_{xx}(10)>E_{yy}(10)$	$E_{xy}(11)>0$	$\Delta_-Z_+\Sigma_-$	$\Delta_+Z_-\Sigma_+$
	$E_{xy}(11)<0$	$\Delta_-Z_+\Sigma_+$	$\Delta_+Z_-\Sigma_-$
$E_{xx}(10)<E_{yy}(10)$	$E_{xy}(11)>0$	$\Delta_+Z_-\Sigma_-$	$\Delta_-Z_+\Sigma_+$
	$E_{xy}(11)<0$	$\Delta_+Z_-\Sigma_+$	$\Delta_-Z_+\Sigma_-$

bands that we designate as upper (+) or lower (−) which are degenerate by symmetry only at Γ and M. For small values of ξ and η near the Γ point, the matrix elements (7.1) reduce to

$$\begin{aligned}
\langle x|\mathcal{E}(\vec{k})|x\rangle &\simeq \alpha-\beta\xi^2-\gamma\eta^2\,, \\
\langle x|\mathcal{E}(\vec{k})|y\rangle &\simeq \delta\xi\eta\,, \qquad (7.2)\\
\langle y|\mathcal{E}(\vec{k})|y\rangle &\simeq \alpha-\gamma\xi^2-\beta\eta^2\,,
\end{aligned}$$

where the constant parameters α, β, γ, and δ are linear combinations of the interaction integrals in (7.1). The matrix (7.2) coincides with the matrix (5.4) for two bands which are degenerate at the Δ line of the Brillouin zone of an fcc lattice, as it must be because C_{4v} is the group of wave vectors at Δ. We can thus proceed as in Sec. V by introducing polar coordinates (ρ,ϕ) about the Γ point. Again, for small values of ρ, the eigenvectors $\vec{U}^{(\pm)}(\rho,\phi)$ are independent of ρ and single valued in ϕ. Therefore, they have a jump discontinuity whenever crossing the Γ point. A similar behavior occurs about the M point. We then conclude that the Wannier functions, corresponding to each one of the two bands, will fall off as r^{-2} for large values of r in any direction in the x-y plane.

VIII. COMPOSITE *s-d* BANDS OF COPPER

The fcc Bravais lattice of metallic copper is invariant under the operations of the point group O_h acting at the lattice nodes $\vec{n}=\frac{1}{2}a(n_x,n_y,n_z)$, where n_x, n_y, and n_z are integers such that $n_x+n_y+n_z$ is an even integer and a is the lattice constant. The lattice is also invariant under the operations of the point group O'_h acting at the interstitial positions $\vec{n}+\vec{t}$, where $\vec{t}=\frac{1}{2}a(1,1,1)$.

The special points (Γ,X,W,L) and the special lines $(\Delta,\Lambda,\Sigma,S,Z,Q)$ in the basic domain of the Brillouin zone are shown in Fig. 2. Table IV lists the symmetry assignment for the Wannier functions corresponding to the eight possible types of bands distinguished by reflection symmetry over the nonsingular portions of the faces of the basic domain. Note, again, the one-to-one correspondence between the possible types of bands and the

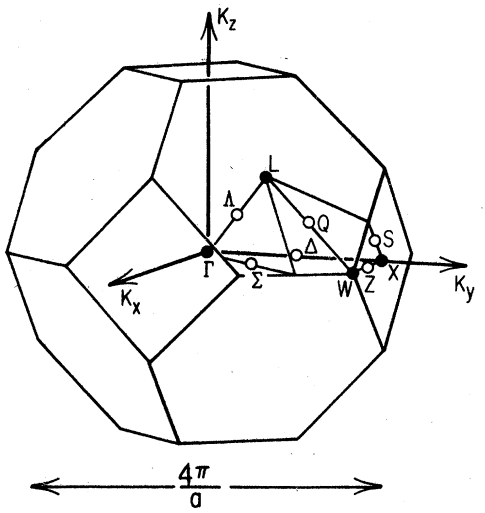

FIG. 2. Brillouin zone of the fcc lattice, showing special lines and points. The basic domain is defined by the inequalities $0 \leq k_z \leq k_x \leq k_y \leq 2\pi/a$ and $k_x+k_y+k_z \leq 3\pi/a$.

eight available one-dimensional irreducible representations, four of O_h and four of O_h'.

