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Review

Group Theory of Wannier Functions Providing the Basis for a Deeper Understanding of Magnetism and Superconductivity

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Abstract: The paper presents the group theory of optimally-localized and symmetry-adapted Wannier functions in a crystal of any given space group G or magnetic group M. Provided that the calculated band structure of the considered material is given and that the symmetry of the Bloch functions at all of the points of symmetry in the Brillouin zone is known, the paper details whether or not the Bloch functions of particular energy bands can be unitarily transformed into optimally-localized Wannier functions symmetry-adapted to the space group G, to the magnetic group M or to a subgroup of G or M. In this context, the paper considers usual, as well as spin-dependent Wannier functions, the latter representing the most general definition of Wannier functions. The presented group theory is a review of the theory published by one of the authors (Ekkehard Krüger) in several former papers and is independent of any physical model of magnetism or superconductivity. However, it is suggested to interpret the special symmetry of the optimally-localized Wannier functions in the framework of a nonadiabatic extension of the Heisenberg model, the nonadiabatic Heisenberg model. On the basis of the symmetry of the Wannier functions, this model of strongly-correlated localized electrons makes clear predictions of whether or not the system can possess superconducting or magnetic eigenstates.

Keywords: Wannier functions; spin-dependent Wannier functions; magnetism; superconductivity; group theory

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1. Introduction

The picture of strongly-correlated localized or nearly-localized electrons is the basis of a successful theoretical description of both high-temperature superconductivity and magnetism (see, e.g., [1–3] and the citations given there). The appertaining localized electron states are often represented by atomic orbitals that define, for instance, partially filled s-, d- or p- bands.

Another option is to represent the localized electron states by optimally-localized and symmetry-adapted Wannier functions. In contrast to atomic functions, Wannier functions situated at adjacent atoms are orthogonal and form a complete set of basis functions within the considered narrow, partially filled band. Consequently, Wannier functions contain all of the physical information about this energy band. At first, however, the use of Wannier functions within the theory of superconductivity and magnetism appears to be hampered by the well-known fact that we need a closed complex of energy bands (Definition 1) for the construction of optimally-localized Wannier functions. Such closed complexes, however, do not exist in the band structures of the metals where all of the bands are connected to each other by band degeneracies.

In the literature, there have been proposed several procedures to tackle this problem; see, e.g., the review article [4]. The present paper, however, and all of the papers of the authors published previously (and cited below) solve this problem in another way, by constructing Wannier functions with the reduced symmetry of a magnetic group or by constructing spin-dependent Wannier functions. In both cases, interfering band degeneracies are sometimes removed in the band structure with the reduced symmetry. The physical power of this natural method of producing closed complexes of energy bands in suitable band structures is corroborated by two observations:

(i) Materials possessing a magnetic structure with the magnetic group M also possess a closed, narrow and roughly half-filled complex of energy bands in their band structure whose Bloch functions can be unitarily transformed into optimally-localized Wannier functions that are symmetry-adapted to the magnetic group M. These energy bands form a "magnetic band"; see Definition 16.

(ii) Both normal and high-temperature superconductors (and only superconductors) possess a closed, narrow and roughly half-filled complex of energy bands in their band structure whose Bloch spinors can be unitarily transformed into optimally-localized spin-dependent Wannier functions that are symmetry-adapted to the (full) space group G of the material. These energy bands form a "superconducting band"; see Definition 22.

The first observation (i) was made at the band structures of Cr [5], Fe [6], La_2CuO_4 [7], $YBa_2Cu_3O_6$ [8], undoped LaFeAsO [9] and $BaFe_2As_2$ [10]; the second observation (ii) at the band structures of numerous elemental superconductors [11] and of the (high-temperature) superconductors La_2CuO_4 [7], $YBa_2Cu_3O_7$ [12], MgB_2 [12] and doped LaFeAsO [13]. It is particularly important that partly filled superconducting bands cannot be found in those elemental metals (such as Li, Na, K, Rb, Cs, Ca, Cu, Ag and Au) that do not become superconducting [11]. An investigation into the band structures of the transition metals in terms of superconducting bands straightforwardly leads to the Matthias rule [14].

These two observations can be interpreted in a clear way within a nonadiabatic extension of the Heisenberg model, the nonadiabatic Heisenberg model [12,15]. This model of strongly-correlated localized electrons is determined by three new postulates and defines a nonadiabatic mechanism stabilizing the hopping motion in narrow bands. On the basis of the symmetry of the Wannier functions, the nonadiabatic model makes clear predictions of whether or not the related nonadiabatic Hamiltonian H^n can possess superconducting or magnetic eigenstates [5,10,11,16]. In this context, the nonadiabatic Heisenberg model no longer uses terms like s-, p- or d-bands, but only speaks of superconducting or magnetic bands.

In some materials, the nonadiabatic Heisenberg model predicts that a small distortion of the lattice or a doping is required for the stability of the superconducting or magnetic state. Thus, in undoped LaFeAsO [9] and in $BaFe_2As_2$ [10], the antiferromagnetic state must be stabilized by an experimentally well-established distortion [17,18], while in $YBa_2Cu_3O_6$ [8], it is stable in the undistorted crystal. Superconductivity in LaFeAsO [9] requires the experimentally-confirmed doping [18–21]. Furthermore, the superconducting state in LiFeAs [22] should be accompanied by a small distortion of the lattice, which, to our knowledge, is experimentally not yet confirmed. Superconductivity in $YBa_2Cu_3O_7$ [12], MgB_2 [12], as well as in the transition elements [11] (such as in Nb [16]), on the other hand, does not require any distortion or doping.

In the case of (conventional and high-T_c [23]) superconductivity, the nonadiabatic Heisenberg model provides a new mechanism of Cooper pair formation, which may be described in terms of constraining forces [16] and spring-mounted Cooper pairs [24].

Any application of the nonadiabatic Heisenberg model starts with an examination of whether or not there exist closed band complexes with optimally-localized symmetry-adapted usual or spin-dependent Wannier functions in the band structure of the material under consideration. In the following (in Sections 2–7), we shall summarize and update the group theory of Wannier functions as published in former papers and give a detailed description of how to determine the symmetry of optimally-localized Wannier functions if they exist in the given band structure. In Sections 2–6, we shall consider usual (*i.e.*, spin-independent) Wannier functions as defined in the first subsection of Section 2. In the following subsections of Section 2 and in Sections 3–5, the spatial symmetry of the Wannier functions will be specified. The central theorem to determine the spatial symmetry of optimally-localized symmetry-adapted Wannier functions will be Theorem 5. Then, in Section 6, we shall consider magnetic groups by adding the time-inversion symmetry. Finally, in Section 7, we shall define and specify spin-dependent Wannier functions.

Since we use the most general definition of Wannier functions, they are identical with the maximally-localized Wannier functions calculated from first principles [25] by minimizing their total spread [26] so long as the latter are symmetry-adapted, too. The methods complement each other, because by group theory, we cannot provide any procedure to calculate the Wannier functions. The present paper only examines the existence of optimally-localized symmetry-adapted Wannier functions.

The closed complexes of energy bands used in this paper, however, differ from the optimal subspaces, as defined by Souza *et al.* [27]: for instance, the subspace method allows the construction of well-localized Wannier-like functions even for the conduction bands of copper. With our methods, on the other hand, we cannot construct optimally-localized symmetry-adapted Wannier functions close to

the Fermi energy in copper, which are centered at the atomic positions. In other words, copper neither possesses a magnetic nor a superconducting band with the physical consequence that copper neither is magnetic nor superconducting. Moreover, our closed complexes of energy bands never comprise all of the partially filled bands near the Fermi level; see, e.g., the superconducting band of niobium depicted in Figure 1 or the numerous magnetic and superconducting bands presented in the papers cited above. The energy bands belonging to our closed complexes are determined by the symmetry of the Bloch functions. Nevertheless, we believe that the subspace method used by Souza *et al.* might be combined with the symmetry method used in this paper.

Though we shall also define the two terms "magnetic" and "superconducting" band (Definitions 16 and 22, respectively), which are related to the nonadiabatic Heisenberg model, the presented group theory is independent of any physical model of magnetism or superconductivity.

2. Usual (Spin-Independent) Wannier Functions

2.1. Definition

Consider a closed complex of μ energy bands in the band structure of a metal or a semiconductor.

Definition 1 (closed)**.** *A complex of energy bands is called closed if the bands are not connected by degeneracies to bands not belonging to the complex.*

Definition 2 (closed band)**.** *In the following, a closed complex of μ energy bands is referred to as a single closed band consisting of μ branches.*

The metals do not possess closed bands in their band structures. However, closed bands may arise after the activation of a perturbation, reducing the symmetry in such a way that interfering band degeneracies are removed. Such a reduction of the symmetry may be caused by a magnetic structure or by a (slight) distortion of the crystal.

Hence, we assume that the Hamiltonian $\mathcal{H}$ of a single electron in the considered material consists of a part $\mathcal{H}_G$ with the unperturbed space group G and a perturbation $\mathcal{H}_H$ with the space group H,

$$\mathcal{H} = \mathcal{H}_G + \mathcal{H}_H, \tag{1}$$

where H is a subgroup of G,

$$H \subset G. \tag{2}$$

In general, the considered closed energy band of μ branches was not closed before the perturbation $\mathcal{H}_H$ was activated.