For this example, two alternative vectors $\vec{h}_R$ should be entered in Eq. (6.10):

(a) $\vec{h}_R = (4\pi/a)(0, \bar{1}, 0)$ for $R = \sigma_y$, corresponding to the SZ plane, which gives $\exp(i\vec{h}_R \cdot \vec{t}) = \exp(-i2\pi) = 1$. According to (6.10), the characters of the operations σ_y and σ_z of the group of the wave vector at the Z line are then equal. As a matter of fact, these two characters differ only when W is a point of degeneracy. However, as we have shown in Sec. V, degeneracy at W requires the presence of a curve of accidental degeneracy in the $k_z = 0$ plane, which in turn implies the presence of a branch cut surface containing the Z line.

(b) $\vec{h}_R = (2\pi/a)(\bar{1}, \bar{1}, \bar{1})$ for $R = C_{2f}$, corresponding

TABLE IV. Symmetry assignment for the Wannier functions of an fcc lattice. [Here "+" or "−" indicates that the Bloch function $\varphi_\mu(\vec{r};\vec{k})$, with $\vec{k}$ belonging to the $\Lambda\Sigma$ and $\Sigma\Delta$ planes and to the Q line, respectively, is even or odd under the symmetry operation, other than the identity, of these planes and line.]

$\Lambda\Sigma$	$\Sigma\Delta$	Q	Irr. rep.	Group
+	+	+	A_{1g}	O_h
+	+	−	A_{1g}	O_h'
−	−	+	A_{1u}	O_h
−	−	−	A_{1u}	O_h'
−	+	−	A_{2g}	O_h
−	+	+	A_{2g}	O_h'
+	−	−	A_{2u}	O_h
+	−	+	A_{2u}	O_h'

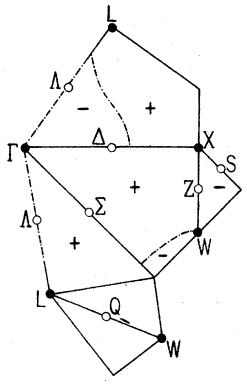

FIG. 3. Conduction band of copper: schematic map of the curves of degeneracy (- • -) on the symmetry planes delimiting the unfolded basic domain.

to the Q line, which gives $\exp(i\vec{h}_R \cdot \vec{t}) = \exp(-i3\pi) = -1$. Thus the symmetry character of the Bloch wave with $\vec{k}$ belonging to the Q line decides whether the Wannier function is symmetry adapted to O_h or to O_h'.

The structure of the s-d bands of copper is quite complex because of the large number of curves of degeneracy occurring between various pairs of bands. We regard these bands as prototypes of composite bands and discuss in this section how to apply the prescriptions of Sec. VI in order to assign: (i) a definite symmetry to the Wannier functions; (ii) a phase of the Bloch waves consistent with the symmetry assignment. We consider these assignments explicitly only for the conduction band of copper ($\mu = 6$), which contributes the density of states at the Fermi level.

As a first step we map the symmetries of the Bloch waves on the four symmetry planes ($\Sigma\Delta$, $\Delta\Lambda, \Lambda\Sigma, SZ$) that delimit the basic domain of the Brillouin zone and on the Q line. We have thus to calculate the eigenvalues $E_\mu(\vec{k})$, and the eigenvectors $\vec{U}^{(\mu)}(\vec{k})$, of the Hamiltonian matrix (3.4) for $\vec{k}$ ranging over a fine mesh of points on these planes and line. To this end, we have estimated the interaction integrals

$$\langle a_{\Gamma i,\gamma}(\vec{r}) | \hat{H}_c | a_{\Gamma' i',\gamma'}(\vec{r}-\vec{n}) \rangle \,, \tag{8.1}$$