Assume the Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ (labeled by the wave vector $\vec{k}$ and the branch index q) as the solutions of the Schrödinger equation of $\mathcal{H}$ to be completely calculated in the first domain of the Brillouin zone.

Definition 3 (first domain)**.** *Let h be the order of the point group H_0 of H. Then, the Brillouin zone is divided by the planes of symmetry into h domains. An arbitrarily chosen domain we call the first domain. This first domain shall comprise the bounding planes, lines and points of symmetry, too.*

As in [28], in the rest of the Brillouin zone, the Bloch functions shall be determined by the equation:

$$\varphi_{\alpha\vec{k},q}(\vec{r}) = P(\{\alpha|\vec{t}_\alpha\})\varphi_{\vec{k},q}(\vec{r}) \text{ for } \alpha \in H_0, \tag{3}$$

where $\vec{k}$ lies in the first domain, and in the $\vec{k}$ space outside the Brillouin zone by the equation:

$$\varphi_{\vec{k}+\vec{K},q}(\vec{r}) = \varphi_{\vec{k},q}(\vec{r}). \tag{4}$$

$\vec{K}$ denotes a vector of the reciprocal lattice and H_0 stands for the point group of H.

Definition 4 (symmetry operator)**.** *$P(a)$ denotes the symmetry operator assigned to the space group operation $a = \{\alpha|\vec{t}_\alpha\}$ consisting of a point group operation α and the associated translation $\vec{t}_\alpha$, acting on a wave function $f(\vec{r})$ according to:*

$$P(a)f(\vec{r}) = f(a^{-1}\vec{r}) = f(\alpha^{-1}\vec{r} - \alpha^{-1}\vec{t}_\alpha). \tag{5}$$

The Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ of the closed band under observation can be unitarily transformed into Wannier functions:

$$w_i(\vec{r} - \vec{R} - \vec{\rho}_i) = \frac{1}{\sqrt{N}} \sum_{\vec{k}}^{BZ} e^{-i\vec{k}(\vec{R}+\vec{\rho}_i)} \widetilde{\varphi}_{\vec{k},i}(\vec{r}) \tag{6}$$

centered at the positions $\vec{R} + \vec{\rho}_i$, where the functions:

$$\widetilde{\varphi}_{\vec{k},i}(\vec{r}) = \sum_{q=1}^{\mu} g_{iq}(\vec{k})\varphi_{\vec{k},q}(\vec{r}) \tag{7}$$

are "generalized" Bloch functions [28]. The sum in Equation (6) runs over the N vectors $\vec{k}$ of the first Brillouin zone (BZ); the sum in Equation (7) over the μ branches of the considered band; $\vec{R}$ denote the vectors of the Bravais lattice; and the coefficients $g_{iq}(\vec{k})$ in Equation (7) are the elements of an unitary matrix $\mathbf{g}(\vec{k})$,

$$\mathbf{g}^{-1}(\vec{k}) = \mathbf{g}^{\dagger}(\vec{k}), \tag{8}$$

in order that the Wannier functions are orthonormal,

$$\int w_i^*(\vec{r} - \vec{R} - \vec{\rho}_i) w_{i'}(\vec{r} - \vec{R}\,' - \vec{\rho}_{i'}) d\vec{r} = \delta_{\vec{R}\vec{R}'}\delta_{ii'}. \tag{9}$$

Definition 5 (optimally-localized)**.** *The Wannier functions are called optimally-localized if the coefficients $g_{iq}(\vec{k})$ may be chosen in such a way that the generalized Bloch functions $\widetilde{\varphi}_{\vec{k},i}(\vec{r})$ move, for fixed $\vec{r}$, continuously through to whole $\vec{k}$ space [28].*

As was already shown in [29], the Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ as the eigenfunctions of the Hamiltonian $\mathcal{H}$ may be chosen in such a way that they vary continuously as functions of $\vec{k}$ through the first domain and, in particular, approach continuously the boundaries of the first domain. From Equations (3) and (4), however, we cannot conclude that they also cross continuously the boundaries of the domains within the Brillouin zone or at the surface of the Brillouin zone. Fortunately, this problem is solvable by group-theoretical methods [28,30]. Theorem 5 shall define the condition for optimally-localized and symmetry-adapted (Definition (7)) Wannier functions.

2.2. Symmetry-Adapted Wannier Functions

In [28], we demanded that symmetry-adapted Wannier functions satisfy the equation:

$$w_i\big(\alpha^{-1}(\vec{r}-\vec{R}-\vec{\rho}_i)\big)=\sum_{j=1}^{\mu}D_{ji}(\alpha)w_j(\vec{r}-\vec{R}-\vec{\rho}_i) \tag{10}$$

for the elements α of the point group H_0 of H, where the $D_{ji}(\alpha)$ are the elements of the matrices:

$$\mathbf{D}(\alpha)=\big[D_{ij}(\alpha)\big] \tag{11}$$

forming a representation $\boldsymbol{D}$ of H_0, which in most cases, is reducible. (It should be noted that the sum in Equation (10) runs over $w_j(\vec{r}-\vec{R}-\vec{\rho}_i)$ and not over $w_j(\vec{r}-\vec{R}-\vec{\rho}_j)$.)

Equation (10) defines the symmetry of Wannier functions in general terms; in particular, they may be centered at a variety of positions $\vec{\rho}_i$ being different from the positions of the atoms. However, in the context of superconducting and magnetic bands, we may restrict ourselves to Wannier functions centered at the positions of the atoms.

Thus, we assume:

(i) that the positions $\vec{\rho}_i$ of the Wannier functions in Equation (6) are the positions of atoms,

(ii) that only atoms of the same sort are considered (although, of course, other atoms may exist) and

(iii) that there is one Wannier function at each atom.

Under these assumptions [15],

- the Wannier functions may be labeled by the positions of the atoms,

$$w_{\vec{T}}(\vec{r})\equiv w_i(\vec{r}-\vec{R}-\vec{\rho}_i), \tag{12}$$

  where

$$\vec{T}=\vec{R}+\vec{\rho}_i, \tag{13}$$

- the matrix representatives $\mathbf{D}(\alpha)$ of the representation $\boldsymbol{D}$ in Equation (10) have one non-vanishing element $D_{ij}(\alpha)$ with:

$$|D_{ij}(\alpha)|=1 \tag{14}$$

  in each row and each column and

- Equation (10) may be written in the considerably simplified form:

$$P(a)w_{\vec{T}}(\vec{r})=D_{ji}(\alpha)w_{\vec{T}'}(\vec{r}) \text{ for } a\in H \tag{15}$$

  where

$$\vec{T}\,'=\alpha\vec{T}+\vec{t}_\alpha \tag{16}$$

  and the subscripts i and j denote the number of the atoms at position $\vec{T}$ and $\vec{T}\,'$, respectively.

Definition 6 (number of the atom)**.** *The subscript i of the vector $\vec{\rho}_i$ in Equation (13) defines the number of the atom at position $\vec{T}$.*

Definition 7 (symmetry-adapted)**.** *We call the Wannier functions symmetry-adapted to H if they satisfy Equation (15).*

Theorem 1. *The third assumption (iii) shows immediately that the number μ of the branches of the band under observation equals the number of the considered atoms in the unit cell.*

Equations (15) and (16) define the non-vanishing elements, and hence, we may write Equation (14) more precisely,

$$|D_{ji}(\alpha)| = \begin{cases} 1 & \text{if } \alpha\vec{\rho}_i + \vec{t}_\alpha = \vec{\rho}_j + \vec{R} \\ 0 & \text{else,} \end{cases} \tag{17}$$

where $\{\alpha|\vec{t}_\alpha\} \in H$ and $\vec{R}$ still denotes a lattice vector.

Definition 8 (the representation defining the Wannier functions)**.** *In what follows, the representation $\boldsymbol{D}$ of H_0 with the matrix representatives*

$$\mathbf{D}(\alpha) = [D_{ij}(\alpha)]$$

defined by Equation (15) shall be referred to in short as "the representation defining the Wannier functions" and its matrix representatives $\mathbf{D}(\alpha)$ as "the matrices defining the Wannier functions".

Definition 9 (unitary generalized permutation matrices)**.** *Since the matrices $\mathbf{D}(\alpha)$ defining the Wannier functions have one non-vanishing element obeying Equation (17) in each row and each column, they are so-called unitary generalized permutation matrices.*

3. Determination of the Representations *D* Defining the Wannier Functions

In the following Section 4, we shall give a simple condition (Theorem 5) for optimally-localized and symmetry-adapted Wannier functions yielding the representations of the Bloch functions at all of the points $\vec{k}$ of symmetry in the Brillouin zone. However, in Theorem 5, the representations $\boldsymbol{D}$ defining the Wannier functions must be known. Hence, first of all, we have to determine in this section all of the possible representations that may define the Wannier functions. In this context, we assume first that all of the atoms are connected by symmetry. This restricting assumption shall not be abandoned until Section 3.4.