up to the second-nearest neighbors. The Slater-Koster interpolation scheme[24] has served to fit the *ab initio* calculation of Burdick,[17] without any advance knowledge of the Kohn's orbitals $\{a_{\Gamma i,\gamma}(\vec{r})\}$. Details of the calculation are described in Ref. 1. In Fig. 3 we report a schematic map of the curves of degeneracy for the conduction band of copper. In the neighborhood of the W point the results from the fitting have been replaced by the *ab initio* data of Burdick's calculation, complemented by the theoretical analysis made in Sec. V (example B). The fitting was, in fact, unable to reproduce the bands at energies of about 0.5 Ry above the Fermi level, such as those for $\vec{k}$ in the vicinity of the W

point. In Fig. 3, the plus or minus sign in a particular symmetry plane indicates that the Bloch function $\varphi_6(\vec{r};\vec{k})$, with $\vec{k}$ in the plane, is even or odd under the reflection through that plane; for the Q line the corresponding symmetry operation is C_{2f}. A curve of degeneracy separates the odd from the even region in a symmetry plane.[25] By comparing Fig. 3 with Table IV we conclude that a consistent symmetry assignment for the Wannier function of the conduction band of copper is $\Gamma(6) = A_{1g}$ of the group O_h' acting at the interstitial position $\vec{t} = \frac{1}{2}a(1,1,1)$ in the central cell.

The discontinuity of the Bloch function when $\vec{k}$ crosses the square face on the boundary of the Brillouin zone is caused by the presence of a curve of accidental degeneracy which surrounds this face and touches it at the four W points. The shift of the Wannier function of this conduction band of copper from the center of the cell to an interstitial position is probably related to strong hybridization with the higher p bands. As a matter of fact, the Bloch function $\varphi_6(\vec{r};\vec{k})$ is completely p-like at the symmetry points X and L on the boundary of the Brillouin zone and almost completely p-like at W.

We now rephrase the criteria of Sec. VI into *practical prescriptions* for defining the phase of the Bloch waves:

(i) Make all matrix elements (3.4) real by taking the orbitals $a_{\Gamma i,\gamma}(\vec{r})$ with even parity under inversion as real and those with odd parity imaginary. The eigenvectors $\vec{U}^{(\mu)}(\vec{k})$, obtained by diagonalization of the Hamiltonian matrix (3.4) at a chosen mesh of points in the basic domain, will then be real, too. Each of them is thus specified to within an overall sign at each $\vec{k}$. We have chosen a cubic mesh of linear size $(2\pi/a)/16$ for a total of 505 points in the basic domain.

(ii) Select a nondegenerate reference point $\vec{k}_i$ in the interior of the basic domain and fix the overall sign of $\vec{U}^{(\mu)}(\vec{k}_i)$ arbitrarily. In fact, as shown in Sec. VI, only this arbitrariness remains in the specification of the phase of the Bloch waves. Moving outward from $\vec{k}_i$ in all directions, we then take the sign that makes $\vec{U}^{(\mu)}(\vec{k})$ a smooth function of $\vec{k}$ throughout the chosen mesh. Care must be used in continuing the eigenvectors analytically when following a path close to any curve of degeneracy in a symmetry plane or close to any curve of accidental degeneracy between equivalent representations in the interior of the basic domain. Typically a component of the normalized eigenvector $\vec{U}^{(\mu)}(\vec{k})$ can vary by ~ 1 over an interval $|\Delta\vec{k}| \sim (2\pi/a)\times 10^{-2}$ at a distance $\sim (2\pi/a)\times 10^{-2}$ from the curve of degeneracy.

(iii) When the center of symmetry of the Wannier function lies in an interstitial position, that is when $\vec{t}_\mu \neq 0$, the real eigenvectors $\vec{U}^{(\mu)}(\vec{k})$ obtained in (ii) within the basic domain must be renormalized by a factor $\exp(-i\vec{k}\cdot\vec{t})$.