Definition 10 (connected by symmetry)**.** *Two atoms at positions $\vec{\rho}_i$ and $\vec{\rho}_j$ are connected by symmetry if there exists at least one element $a = \{\alpha|\vec{t}_\alpha\}$ in the space group H satisfying the equation:*

$$\alpha\vec{\rho}_i + \vec{t}_\alpha = \vec{\rho}_j + \vec{R}, \tag{18}$$

where $\vec{R}$ is a lattice vector.

3.1. General Properties of the Representatives $\mathbf{D}(\alpha)$ *of* $\boldsymbol{D}$

First consider the diagonal elements:

$$d_i(\alpha) = D_{ii}(\alpha) \tag{19}$$

of the matrices $\mathbf{D}(\alpha)$ defining the Wannier functions. From Equation (17), we obtain:

$$|d_i(\alpha)| = \begin{cases} 1 & \text{if } \alpha\vec{\rho}_i + \vec{t}_\alpha = \vec{\rho}_i + \vec{R} \\ 0 & \text{else} \end{cases} \tag{20}$$

where $\vec{R}$ denotes a lattice vector. This equation demonstrates that the matrix $\mathbf{D}(\alpha)$ has non-vanishing diagonal elements $d_i(\alpha)$ if the space group operation $a = \{\alpha|\vec{t}_\alpha\}$ leaves invariant the position $\vec{\rho}_i$ of the i-th atom. These space group operations form a group, namely the group $G_{\vec{\rho}_i}$ of the position $\vec{\rho}_i$.

Definition 11 (group of position)**.** *The group $G_{\vec{\rho}_i}$ of the position $\vec{\rho}_i$ is defined by:*

$$a \in G_{\vec{\rho}_i} \textit{ if } a \in H \textit{ and } \alpha\vec{\rho}_i + \vec{t}_\alpha = \vec{\rho}_i + \vec{R}. \tag{21}$$

$G_{0\vec{\rho}_i}$ denotes the point group of $G_{\vec{\rho}_i}$.

Hence, the non-vanishing diagonal elements $d_i(\alpha)$ of the matrices $\mathbf{D}(\alpha)$ form a one-dimensional representation $\boldsymbol{d}_i$ of the point group $G_{0\vec{\rho}_i}$ of $G_{\vec{\rho}_i}$. The Wannier functions transform according to:

$$P(a)w_{\vec{T}}(\vec{r}) = d_i(\alpha)w_{\vec{T}+\vec{R}}(\vec{r}) \text{ for } \alpha \in G_{0\vec{\rho}_i} \tag{22}$$

(*cf.*, Equation (15)) by application of a space group operator $P(a)$ (where $\vec{R}$ still denotes a vector of the Bravais lattice). From Equation (10), we may derive the equivalent equation:

$$w_i\big(\alpha^{-1}(\vec{r} - \vec{R} - \vec{\rho}_i)\big) = d_i(\alpha)w_i(\vec{r} - \vec{R} - \vec{\rho}_i) \text{ for } \alpha \in G_{0\vec{\rho}_i} \tag{23}$$

or, after shifting the origin of the coordinate system into the center of the function $w_i(\vec{r} - \vec{R} - \vec{\rho}_i)$,

$$\vec{r}\,' = \vec{r} - \vec{R} - \vec{\rho}_i,$$

we receive an equation:

$$w_i(\alpha^{-1}\vec{r}\,') = d_i(\alpha)w_i(\vec{r}\,') \text{ for } \alpha \in G_{0\vec{\rho}_i} \tag{24}$$

emphasizing the point-group symmetry of the Wannier function at position $\vec{R} + \vec{\rho}_i$.

In constructing the representation $\boldsymbol{D}$ defining the Wannier functions, we cannot arbitrarily choose the one-dimensional representations $\boldsymbol{d}_i$ of $G_{0\vec{\rho}_i}$, because they must be chosen in such a way that the matrix representatives $\mathbf{D}(\alpha)$ form a representation of the point group H_0, *i.e.*, they must obey the multiplication rule:

$$\mathbf{D}(\alpha\beta) = \mathbf{D}(\alpha)\mathbf{D}(\beta) \tag{25}$$

for all of the elements α and β in H_0.

In what follows, we assume that all of the groups $G_{\vec{\rho}_i}$ are normal subgroups of H. In fact, in all of the crystal structures that we examined in the past, $G_{\vec{\rho}_i}$ was a normal subgroup, be it because it was a

subgroup of Index 2 or be it because it was the intersection of two subgroups of Index 2. Both cases are sufficient for a normal subgroup. We believe that in all physically-relevant crystal structures, $G_{\vec{\rho}_i}$ is a normal subgroup of H. If not, the present formalism must be extended for these structures.

When the groups $G_{\vec{\rho}_i}$ are normal subgroups of H, each of the groups $G_{\vec{\rho}_i}$ contains only complete classes of H,

$$b^{-1}ab \in G_{\vec{\rho}_i} \text{ if } a \in G_{\vec{\rho}_i} \text{ and } b \in H. \tag{26}$$

We now show that, as a consequence, all of the groups $G_{\vec{\rho}_i}$ contain the same space group operations.

Let $b = \{\beta|\vec{t}_\beta\}$ be a space group operation of H moving ρ_i into ρ_j,

$$\beta\vec{\rho}_i + \vec{t}_\beta = \vec{\rho}_j + \vec{R},$$

then

$$c = b^{-1}ab \tag{27}$$

is an element of $G_{\vec{\rho}_i}$ if $a \in G_{\vec{\rho}_j}$. Equation (27) even yields all of the elements c of $G_{\vec{\rho}_i}$ when a runs throw all of the elements of $G_{\vec{\rho}_j}$, because we may write Equation (27) in the form:

$$bcb^{-1} = a$$

showing that we may determine from any element $c \in G_{\vec{\rho}_i}$ an element $a \in G_{\vec{\rho}_j}$.

On the other hand, Equation (26) shows that c is an element of $G_{\vec{\rho}_j}$, too. When a runs through all of the elements of $G_{\vec{\rho}_j}$, then also c runs through all of the elements of $G_{\vec{\rho}_j}$. Consequently, all of the groups $G_{\vec{\rho}_i}$, as well as all of the related point groups $G_{0\vec{\rho}_i}$ contain the same elements.

Thus, we may omit the index i and define:

Definition 12 (group of position)**.** *The group G_p and the related point group G_{0p} of the positions of the atoms are defined by:*

$$G_p \equiv G_{\vec{\rho}_i} \tag{28}$$

and

$$G_{0p} \equiv G_{0\vec{\rho}_i}, \tag{29}$$

respectively, where $G_{\vec{\rho}_i}$ and $G_{0\vec{\rho}_i}$ are given by Definition 11.

3.2. Necessary condition for of the representatives $\mathbf{D}(\alpha)$ of $\boldsymbol{D}$

The one-dimensional representations $\boldsymbol{d}_i$ of G_{0p} must be chosen in such a way that the matrices $\mathbf{D}(\alpha)$ defining the Wannier functions form a representation $\boldsymbol{D}$ of the complete point group H_0. A necessary condition is given by the evident Theorem 2.

Theorem 2. *If the matrices $\mathbf{D}(\alpha)$ cannot be completely reduced into the irreducible representations of H_0, then they do not form a representation of the point group H_0.*

This theorem is necessary, but not sufficient: even if the matrices $\mathbf{D}(\alpha)$ can be completely reduced into the irreducible representations of H_0, then they need not form a representation of the point group H_0 [31]. The complete decomposition of a reducible representation is described, e.g., in [31,32]; in particular, see Equation (1.3.18) of [32]. Theorem 2 leads to three important cases:

– Case (i): If all of the representations $\boldsymbol{d}_i$ are subduced from one-dimensional representations of H_0, then all of the representations $\boldsymbol{d}_i$ are equal,

$$\boldsymbol{d}_i = \boldsymbol{d} \quad \text{for all of the positions } \vec{\rho}_i. \tag{30}$$

The representation $\boldsymbol{d}$ may be equal to any one-dimensional representation of G_{0p} subduced from a one-dimensional representation of H_0.

– Case (ii): If all of the representations $\boldsymbol{d}_i$ are subduced from two-dimensional representations of H_0, then one half of the representations $\boldsymbol{d}_i$ is equal to $\boldsymbol{d}_A$, and the other half is equal to $\boldsymbol{d}_B$,

$$\begin{array}{rcll} \boldsymbol{d}_i & = & \boldsymbol{d}_A & \text{for one half of the positions } \vec{\rho}_i \\ \boldsymbol{d}_i & = & \boldsymbol{d}_B & \text{for the remaining positions } \vec{\rho}_i, \end{array} \tag{31}$$

where $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ are subduced from the same two-dimensional representation of H_0. In special cases, the two representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ may be equal; see below.

– Case (iii): "Mixed" representations $\boldsymbol{D}$ consisting of both representations $\boldsymbol{d}_i$ subduced from one- and two-dimensional representations of H_0 do not exist.

A further case that the representations $\boldsymbol{d}_i$ are subduced from three-dimensional representations of H_0 may occur in crystals of high symmetry, but is not considered in this paper.

These results, (i)–(iii), follow from the very fact that Equation (15) describes an interchange of the Wannier functions at different positions $\vec{\rho}_i$. Such an interchange, however, does not alter the symmetry of the Wannier functions.

3.3. Sufficient Condition for of the Representatives $\mathbf{D}(\alpha)$ *of* $\boldsymbol{D}$

For $\alpha \in G_{0p}$ the matrices $\mathbf{D}(\alpha)$ defining the Wannier functions are diagonal, while the remaining matrices $\mathbf{D}(\alpha)$ (for $\alpha \in H_0 - G_{0p}$) do not possess any diagonal element. Theorem 2 only gives information about the diagonal matrices $\mathbf{D}(\alpha)$. Hence, this theorem indeed cannot be sufficient, because we do not know whether or not the remaining matrices obey the multiplication rule (25).

In this section, we assume that the matrices $\mathbf{D}(\alpha)$ already satisfy Theorem 2 and examine the conditions under which they actually form a (generally reducible) representation of H_0. In doing so, we consider separately the two cases, (i) and (ii), of the preceding Section 3.2.

3.3.1. Case (i) of Section 3.2

No further problems arises when Case (i) of Section 3.2 is realized. In this case, Theorem 2 is necessary and sufficient. To justify this assertion, we write down explicitly the non-diagonal elements of the matrices $\mathbf{D}(\alpha)$.

Let $\boldsymbol{\delta}$ be any one-dimensional representation of H_0 subducing the representation $\boldsymbol{d}$ in Equation (30). If we put all of the non-vanishing elements of the matrices $\mathbf{D}(\alpha)$ equal to the elements $\delta(\alpha)$ of $\boldsymbol{\delta}$,

$$D_{ji}(\alpha) = \begin{cases} \delta(\alpha) & \text{if } \alpha\vec{\rho}_i + \vec{t}_\alpha = \vec{\rho}_j + \vec{R} \\ 0 & \text{else,} \end{cases} \tag{32}$$

then we receive matrices $\mathbf{D}(\alpha)$ evidently multiplying as the elements of the representation $\boldsymbol{\delta}$ and, consequently, obeying the multiplication rule in Equation (25).

3.3.2. Case (ii) of Section 3.2

The situation is a little more complicated when Case (ii) of Section 3.2 is realized. Now, the representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ in Equation (31) may be distributed across the positions $\vec{\rho}_i$ in such a way that the matrices $\mathbf{D}(\alpha)$ form a representation of H_0 or do not. Though we always find a special distribution of the $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ yielding matrices $\mathbf{D}(\alpha)$ actually forming a representation of H_0, we have to rule out those distributions not leading to a representation of H_0, because in the following (in Equations (38), (66) and (111)), we need the matrices $\mathbf{D}(\alpha)$ explicitly.

Let $\boldsymbol{\Delta}$ be (with the matrix representatives $\boldsymbol{\Delta}(\alpha)$) a two-dimensional representation of H_0 subducing the two representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ of G_{0p}. The matrix representatives $\boldsymbol{\Delta}(\alpha)$ may be determined, e.g., from Table 5.1 of [32].

As a first step, $\boldsymbol{\Delta}$ must be unitarily transformed (by a matrix $\mathbf{Q}$) in such a way that the matrices $\boldsymbol{\Delta}(\alpha)$ are diagonal for $\alpha \in G_{0p}$,

$$\overline{\boldsymbol{\Delta}}(\alpha) = \mathbf{Q}^{-1}\boldsymbol{\Delta}(\alpha)\mathbf{Q} \quad = \text{ diagonal for } \alpha \in G_{0p}. \tag{33}$$

Now, consider a certain distribution of the representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ across the positions $\vec{\rho}_i$. Then, we may determine the elements of the matrices $\mathbf{D}(\alpha)$, if they exist, be means of the formula:

$$\text{if} \quad \alpha\vec{\rho}_i + \vec{t}_\alpha = \vec{\rho}_j + \vec{R}$$

$$D_{ji}(\alpha) = \begin{cases} \overline{\Delta}_{12}(\alpha) & \text{if } \boldsymbol{d}_j = \boldsymbol{d}_A \quad \text{and } \boldsymbol{d}_i = \boldsymbol{d}_B, \\ \overline{\Delta}_{21}(\alpha) & \text{if } \boldsymbol{d}_j = \boldsymbol{d}_B \quad \text{and } \boldsymbol{d}_i = \boldsymbol{d}_A, \\ \overline{\Delta}_{11}(\alpha) & \text{if } \boldsymbol{d}_j = \boldsymbol{d}_A \quad \text{and } \boldsymbol{d}_i = \boldsymbol{d}_A, \\ \overline{\Delta}_{22}(\alpha) & \text{if } \boldsymbol{d}_j = \boldsymbol{d}_B \quad \text{and } \boldsymbol{d}_i = \boldsymbol{d}_B, \end{cases} \tag{34}$$

else

$$D_{ji}(\alpha) = 0,$$

where the $\overline{\Delta}_{ij}(\alpha)$ denote the elements of $\overline{\boldsymbol{\Delta}}(\alpha)$.

It turns out that in each case, the matrices determined by Equation (34) satisfy the multiplication rule in Equation (25) if Equation (34) produces for each space group operation $a \in H$ a unitary generalized permutation matrix $\mathbf{D}(\alpha)$. This may be understood because Equation (34) defines the complex numbers $D_{ji}(\alpha)$ in such a way that the Wannier functions transform in Equation (15) in an unequivocal manner like the basis functions for $\overline{\boldsymbol{\Delta}}$. With "like" the basis functions, we want to express that by application of any space group operator $P(\{\alpha|\vec{t}_\alpha\})$, they are multiplied in Equation (15) by the same complex number

$\overline{\Delta}_{ij}(\alpha)$ as the basis functions for $\overline{\mathbf{\Delta}}$. The Wannier functions would indeed be basis functions for $\overline{\mathbf{\Delta}}$ if they would not be moved from one position $\vec{\rho}_i$ to another by some space group operations. Hence, we may expect that the matrices $\mathbf{D}(\alpha)$ satisfy the multiplication rule in Equation (25) just as the matrices $\overline{\mathbf{\Delta}}(\alpha)$ do. Nevertheless, the multiplication rule should be verified numerically in any case.

When using this Equation (34), a little complication arises if the group of position G_{0p} contains so few elements that the two one-dimensional representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ subduced from $\overline{\mathbf{\Delta}}$ are equal. Thus, in this case, we have no problem with the distribution of $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ across the positions $\vec{\rho}_i$. Theorem 2 is necessary and sufficient, and we may directly solve Equation (38) of Theorem 5.

However, when in Section 6 or in Section 7.3 we will consider magnetic groups, we need all of the representatives $\mathbf{D}(\alpha)$ of the representation $\boldsymbol{D}$ explicitly. Fortunately, also when the representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ are equal, Equation (34) is applicable: in this case, their exists at least one diagonal matrix representative $\overline{\mathbf{\Delta}}(\gamma)$ of $\overline{\mathbf{\Delta}}$ with vanishing trace and $\gamma \notin G_{0p}$. We may define pairs:

$$(\vec{\rho}_a, \vec{\rho}_b), \quad (\vec{\rho}_c, \vec{\rho}_d), \quad \ldots \tag{35}$$

of positions ρ_i where the positions in each pair are connected by the space group operation $\{\gamma|\vec{t}_\gamma\}$. In the simplest case, we receive two pairs. Then, in Equation (34), we may identify the two representations at $\vec{\rho}_a$ and $\vec{\rho}_b$ by $\boldsymbol{d}_A$ and the representations at the other two positions $\vec{\rho}_c$ and $\vec{\rho}_d$ by $\boldsymbol{d}_B$. If we find four pairs of positions, we may look for a second matrix representative $\overline{\mathbf{\Delta}}(\gamma')$ in $\overline{\mathbf{\Delta}}$ with vanishing trace and $\gamma' \notin G_{0p}$. Then, we may repeat the above procedure and receive again four pairs of positions. Now, we associate the two representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ to the positions $\vec{\rho}_i$ under the provision that positions of the same pair are always associated with the same representation $\boldsymbol{d}_A$ or $\boldsymbol{d}_B$.

Finally, it should be mentioned that the elements of the non-diagonal matrices $\mathbf{D}(\alpha)$ are not fully fixed (as already remarked in [30]): In Equation (32), we may use the elements $\delta(\alpha)$ of any one-dimensional representation $\boldsymbol{\delta}$ subducing the representation $\boldsymbol{d}$. We receive in each case the same diagonal, but different non-diagonal matrices nevertheless satisfying the multiplication rule (25). Analogously, in Equation (34), we may determine the matrices $\mathbf{D}(\alpha)$ by means of any two-dimensional representation $\overline{\mathbf{\Delta}}$ subducing $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$.

In the following Theorem 3, we summarize our results in the present Section 3.3.

Theorem 3. *The Wannier function $w_i(\vec{r}-\vec{R}-\vec{\rho}_i)$ at the position $\vec{\rho}_i$ is basis function for a one-dimensional representation $\boldsymbol{d}_i$ of the "point group of position" $G_{0p} \subset H_0$ (Definition 12); cf. Equation (24). The representations $\boldsymbol{d}_i$ fix the (generally reducible) representation $\boldsymbol{D}$ of H_0 defining the Wannier functions (Definition 8). The matrix representatives $\mathbf{D}(\alpha)$ of $\boldsymbol{D}$ are unitary generalized permutation matrices. We distinguish between two cases, (i) and (ii).*

Case (i): If the representations $\boldsymbol{d}_i$ are subduced from one-dimensional representations of the point group H_0, then all of the Wannier functions of the band under observation are basis functions for the same representation $\boldsymbol{d}$, which may be any one-dimensional representation of G_{0p} subduced from a one-dimensional representation of H_0. The representation $\boldsymbol{D}$ exists always; its matrix representatives $\mathbf{D}(\alpha)$ may be calculated by Equation (32).