(iv) Having calculated the eigenvalues $E_\mu(\vec{k})$ and the eigenvectors $\vec{U}^{(\mu)}(\vec{k})$ in the basic domain, obtain their numerical values in the rest of the Brillouin zone by the symmetry relations

$$E_\mu(R\vec{k}) = E_\mu(\vec{k}), \tag{8.2}$$

$$U^{(\mu)}_{\Gamma i,\gamma}(R\vec{k}) = \exp[-i\tau^{(R)}_\mu(R\vec{k})] \times \sum_{j=1}^{\dim(\Gamma)} U^{(\mu)}_{\Gamma j,\gamma}(\vec{k}) D^{(\Gamma)}_{ji}(R^{-1}), \tag{8.3}$$

for each operation R of the crystal point group and for all μ. The value of the phase factor $\exp[-i\tau^{(R)}_\mu(R\vec{k})]$ has been discussed in Sec. VI, with reference to the construction of a symmetry-adapted Wannier function.

(v) With these definitions of phase, the Wannier function $a_\mu(\vec{r})$ is real or imaginary depending whether $\Gamma(\mu)$ is even or odd under inversion. A real Wannier function could be obtained instead by multiplying the eigenvector $\vec{U}^{(\mu)}(\vec{k})$ by an additional factor of i for all $\vec{k}$ in the Brillouin zone.

IX. SYMMETRIES OF THE MULTIPOLE WAVE FUNCTIONS

We return now to the set of multipole wave functions defined in Ref. 1 as

$$\begin{aligned}\mathfrak{R}^{(\Gamma iLq)}(\vec{r};E_\mu) &\equiv \oint_{E_\mu(\vec{k})=E} d\xi\, d\eta\, \varphi_\mu(\vec{r};E,\xi,\eta) \times \langle \xi\eta|\Gamma iLq\rangle_{E_\mu} \\ &= \frac{1}{\sqrt{\Omega}} \int_\Omega d\vec{k}\, \delta(E - E_\mu(\vec{k}))\varphi_\mu(\vec{r};\vec{k}) \times e^{i\vec{k}\cdot\vec{t}_\mu} P^{(\Gamma i)}_{Lq}(\vec{k};E_\mu).\end{aligned} \tag{9.1}$$

Here

(a) $\{P^{(\Gamma i)}_{Lq}(\vec{k};E_\mu)\}$ is a complete and orthonormal set of polynomials belonging to the non-negative density function $\delta(E - E_\mu(\vec{k}))/\Omega$ with the Brillouin zone Ω as its fundamental domain. Examples of $\{P^{(\Gamma i)}_{Lq}(\vec{k};E_\mu)\}$ for the s-d bands of copper have been calculated in Ref. 1. By construction, the polynomial $P^{(\Gamma i)}_{Lq}(\vec{k};E_\mu)$ belongs to the ith row of the irreducible representation Γ of the crystal point group, i.e.,

$$P^{(\Gamma i)}_{Lq}(R^{-1}\vec{k};E_\mu) = \sum_{j=1}^{\dim(\Gamma)} P^{(\Gamma j)}_{Lq}(\vec{k};E_\mu) D^{(\Gamma)}_{ji}(R) \tag{9.2}$$

for any operation R of the point group.

(b) The phase factor $\exp(i\vec{k}\cdot\vec{t}_\mu)$ in Eq. (9.1) is the same for all constant-energy surfaces $E_\mu(\vec{k}) = E$ of the μth band and for all indices ΓiLq which label the polynomials; it depends only on the band index μ. This factor depends on the phase of

$\varphi_\mu(\vec{r};\vec{k})$ adopted in Sec. VI and was indicated in Ref. 1 generally as $\exp[i\Theta_\mu(\vec{k})]$. It serves to compensate the shift of the Wannier function to $\vec{t}_\mu$ thus restoring the symmetry adaptation of the multipole function to the point $\vec{r}=0$, as will be shown below.

(c) The multipole wave functions are normalized according to

$$\int d\vec{r}\,\mathcal{R}^{(\Gamma i L q)}(\vec{r};E_\mu)^*\mathcal{R}^{(\Gamma' i' L' q')}(\vec{r};E'_{\mu'}) = \delta(E-E')\delta_{\mu\mu'}\delta_{\Gamma\Gamma'}\delta_{ii'}\delta_{LL'}\delta_{qq'}, \quad (9.3)$$

where the integration extends over the whole (infinite) crystal.