Case (ii): If the representations $\boldsymbol{d}_i$ are subduced from two-dimensional representations of the point group H_0, then the Wannier functions are basis functions for the two one-dimensional representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ of G_{0p} subduced from the same two-dimensional representation of H_0. One half of the Wannier

functions is the basis function for $\boldsymbol{d}_A$ and the other half for $\boldsymbol{d}_B$. In special cases, the representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ may be equal; see above. The representation $\boldsymbol{D}$ exists for a given distribution of the representations $\boldsymbol{d}_A$ and $\boldsymbol{d}_B$ across the positions $\vec{\rho}_i$ if Equation (34) yields unitary generalized permutation matrices $\mathbf{D}(\alpha)$ satisfying the multiplication rule in Equation (25).

A third case with representations $\boldsymbol{d}_i$ subduced from one-dimensional, as well as from two-dimensional representations of H_0 does not exist.

3.4. Not All of the Atoms Are Connected by Symmetry

If not all of the atoms at the positions $\vec{\rho}_i$ are connected by symmetry (Definition 10), the representation $\boldsymbol{D}$ defining the Wannier functions consists of representatives $\mathbf{D}(\alpha)$, which may be written in block-diagonal form:

$$\mathbf{D}(\alpha) = \begin{pmatrix} \begin{pmatrix} \text{block 1} \end{pmatrix} & 0 & \cdots \\ 0 & \begin{pmatrix} \text{block 2} \end{pmatrix} & \cdots \\ \vdots & \vdots & \end{pmatrix}, \tag{36}$$

where each block comprises the matrix elements $D_{ij}(\alpha)$ belonging to positions connected by symmetry. Otherwise, when the matrices $\mathbf{D}(\alpha)$ would not possess the block-diagonal form, Equation (10) would falsely connect atomic positions that are not at all connected by symmetry. As a consequence of the block-diagonal form, the representation $\boldsymbol{D}$ is the direct sum over representations $\boldsymbol{D}^q$ related to the individual blocks,

$$\begin{aligned} \boldsymbol{D} &= \boldsymbol{D}^1 \oplus \boldsymbol{D}^2 \oplus \ldots \\ &= \sum_q \boldsymbol{D}^q. \end{aligned} \tag{37}$$

We may summarize as follows.

Theorem 4. *Each block $\boldsymbol{D}^q$ in Equation (37) forms its own representation of H_0 and, hence, must comply separately and independently with the criteria given in Theorem 3.*

The groups of position G_p belonging to different blocks may (but need not) be different. However, we assume that the sum in Equation (37) consists only of blocks with coinciding groups of position. If this is not true in special cases, the number μ of the atoms in Equation (7) must be reduced until the groups of position coincide in the sum in Equation (37). Briefly speaking, in such a (probably rare) case, atoms of the same sort must be treated like different atoms.

4. Condition for Optimally-Localized Symmetry-Adapted Wannier Functions

Remember that we consider a closed energy band of μ branches and let a representation $\boldsymbol{D}$ defining the Wannier functions be given, which was determined according to Theorems 3 and 4. Then, we may give a simple condition for optimally-localized symmetry-adapted Wannier functions based on the theory of Wannier functions published in [28,30].

Theorem 5. *Let $\vec{k}$ be a point of symmetry in the first domain of the Brillouin zone for the considered material, and let $H_{\vec{k}} \subset H$ be the little group of $\vec{k}$ in Herrings sense. That means, $H_{\vec{k}}$ is the finite group denoted in* [32] *by ${}^{H}G^{\vec{k}}$ (and listed for all of the space groups in Table 5.7 ibidem). Furthermore, let $\boldsymbol{D}_{\vec{k}}$ be the μ-dimensional representation of $H_{\vec{k}}$ whose basis functions are the μ Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ with wave vector $\vec{k}$ and $\chi_{\vec{k}}(a)$ (with $a \in H_{\vec{k}}$) the character of $\boldsymbol{D}_{\vec{k}}$. $\boldsymbol{D}_{\vec{k}}$ either is irreducible or the direct sum over small irreducible representations of $H_{\vec{k}}$.*

We may choose the coefficients $g_{iq}(\vec{k})$ in Equation (7) in such a way that the Wannier functions are optimally-localized (Definition 1) and symmetry-adapted to H (Definition 7) if the character $\chi_{\vec{k}}(a)$ of $\boldsymbol{D}_{\vec{k}}$ satisfies at each point $\vec{k}$ of symmetry in the first domain of the Brillouin zone the equation:

$$\chi_{\vec{k}}(a) = e^{-i\alpha\vec{k}\cdot\vec{t}_\alpha} \sum_{i=1}^{\mu} n_i(a) e^{-i\vec{\rho}_i\cdot(\vec{k}-\alpha\vec{k})} \text{ for } a \in H_{\vec{k}}, \tag{38}$$

where $a = \{\alpha|\vec{t}_\alpha\}$ and:

$$n_i(a) = \begin{cases} d_i(\alpha) & \text{if} \quad \alpha \in G_{0p} \\ 0 & \text{else.} \end{cases} \tag{39}$$

The complex numbers $d_i(\alpha)$ stand for the elements of the one-dimensional representations $\boldsymbol{d}_i$ of G_{0p} fixing the given μ-dimensional representation $\boldsymbol{D}$ defining the Wanner functions.

Definition 13 (point of symmetry)**.** *The term point of symmetry we use as defined in* [32]*: $\vec{k}$ is a point of symmetry if there exists a neighborhood of $\vec{k}$ in which no point except $\vec{k}$ has the symmetry group $H_{\vec{k}}$.*

Thus, a point $\vec{k}$ of symmetry has a higher symmetry than all surrounding points.

We add a few comments on Theorem 5.

- In Equation (39), we write $n_i(a)$, rather than $n_i(\alpha)$, because the group G_{0p} depends on $a = \{\alpha|\vec{t}_\alpha\}$.
- The representation $\boldsymbol{D}$ defining the Wannier functions is equivalent to the representation $\boldsymbol{D}_{\vec{0}}$, *i.e.*, to the representation $\boldsymbol{D}_{\vec{k}}$ for $\vec{k} = \vec{0}$; see Equation (50).
- In the majority of cases, all of the representations $\boldsymbol{d}_i$ in Equation (39) are equal. The only exceptions arises when:
  - (i) not all of the positions $\vec{\rho}_i$ are connected by symmetry or
  - (ii) the one-dimensional representations $\boldsymbol{d}_i$ of G_{0p} are subduced from a higher-dimensional representation of H_0.
- a basic form of Theorem 5 was published first in Equation (23) of [7] and used in several former papers; Equation (23) of [7] yields the same results as Theorem 5

(i) if all of the $\vec{\rho}_i$ are connected by symmetry and

(ii) if all of the representations $\boldsymbol{d}_i$ of G_{0p} are subduced from one-dimensional representations of H_0.

These two conditions were satisfied in our former papers.

– The irreducible representations of the Bloch functions of the considered band at the points $\vec{k}$ of symmetry may be determined from the representations $\boldsymbol{D}_{\vec{k}}$ as follows:

Theorem 6. *Let $H_{\vec{k}}$ possess r irreducible representations with the characters $\chi_{\vec{k},m}(a) \quad (1 \leq m \leq r)$, and assume that $\boldsymbol{D}_{\vec{k}}$ contains the m-th irreducible representation, say, c_m times. Then, the numbers c_m may be calculated by means of Equation (1.3.18) of* [32],

$$c_m = \frac{1}{|H_{\vec{k}}|} \sum_{a}^{H_{\vec{k}}} \chi_{\vec{k},m}(a) \chi^*_{\vec{k}}(a), \tag{40}$$

where $\chi_{\vec{k}}(a)$ denotes the character of $\boldsymbol{D}_{\vec{k}}$ as determined by Equation (38) and the sum runs over the $|H_{\vec{k}}|$ elements a of $H_{\vec{k}}$. Remember (Theorem 5) that $H_{\vec{k}}$ is a finite group.

5. Proof of Theorem 5

The existence of the optimally-localized symmetry-adapted Wannier functions is defined in Satz 4 of [28]: such Wannier functions exist in a given closed energy band of μ branches if Equations (4.28) and (4.17) of [28] are satisfied. We show in this section that the fundamental Theorem 5 complies with these two equations if the Wannier functions meet Assumptions (i)–(iii) in Section 2.2.