As mentioned in Sec. VI, we require the multipole wave functions to be symmetry adapted to the crystal point group for the node of the Bravais lattice belonging to the "central" cell that serves as the origin. This node is intended to coincide with a physical impurity, such as the inner-shell vacancy left behind by a photoelectron. We shall now determine explicitly the symmetry species of the multipole wavefunction (9.1) by replacing $\vec{r}$ by $R^{-1}\vec{r}$ on both sides. The transformed Bloch function $\varphi_\mu(R^{-1}\vec{r};\vec{k})$ is given by Eqs. (6.2) and (6.6). From these equations it follows that

$$\varphi_\mu(R^{-1}\vec{r};\vec{k})e^{(i\vec{k}\cdot\vec{t}_\mu)} = \chi^{\Gamma(\mu)}(R)\varphi_\mu(\vec{r};R\vec{k})e^{(iR\vec{k}\cdot\vec{t}_\mu)}. \quad (9.4)$$

Considering the point group invariance of the integration over $\vec{k}$ and of the constant-energy surface and using the transformation (9.2), we have

$$\mathcal{R}^{(\Gamma i L q)}(R^{-1}\vec{r};E_\mu) = \chi^{[\Gamma(\mu)]}(R)\frac{1}{\sqrt{\Omega}}\int_\Omega d\vec{k}\,\delta(E-E_\mu(\vec{k}))\varphi_\mu(\vec{r};\vec{k})\,e^{i\vec{k}\cdot\vec{t}_\mu}P^{(\Gamma i)}_{Lq}(R^{-1}\vec{k};E_\mu)$$
$$= \sum_{j=1}^{\dim(\Gamma)}\mathcal{R}^{(\Gamma j L q)}(\vec{r};E_\mu)\chi^{[\Gamma(\mu)]}(R)D^{(\Gamma)}_{ji}(R). \quad (9.5)$$

Therefore, the set $\{\mathcal{R}^{(\Gamma i L q)}(\vec{r};E_\mu)\ [i=1,\ldots,\dim(\Gamma)]\}$ forms a basis of the *Kronecker product representation* $\Gamma(\mu)\times\Gamma$ of the crystal point group acting at $\vec{n}=0$. This Kronecker product reduces in a simple way because $\Gamma(\mu)$ is one dimensional, as shown in tables of the coupling coefficients.[26] For instance, $\{\mathcal{R}^{(E_g 2 L q)}(\vec{r};E_\mu), -\mathcal{R}^{(E_g 1 L q)}(\vec{r};E_\mu)\}$ forms an irreducible basis of E_g when $\Gamma(\mu)=A_{2g}$ and $\Gamma=E_g$ of the group O_h. Thus each multipole wave function is readily assigned to a specific row of an irreducible representation of the crystal point group.

We now consider the expansion of the multipole wave functions in series of Wannier functions, by inserting the Wannier expansion of the Bloch wave, Eq. (2.2), into Eq. (9.1):

$$\mathcal{R}^{(\Gamma i L q)}(\vec{r};E_\mu) = \frac{1}{\sqrt{\Omega}}\int_\Omega d\vec{k}\,\delta(E-E_\mu(\vec{k}))\times\left(\frac{1}{\sqrt{\Omega}}\sum_{\vec{n}}a_\mu(\vec{r}-\vec{n})e^{i\vec{n}\cdot\vec{k}}\right)\times e^{i\vec{k}\cdot\vec{t}_\mu}P^{(\Gamma i)}_{Lq}(\vec{k};E_\mu)$$
$$= \sum_{\vec{n}}a_\mu(\vec{r}-\vec{n})\langle\vec{n}+\vec{t}_\mu|\Gamma i L q\rangle_{E_\mu}. \quad (9.6)$$

We have here introduced the *lattice multipoles*, defined as

$$\langle\vec{n}+\vec{t}_\mu|\Gamma i L q\rangle_{E_\mu} \equiv \frac{1}{\Omega}\int_\Omega d\vec{k}\,\delta(E-E_\mu(\vec{k}))\times P^{(\Gamma i)}_{Lq}(\vec{k};E_\mu)e^{i\vec{k}\cdot(\vec{n}+\vec{t}_\mu)}. \quad (9.7)$$