5.1. Equation (4.28) of [28]

As the first step, consider Equation (4.28) of [28] stating that optimally-localized and symmetry-adapted Wannier functions may exist only if two representations $\widehat{\boldsymbol{D}}_{\vec{k}'_{\Sigma R}}$ and $\boldsymbol{D}_{\vec{k}'_{\Sigma R}}$ are equivalent,

$$\widehat{\boldsymbol{D}}_{\vec{k}} \text{ equivalent to } \boldsymbol{D}_{\vec{k}}, \tag{41}$$

where we have abbreviated $\vec{k}'_{\Sigma R}$ by $\vec{k}$ denoting a point of symmetry lying in the first domain of the Brillouin zone. Consequently, our first task will be to determine the character of $\widehat{\boldsymbol{D}}_{\vec{k}}$, as well as of $\boldsymbol{D}_{\vec{k}}$,

The representation $\boldsymbol{D}_{\vec{k}}$ as defined in Theorem 5 is the direct sum of the representations of the Bloch functions of the considered band at point $\vec{k}$. The character $\chi_{\vec{k}}(a)$ of the representation $\boldsymbol{D}_{\vec{k}}$ is simply given by:

$$\chi_{\vec{k}}(a) = \text{trace } \mathbf{D}_{\vec{k}}(a) \tag{42}$$

where the matrices $\mathbf{D}_{\vec{k}}(a)$ are the matrix representatives of $\boldsymbol{D}_{\vec{k}}$.

The matrix representatives $\widehat{\mathbf{D}}_{\vec{k}}(a)$ of $\widehat{\boldsymbol{D}}_{\vec{k}}$ are defined in Equation (4.26) of [28],

$$\widehat{\mathbf{D}}_{\vec{k}}(a) = \mathbf{S}^*(\vec{K}_\alpha) \mathbf{D}_{\vec{0}}(\alpha) e^{-i\alpha\vec{k}\vec{t}_\alpha} \tag{43}$$

where

$$\vec{K}_\alpha = \vec{k} - \alpha\vec{k} \tag{44}$$

is a vector of the reciprocal lattice. Again, we have abbreviated $\vec{k}'_{SR}$ by $\vec{k}$ denoting a point of symmetry. The matrices $\mathbf{S}(\vec{K})$ as defined in Equation (4.13) of [28] are responsible for a continuous transition of the generalized Bloch functions between neighboring Brillouin zones. The matrices $\mathbf{D}_{\vec{0}}(\alpha)$ are the matrix representatives of the representation $\boldsymbol{D}_{\vec{k}}$ for $\vec{k} = \vec{0}$ as defined in Theorem 5. $\boldsymbol{D}_{\vec{0}}$ is the direct sum of the irreducible representations of the Bloch functions of the considered band at point Γ.

The traces of the matrices $\widehat{\mathbf{D}}_{\vec{k}}(a)$ can be determined by transforming Equation (43) with the complex conjugate of the matrix $\mathbf{M}$ defined by Equation (2.1) of [30],

$$\begin{aligned} \mathbf{M}^*\widehat{\mathbf{D}}_{\vec{k}}(a)\mathbf{M}^{*-1} &= \mathbf{M}^*\mathbf{S}^*(\vec{K}_\alpha)\mathbf{M}^{*-1} \times \\ &\quad \mathbf{M}^*\mathbf{D}_{\vec{0}}(\alpha)\mathbf{M}^{*-1} \times \\ &\quad e^{-i\alpha k\cdot\vec{t}_\alpha}, \end{aligned} \tag{45}$$

where $a = \{\alpha|\vec{t}_\alpha\}$ still denotes an element of the space group H. By definition, the matrix $\mathbf{M}$ diagonalizes the matrices $\mathbf{S}(\vec{K})$, which is possible, since all of the $\mathbf{S}(\vec{K})$ commute. Thus, the first factor $\mathbf{M}^*\mathbf{S}^*(\vec{K}_\alpha)\mathbf{M}^{*-1}$ in Equation (45) is the diagonal matrix:

$$\overline{\mathbf{S}}^*(\vec{K}_\alpha) = e^{-i\vec{K}_\alpha\cdot\overline{\mathbf{T}}}, \tag{46}$$

where, according to Equation (2.7) of [30], also $\overline{\mathbf{T}}$ is a diagonal matrix with:

$$\vec{\overline{T}}_{ii} = \vec{\rho}_i. \tag{47}$$

Hence, the first factor in Equation (45) may be written as:

$$\mathbf{M}^*\mathbf{S}^*(\vec{K}_\alpha)\mathbf{M}^{*-1} = \overline{\mathbf{S}}^*(\vec{K}_\alpha) =$$

$$\begin{pmatrix} e^{-i\vec{\rho}_\mu\cdot(\vec{k}-\alpha\vec{k})} & \dots & 0 & 0 \\ 0 & \ddots & 0 & 0 \\ 0 & \dots & e^{-i\vec{\rho}_2\cdot(\vec{k}-\alpha\vec{k})} & 0 \\ 0 & \dots & 0 & e^{-i\vec{\rho}_1\cdot(\vec{k}-\alpha\vec{k})} \end{pmatrix}. \tag{48}$$

Definition 14 (horizontal bar)**.** *In line with* [30]*, we denote matrices transformed with* $\mathbf{M}$ *(or* $\mathbf{M}^*$*) by a horizontal bar to indicate that these matrices belong to the diagonal matrices* $\overline{\mathbf{S}}(\vec{K})$*.*

As shown in [30] (see Equations (2.18) and (2.19) of [30]), the second factor:

$$\overline{\mathbf{D}}_{\vec{0}}(\alpha) = \mathbf{M}^*\mathbf{D}_{\vec{0}}(\alpha)\mathbf{M}^{*-1} \tag{49}$$

in Equation (45) is a matrix representative $\mathbf{D}(\alpha)$ of the representation $\boldsymbol{D}$ defining the Wannier functions,

$$\overline{\mathbf{D}}_{\vec{0}}(\alpha) = \mathbf{D}(\alpha). \tag{50}$$

Thus, the matrices:

$$\begin{aligned} \overline{\widehat{\mathbf{D}}}_{\vec{k}}(a) &= \mathbf{M}^*\widehat{\mathbf{D}}_{\vec{k}}(a)\mathbf{M}^{*-1} \\ &= \overline{\mathbf{S}}^*(\vec{K}_\alpha)\mathbf{D}(\alpha)e^{-i\alpha\vec{k}\cdot\vec{t}_\alpha} \end{aligned} \tag{51}$$

are the matrix representatives of a representation $\overline{\widehat{\boldsymbol{D}}}_{\vec{k}}$ equivalent to $\widehat{\boldsymbol{D}}_{\vec{k}}$.

The character of $\overline{\widehat{\boldsymbol{D}}}_{\vec{k}}$ may be easily determined: the diagonal elements $d_i(\alpha)$ of the matrices $\mathbf{D}(\alpha)$ are fixed by Theorems 3 and 4. Since the matrix $\overline{\mathbf{S}}^*(\vec{K}_\alpha)$ is diagonal, the diagonal elements $\widehat{d}_i(a)$ of the matrices $\overline{\widehat{\mathbf{D}}}_{\vec{k}}(a)$ may be written as:

$$\widehat{d}_i(a) = e^{-i\alpha\vec{k}\cdot\vec{t}_\alpha} d_i(\alpha) e^{-i\vec{\rho}_i\cdot(\vec{k}-\alpha\vec{k})} \text{ for } a \in H_{\vec{k}}, \tag{52}$$

where still $a = \{\alpha|\vec{t}_\alpha\}$. The diagonal elements $d_i(\alpha)$ of the matrices $\mathbf{D}(\alpha)$ vanish if $\alpha \notin G_{0p}$; see Equation (20). Hence, the term on the right-hand side of Equation (38) is the sum over the diagonal elements $\widehat{d}_i(a)$, *i.e.*, it is the trace of the matrices $\overline{\widehat{\mathbf{D}}}_{\vec{k}}(a)$. Consequently, if Equation (38) is satisfied, then Condition (41) is true.

Strictly speaking, in [28], we have proven that the condition (41) must be satisfied for the points of symmetry lying in the first domain on the surface of the Brillouin zone. Equation (38) demands that in addition, the representation $\boldsymbol{D}_{\vec{0}}$ is equivalent to the representation $\boldsymbol{D}$, which is evidently true; see Equation (50).

5.2. Equation (4.17) of [28]

As the second step, we show that Equation (4.17) of [28] does not reduce the validity of Theorem 5, but this equation is satisfied whenever Assumptions (i)–(iii) in Section 2.2 are valid. Taking the complex conjugate of Equation (4.17) of [28] and transforming this equation with the matrix $\mathbf{M}^*$ already used in Equation (45), we receive the equation:

$$\overline{\mathbf{S}}^*(\alpha\vec{K}) = \mathbf{D}(\alpha)\overline{\mathbf{S}}^*(\vec{K})\mathbf{D}^{-1}(\alpha)e^{-i\alpha\vec{K}\cdot\vec{t}_\alpha}, \tag{53}$$

cf. Equations (48) and (50), which must be satisfied for all $a = \{\alpha|\vec{t}_\alpha\} \in H$ and all of the vectors $\vec{K}$ of the reciprocal lattice.