Equation (9.6) involves the term-by-term integration of the infinite Wannier series. Note that the series (2.2) cannot converge uniformly everywhere in the Brillouin zone and term-by-term integration must be handled with some care if the μth band has points of degeneracy. However, term-by-term integration in Eq. (9.6) is justified by the Lebesgue convergence theorem[27] under the following conditions:

(i) The measure

$$m_\Omega(E_\mu) \equiv \frac{1}{\Omega}\int_\Omega d\vec{k}\,\delta(E-E_\mu(\vec{k})) = \frac{1}{\Omega}\oint_{E_\mu(\vec{k})=E}\frac{dS_{E\mu}}{|\vec{\nabla}_{\vec{k}}E_\mu(\vec{k})|} \quad (9.8)$$

must be finite. This is certainly true because $m_\Omega(E_\mu)$ represents the density of states contributed by the μth band per crystal cell.

(ii) The (spherical) partial sums of the series (2.2) are uniformly bounded, i.e., their absolute value must be smaller than a chosen constant, as the number of shells included in the sum increases without bound. This is certainly true for the Fourier partial sums of piecewise smooth functions of one variable. In fact, the worst situation one faces in the case of one variable is the Gibbs phenomenon, from which one can easily visualize the boundedness of the partial sums. Although this result seems also plausible for piecewise smooth functions of three variables, such as our Bloch functions $\varphi_\mu(\vec{r};\vec{k})$, we lack a general proof of this nontrivial theorem for several variables.

For practical purposes we might proceed, in any event, as follows:

(a) We split any Bloch function, $\varphi_\mu(\vec{r};\vec{k})$, as in Eq. (2.6) and expand in Fourier series *only* its smooth, well-behaved part, $\bar{\varphi}_\mu(\vec{r};\vec{k})$. Term-by-term integration is thus fully justified because the Fourier series of $\bar{\varphi}_\mu(\vec{r};\vec{k})$ converges uniformly everywhere in the Brillouin zone. Moreover, the rate of convergence of the series can be improved by properly defining $\bar{\varphi}_\mu(\vec{r};\vec{k})$.

(b) The contribution to the multipole wave functions of the remainder, $\Phi_\mu(\vec{r};\vec{k}) \equiv \varphi_\mu(\vec{r};\vec{k}) - \bar{\varphi}_\mu(\vec{r};\vec{k})$, can be estimated from Eq. (9.1) by explicit integration over the portion Ω_0 of Ω, where $\Phi_\mu(\vec{r};\vec{k})$ is appreciably different from zero. This contribution might be neglected, particularly when the factor P_{Lq} in that equation has low value of L, and hence oscillates slowly. The error thus made in reproducing $\mathfrak{R}^{(\Gamma i Lq)}(\vec{r};E_\mu)$ will be smaller than the error in the Bloch function because of the averaging action of the integration. From the numerical point of view, any interpolation scheme, such as the QUAD scheme,[28] can in fact serve well for smoothing the Bloch functions.

X. PROPERTIES OF THE LATTICE MULTIPOLES $\langle \vec{n}+\vec{t}_\mu | \Gamma i L q\rangle_{E_\mu}$

The analogy between the multipole wave functions, Eq. (9.1), and the ordinary spherical Bessel functions is most evident when the wave functions are represented through their Wannier series, Eq. (9.6). In fact, in the degenerate limit of a spherical constant-energy surface, $E=k^2$, the lattice multipoles (9.7) reduce to

$$\langle \vec{n}+\vec{t}_\mu | lm\rangle_E = \left(\frac{k}{2\Omega}\right)^{1/2} 4\pi i^l j_l(k|\vec{n}+\vec{t}_\mu|)\, Y_{lm}\left(\frac{\vec{n}+\vec{t}_\mu}{|\vec{n}+\vec{t}_\mu|}\right). \tag{10.1}$$

In this section we carry the analogy further by discussing a few properties of the lattice multipoles, which hold for a generic constant-energy surface.