Just as the matrix:

$$\overline{\mathbf{S}}^*(\vec{K}) = \begin{pmatrix} e^{-i\vec{\rho}_\mu\cdot\vec{K}} & \dots & 0 & 0 \\ 0 & \ddots & 0 & 0 \\ 0 & \dots & e^{-i\vec{\rho}_2\cdot\vec{K}} & 0 \\ 0 & \dots & 0 & e^{-i\vec{\rho}_1\cdot\vec{K}} \end{pmatrix}, \tag{54}$$

also the matrix $\mathbf{D}(\alpha)\overline{\mathbf{S}}^*(\vec{K})\mathbf{D}^{-1}(\alpha)$ in Equation (53) is diagonal with the same diagonal elements, which, however, may stand in a new order. In fact, if $D_{ji}(\alpha) \neq 0$, the element $e^{-i\vec{\rho}_i\cdot\vec{K}}$ of $\overline{\mathbf{S}}^*(\vec{K})$ at position i stands at position j in the matrix $\mathbf{D}(\alpha)\overline{\mathbf{S}}^*(\vec{K})\mathbf{D}^{-1}(\alpha)$. Thus, from Equation (53), we receive the μ equations:

$$e^{-i\alpha\vec{K}\cdot\vec{\rho}_j} = e^{-i\vec{K}\cdot\vec{\rho}_i} \cdot e^{-i\alpha\vec{K}\cdot\vec{t}_\alpha} \text{ if } D_{ji}(\alpha) \neq 0, \tag{55}$$

yielding μ equations for the positions $\vec{\rho}_i$,

$$\vec{\rho}_j = \alpha\vec{\rho}_i + \vec{t}_\alpha + \vec{R}_j \text{ if } D_{ji}(\alpha) \neq 0, \tag{56}$$

where $\vec{R}_j$ is a lattice vector, which may be different in each equation. In fact, these last μ equations (56) are satisfied; see Equation (17).

6. Magnetic Groups

Assume a magnetic structure to be given in the considered material,, and let:

$$M = H + K\{\gamma|\vec{\tau}\}H \tag{57}$$

be the magnetic group of this magnetic structure, where:

$$\{\gamma|\vec{\tau}\} \in G \tag{58}$$

and K denotes the operator of time inversion acting on a function $f(\vec{r})$ of position according to:

$$Kf(\vec{r}) = f^*(\vec{r}). \tag{59}$$

We demand that the equation:

$$Kw_i\big(\gamma^{-1}(\vec{r} - \vec{R} - \vec{\rho}_i)\big) = \sum_{j=1}^{\mu} N_{ji} w_j(\vec{r} - \vec{R} - \vec{\rho}_i) \tag{60}$$

is satisfied in addition to Equation (10), where the matrix $\mathbf{N} = [N_{ij}]$ is the representative of the anti-unitary symmetry operation $K\gamma$ in the co-representation of the point group:

$$M_0 = H_0 + K\gamma H_0 \tag{61}$$

of M derived from [32] the representation $\boldsymbol{D}$ of H_0 defining the Wannier functions.

Still, we assume that there is exactly one Wannier function at each position $\vec{\rho}_i$, *i.e.*, the three assumptions, (i)–(iii), of Section 2.2 remain valid. Thus, [15], Equation (60) may be written in the more compact form:

$$KP(\{\gamma|\vec{\tau}\})w_{\vec{T}}(\vec{r}) = N_{ji} w_{\vec{T}'}(\vec{r}) \tag{62}$$

with:

$$\vec{T}\,' = \gamma\vec{T} + \vec{\tau} \tag{63}$$

and the subscripts i and j denote the number of the atoms at position $\vec{T}$ and $\vec{T}\,'$, respectively; see Definition 6.

Definition 15 (symmetry-adapted to a magnetic group)**.** *We call the Wannier functions symmetry-adapted to the magnetic group M if, in addition to Equation (15), Equation (62) is satisfied.*

Again (*cf.* Section 2.2), Equation (62) defines the non-vanishing elements of the matrix $\mathbf{N}$. Hence, also, $\mathbf{N}$ has one non-vanishing element in each row and each column,

$$|N_{ji}| = \begin{cases} 1 & \text{if } \gamma\vec{\rho}_i + \vec{\tau} = \vec{\rho}_j + \vec{R} \\ 0 & \text{else.} \end{cases} \tag{64}$$

As already expressed by Equation (60), we only consider bands of μ branches, which are not connected to other bands, also after the introduction of the new anti-unitary operation $K\{\gamma|\vec{\tau}\}$. That

means that the considered band consists of μ branches, as well, after, as before the introduction of $K\{\gamma|\vec{\tau}\}$. Hence, the matrix $\mathbf{N}$ must satisfy the equations:

$$\mathbf{N}\mathbf{N}^* = \mathbf{D}(\gamma^2) \tag{65}$$

and

$$\mathbf{D}(\alpha) = \mathbf{N}\mathbf{D}^*(\gamma^{-1}\alpha\gamma)\mathbf{N}^{-1} \text{ for } \alpha \in H_0, \tag{66}$$

see Equation (7.3.45) of [32]. Still, the matrices $\mathbf{D}(\alpha)$ are the representatives of the representation $\boldsymbol{D}$ of H_0 defining the Wannier functions. In [32], Equation (7.3.45) was established for irreducible representations. However, this, proven in Section 7.3 *ibidem*, shows that Equation (7.3.45) holds for reducible representations, too, if Equation (65) is satisfied.

Assume Theorem 5 to be satisfied in the considered energy band and remember that then, the coefficients $g_{iq}(\vec{k})$ in Equation (7) can be chosen in such a way that the Wannier functions of this band are optimally-localized and symmetry-adapted to H. In [33], we have shown that the Wannier functions may even be chosen symmetry-adapted to the magnetic group M if Equation (7.1) of [33],

$$\mathbf{S}(-\gamma\vec{K}) = \mathbf{D}^*_{\vec{0}}(K\gamma)\mathbf{S}^*(\vec{K})\mathbf{D}^{*-1}_{\vec{0}}(K\gamma)e^{-i\gamma\vec{K}\cdot\vec{\tau}}, \tag{67}$$

is valid for each vector $\vec{K}$ of the reciprocal lattice (which should not be confused with the operator K of time inversion). The matrix $\mathbf{S}(\vec{K})$ is defined in Equation (4.13) of [28], and the matrix $\mathbf{D}_{\vec{0}}(K\gamma)$ is the representative of the symmetry operation $K\gamma$ in the co-representation of M_0 derived from the representation $\boldsymbol{D}_{\vec{0}}$, *i.e.*, from the representation $\boldsymbol{D}_{\vec{k}}$ for $\vec{k} = \vec{0}$, as introduced in Theorem 5.

Transforming Equation (67) with the matrix $\mathbf{M}^*$ already used in Equation (45) and using:

$$\begin{array}{rcll} \mathbf{N} & = & \mathbf{M}^*\mathbf{D}_{\vec{0}}(K\gamma)\mathbf{M}^{-1} & \text{(Equation (11.29) of [33])} \\ \overline{\mathbf{S}}(\vec{K}) & = & \mathbf{M}\mathbf{S}(\vec{K})\mathbf{M}^{-1} & \text{= diagonal, Equation (54)} \\ \overline{\mathbf{S}}^*(\gamma\vec{K}) & = & \overline{\mathbf{S}}(-\gamma\vec{K}) & \text{(see Equation (54))} \end{array} \tag{68}$$

we receive an equation:

$$\overline{\mathbf{S}}^*(\gamma\vec{K}) = \mathbf{N}^*\overline{\mathbf{S}}^*(\vec{K})\mathbf{N}^{*-1}e^{-i\gamma\vec{K}\cdot\vec{\tau}} \tag{69}$$

identical to Equation (53) when we replace the space group operation $\{\alpha|\vec{t}_\alpha\}$ by $\{\gamma|\vec{\tau}\}$ and $\mathbf{D}(\alpha)$ by $\mathbf{N}^*$. In Section 5.2, we have shown that Equation (53) is satisfied if the matrices $\mathbf{D}(\alpha)$ follow Equation (17). In the same way, Equation (69) is true if the elements of $\mathbf{N}$ (as well as of $\mathbf{N}^*$) obey Equation (64). Thus, Equations (64)–(66) are the only additional conditions for the existence of optimally-localized Wannier functions that are symmetry-adapted to the magnetic group M.

We summarize the results of the present Section 6 in:

Theorem 7. *The coefficients $g_{iq}(\vec{k})$ in Equations (7) may be chosen in such a way that the Wannier functions are optimally-localized (Definition 5) and even symmetry-adapted to the magnetic group M in Equation (57) (Definition 15) if, according to Theorem 5, they may be chosen symmetry-adapted to H and if, in addition, there exists a μ-dimensional matrix $\mathbf{N}$ satisfying Equations (64)–(66).*

The representation $\boldsymbol{D}$ in Equations (65) and (66) is the representation defining the Wannier functions as used in Theorem 5.

In most cases, we may set the non-vanishing elements of $\mathbf{N}$ equal to one.

Definition 16 (magnetic band)**.** *If, according to Theorem 7, the unitary transformation in Equation (6) may be chosen in such a way that the Wannier functions are optimally-localized and symmetry-adapted to the magnetic group M in Equation (57), we call the band under consideration (as defined by the representations $\boldsymbol{D}_{\vec{k}}$ in Equation (38)) a "magnetic band related to the magnetic group M".*

Within the nonadiabatic Heisenberg model, the existence of a narrow, roughly half-filled magnetic band in the band structure of a material is a precondition for the stability of a magnetic structure with the magnetic group M in this material. However, the magnetic group M must be "allowed" in order that the time-inversion symmetry does not interfere with the stability of the magnetic state [10].