(i) By construction,[1] the polynomials $P_{Lq}^{(\Gamma i)}(\vec{k};E_\mu)$ are real and have parity,

$$P_{Lq}^{(\Gamma i)}(-\vec{k};E_\mu) = (-1)^L P_{Lq}^{(\Gamma i)}(\vec{k};E_\mu). \tag{10.2}$$

Hence

$$\langle \vec{n}+\vec{t}_\mu | \Gamma i L q\rangle^*_{E_\mu} = (-1)^L \langle \vec{n}+\vec{t}_\mu | \Gamma i L q\rangle_{E_\mu}, \tag{10.3}$$

and $i^L \mathfrak{R}^{(\Gamma i Lq)}(\vec{r};E_\mu)$ is real because we have constructed real Wannier functions.

(ii) The lattice multipoles can be expanded in power series of the components of $\vec{n}+\vec{t}_\mu$:

$$\langle \vec{n}+\vec{t}_\mu | \Gamma i L q\rangle_{E_\mu} = \sum_{l=L}^{\infty} \sum_{s\lambda} i^l v_{ls\lambda}^{(\Gamma i)}(\vec{n}+\vec{t}_\mu) \times \langle v_{ls\lambda} | W_{E_\mu}(\Gamma)\, | P_{Lq}\rangle \tag{10.4}$$

in the notation of Sec. III of Ref. 1. The polynomials $v_{ls\lambda}^{(\Gamma i)}(\vec{n}+\vec{t}_\mu)$ are homogeneous of degree l in the components of $\vec{n}+\vec{t}_\mu$. As for the power series of the spherical Bessel function $j_L(kr)$,[29] the expansion (10.4) starts with terms of degree $l=L$. Moreover, at fixed $|\vec{n}|$, $|v_{ls\lambda}^{(\Gamma i)}(\vec{n}/a)|$ tends to zero with increasing l, and roughly speaking, is rather small for $la \gg |\vec{n}|$. Therefore, *only the multipoles with relatively small L are appreciably different from zero in the vicinity of the "central" cell* $(\vec{n}=0)$.

(iii) An estimate of the value of the lattice multipoles for $|\vec{n}| \to \infty$ can be obtained from their integral representation, Eq. (9.7), by using the method of stationary phase. We follow the treatment of Koster[30] and Callaway[31] and rewrite Eq. (9.7) as

$$\langle \vec{n}+\vec{t}_\mu | \Gamma i L q\rangle_{E_\mu} = \frac{1}{2\pi\Omega} \int_{-\infty}^{+\infty} d\tau \int_\Omega d\vec{k}\, P_{Lq}^{(\Gamma i)}(\vec{k};E_\mu) \times \exp\{i[\vec{k}\cdot(\vec{n}+\vec{t}_\mu) + [E - E_\mu(\vec{k})]\tau\}). \tag{10.5}$$

For $|\vec{n}|$ large, the principal contribution to the integral comes from the neighborhoods of points $(\tau_0,\vec{k}_0)$ where the variation of the exponent is small. That is, $(\tau_0,\vec{k}_0)$ are determined by the condition

$$E = E_\mu(\vec{k}_0), \qquad \vec{n}+\vec{t}_\mu = \tau_0[\vec{\nabla}_{\vec{k}} E_\mu(\vec{k})]_{\vec{k}_0}. \tag{10.6}$$

Physically, this condition means that an electron, in a Bloch state with momentum $\vec{k}_0$ and energy E, will reach the $\vec{n}$th cell only if its (group) velocity has the direction of $\vec{n}$. Assuming that $E_\mu(\vec{k})$ is analytic about $\vec{k}_0$ so that it can be expanded in a convergent Taylor series about this point, and keeping only terms up to second order we readily get

$$\langle \vec{n}+\vec{t}_\mu | \Gamma i L q\rangle_{E_\mu} \xrightarrow[|\vec{n}|\to\infty]{} C_0 i^L P_{Lq}^{(\Gamma i)}(\vec{k}_0;E_\mu) \times \frac{\sin[\vec{k}_0\cdot(\vec{n}+\vec{t}_\mu) - L\pi/2]}{|\vec{n}+\vec{t}_\mu|} \tag{10.7}$$

Here C_0 is a constant that depends only on the derivatives of $E_\mu(\vec{k})$ at $\vec{k}_0$. In deriving Eq. (10.7) we have made use of the property that, if $(\tau_0,\vec{k}_0)$ satisfies the condition (10.6), $(-\tau_0,-\vec{k}_0)$ does too. Moreover, if several points $(\tau_0,\vec{k}_0)$ satisfy (10.6), Eq. (10.7) is naturally generalized to a sum of contributions from the various points. Equation (10.7)

is, of course, analogous to the asymptotic expansion of the spherical Bessel function for large values of the argument.[29]

That $|\langle\vec{n}+\vec{t}_\mu|\Gamma i L q\rangle_{E_\mu}| = 0(1/|\vec{n}|)$ follows on dimensional grounds as for all spherical waves. The "normalization" condition of the lattice multipoles

$$\sum_{\vec{n}} {}_{E_\mu}\langle\Gamma i L q|\vec{n}\rangle\langle\vec{n}|\Gamma' i' L' q'\rangle_{E'_\mu} = \delta(E-E')\delta_{\Gamma\Gamma'}\delta_{ii'}\delta_{LL'}\delta_{qq'}\,, \quad (10.8)$$

shows that, for large N,

$$\sum_{|\vec{n}|\le N} |\langle\vec{n}|\Gamma i L q\rangle_{E_\mu}|^2 \sim N\,, \quad (10.9)$$

while

$$\sum_{|\vec{n}|\le N} \sim N^3\,. \quad (10.10)$$

We have then $|\langle\vec{n}|\Gamma i L q\rangle_{E_\mu}| \sim 1/N$ for $|\vec{n}| \sim N$, showing that *the Wannier series of the multipole wave functions*, Eq. (9.6), *converges faster than the corresponding Wannier series of Bloch functions*.

XI. DISCUSSION

Wannier functions have traditionally been regarded as a tool for discussing local phenomena in crystals, e.g., impurities problems, *but only to the extent* that these functions are well "localized," i.e., only in a tight-binding limit, when their tails fall off exponentially.[32] In realistic situations, however, bands are degenerate and the associated Wannier functions suffer "slow" decay. Our main point has been to restore the practical role of Wannier functions by remarking that the undesirable tails originate from singularities of the Bloch waves whose effects on the norm of the Wannier functions are of the order of the *volume of a small portion of the Brillouin zone* [Eq. (5.10)]. To this extent, the contributions of the tails may be neglected in the construction of superpositions of Bloch waves, such as the multipole wave functions (9.1).

The singularities of the Bloch waves have been studied here in a few examples. Specifically, we have determined whether or not a branch cut surface must be introduced by determining the form of the Hamiltonian matrix (3.4) in small neighborhoods of loci of degeneracy. Procedures to obtain the expansion of the Hamiltonian matrix in neighborhoods of points of symmetry have been developed by group-theoretical considerations[33] and used recently to obtain densities of states contributed by neighborhoods of high degeneracy points in complex compounds.[34] We plan to apply similar methods to determine the behavior of the eigenvectors of the Hamiltonian about the loci of degeneracy.

The problem of establishing a rational normalization of the phases of the Bloch waves had been raised repeatedly over the years.[2,12,13] This problem appears to have been solved in Sec. VI, at least for the class of crystals considered explicitly. Not surprisingly, the problem had to be set in the context of unitary transformations of the whole set of Bloch waves onto alternative bases.

Certain questions emerging from this paper remain to be explored. Firstly, as noted in Sec. VI, one should consider whether and how the shift of the center of symmetry of certain Wannier functions to an interstitial position relates to chemical properties of crystal, for instance, to hybridization and bonding. Another open question concerns the possible observable implications of long-range order related to degeneracies in the spectrum of the Hamiltonian (3.4), especially when a degeneracy occurs near the Fermi level, as in the case of nickel.

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