7. Spin-Dependent Wannier Functions

7.1. Definition

Assume the Hamiltonian $\mathcal{H}$ of a single electron in the considered material to be given, and assume $\mathcal{H}$ to consist of a spin-independent part $\mathcal{H}_i$ and a spin-dependent perturbation $\mathcal{H}_s$,

$$\mathcal{H} = \mathcal{H}_i + \mathcal{H}_s. \tag{70}$$

Further, assume the Bloch spinors $\psi_{\vec{k},q,s}(\vec{r},t)$ as the exact solutions of the Schrödinger equation:

$$\mathcal{H}\psi_{\vec{k},q,s}(\vec{r},t) = E_{\vec{k},q,s}\psi_{\vec{k},q,s}(\vec{r},t) \tag{71}$$

to be completely determined in the first domain of the Brillouin zone. Just as the Bloch functions, they are labeled by the wave vector $\vec{k}$ and the branch index q. In addition, they depend on the spin coordinate $t = \pm\frac{1}{2}$ and are labeled by the spin quantum number $s = \pm\frac{1}{2}$.

Consider again a closed energy band of μ branches that, in general, was not closed before the perturbation $\mathcal{H}_s$ was activated. Now, each branch is doubled, which means that it consists of two bands related to the two different spin directions. Just as in Section 2.1, we assume that the Bloch spinors $\psi_{\vec{k},q,s}(\vec{r},t)$ are chosen in such a way that they vary continuously through the first domain and approach continuously the boundaries of the first domain. In the rest of the Brillouin zone and in the remaining $\vec{k}$ space, they shall be given again by Equations (3) and (4) [33], where, however, $P(a)$ acts now on both $\vec{r}$ and t; see Equation (85).

We define "spin-dependent Wannier functions" by replacing the Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ in Equation (7) by linear combinations:

$$\varphi_{\vec{k},q,m}(\vec{r},t) = \sum_{s=-\frac{1}{2}}^{+\frac{1}{2}} f_{ms}(q,\vec{k})\psi_{\vec{k},q,s}(\vec{r},t) \tag{72}$$

of the given Bloch spinors. Thus, Equation (7) becomes:

$$\widetilde{\varphi}_{\vec{k},i,m}(\vec{r},t) = \sum_{q=1}^{\mu} g_{iq}(\vec{k})\varphi_{\vec{k},q,m}(\vec{r},t) \tag{73}$$

and finally, the spin-dependent Wannier functions my be written as:

$$w_{i,m}(\vec{r}-\vec{R}-\vec{\rho}_i,t) = \frac{1}{\sqrt{N}}\sum_{\vec{k}}^{BZ} e^{-i\vec{k}(\vec{R}+\vec{\rho}_i)}\widetilde{\varphi}_{\vec{k},i,m}(\vec{r},t). \tag{74}$$

Furthermore, the spin-dependent Wannier functions depend on t and are labeled by a new quantum number $m = \pm\frac{1}{2}$, which, in the framework of the nonadiabatic Heisenberg model, is interpreted as the quantum number of the "crystal spin" [15,34,35]. The sum in Equation (73) runs over the μ branches of the given closed energy band, where μ still is equal to the number of the considered atoms in the unit cell.

The matrices:

$$\mathbf{g}(\vec{k}) = [g_{iq}(\vec{k})] \tag{75}$$

still are unitary (see Equation (8)), and also, the coefficients $f_{ms}(q, \vec{k})$ in Equation (72) form for each $\vec{k}$ and q a two-dimensional matrix:

$$\mathbf{f}(q, \vec{k}) = [f_{ms}(q, \vec{k})] \tag{76}$$

which is unitary,

$$\mathbf{f}^{-1}(q, \vec{k}) = \mathbf{f}^{\dagger}(q, \vec{k}), \tag{77}$$

in order that the spin-dependent Wannier functions are orthonormal,

$$\begin{aligned} &\sum_{t=-\frac{1}{2}}^{+\frac{1}{2}} \int w^{*}_{i,m}(\vec{r} - \vec{R} - \vec{\rho}_i, t) w_{i',m'}(\vec{r} - \vec{R}\,' - \vec{\rho}_{i'}, t) d\vec{r} \\ &= \delta_{\vec{R}\vec{R}'} \delta_{ii'} \delta_{mm'}. \end{aligned} \tag{78}$$

Within the nonadiabatic Heisenberg model, we strictly consider the limiting case of vanishing spin-orbit coupling,

$$\mathcal{H}_s \to 0, \tag{79}$$

by approximating the Bloch spinors $\psi_{\vec{k},q,s}(\vec{r}, t)$ by means of the spin-independent Bloch functions $\varphi_{\vec{k},q}(\vec{r})$. In this context, we should distinguish between two kinds of Bloch states $\varphi_{\vec{k},q}(\vec{r})$ in the considered closed band:

(i) If $\varphi_{\vec{k},q}(\vec{r})$:

- was the basis function for a non-degenerate representation already before the spin-dependent perturbation $\mathcal{H}_s$ was activated or
- was the basis function for a degenerate representation before $\mathcal{H}_s$ was activated and this degeneracy is not removed by $\mathcal{H}_s$ (see Section 7.4.2),

then we may approximate the Bloch spinors by:

$$\psi_{\vec{k},q,s}(\vec{r}, t) = u_s(t) \varphi_{\vec{k},q}(\vec{r}) \tag{80}$$

where the functions $u_s(t)$ denote Pauli's spin functions:

$$u_s(t) = \delta_{st}, \tag{81}$$

with the spin quantum number $s = \pm\frac{1}{2}$ and the spin coordinate $t = \pm\frac{1}{2}$. Equation (80) applies to the vast majority of points $\vec{k}$ in the Brillouin zone.

(ii) If, at a special point $\vec{k}$, the Bloch function $\varphi_{\vec{k},q}(\vec{r})$ were the basis function for a degenerate single-valued representation before the perturbation $\mathcal{H}_s$ was activated and if this degeneracy were removed by $\mathcal{H}_s$, then Equation (80) is unusable for the sole reason that we do not know which of the basis functions of the degenerate representation we should avail ourselves of in this equation. In fact, in this case, the Bloch spinors $\psi_{\vec{k},q,s}(\vec{r},t)$ are well-defined linear combinations of the functions $u_s(t)\varphi_{\vec{k},q}(\vec{r})$ comprising all of the basis functions $\varphi_{\vec{k},q}(\vec{r})$ of the degenerate single-valued representation (as given, e.g., in Table 6.12 of [32]). These specific linear combinations are not, considered because, at this stage, they are of no importance within the nonadiabatic Heisenberg model.

In the framework of the approximation defined by Equation (80), the two functions $\varphi_{\vec{k},q,m}(\vec{r},t)$ in Equation (72) (with $m = \pm\frac{1}{2}$) are usual Bloch functions with the spins lying in the $\pm z$ direction if:

$$f_{ms}(q,\vec{k}) = \delta_{ms}. \tag{82}$$

Otherwise, if the coefficients $f_{ms}(q,\vec{k})$ cannot be chosen independent of $\vec{k}$, the spin-dependent Wannier functions cannot be written as a product of a local function with the spin function $u_s(t)$, even if the approximation defined by Equation (80) is valid. Consequently, even in the limit of vanishing spin-orbit coupling, the spin-dependent Wannier functions are neither orthonormal in the local space $\mathcal{L}$ nor in the spin space $\mathcal{S}$, but in $\mathcal{L}\times\mathcal{S}$ only; see Equation (78). Thus, also in the case

$$\mathcal{H}_s \to 0,$$

spin-dependent Wannier functions clearly differ from the usual Wannier functions characterized by

$$\mathcal{H}_s = 0.$$

Ansatz (74) presents the most general definition of Wannier functions. While their localization can be understood only in terms of the exact solutions of the Schrödinger equation (71), the limiting case of vanishing spin-orbit coupling characterized by Equation (80) yields fundamental properties of these Wannier functions, leading finally to an understanding of the material properties of superconductors [16,35,36].

7.2. Symmetry-Adapted Spin-Dependent Wannier Functions

We demand that symmetry-adapted spin-dependent Wannier functions satisfy, in analogy to Equation (15), the equation:

$$P(a)w_{\vec{T},m}(\vec{r},t) = D_{ji}(\alpha)\sum_{m'=-\frac{1}{2}}^{\frac{1}{2}} d_{m'm}(\alpha)w_{\vec{T}',m'}(\vec{r},t) \tag{83}$$

for $a \in H$ since, still, Assumptions (i)–(iii) of Section 2.2 are valid. Merely the third assumption (iii) is modified: now, the two Wannier functions $w_{\vec{T},+\frac{1}{2}}(\vec{r},t)$ and $w_{\vec{T},-\frac{1}{2}}(\vec{r},t)$ are situated at the same atom, and consequently, we now put:

$$w_{\vec{T},m}(\vec{r},t) \equiv w_{i,m}(\vec{r}-\vec{R}-\vec{\rho}_i,t), \tag{84}$$

where $m = \pm\frac{1}{2}$.

The vectors $\vec{T}$ and $\vec{T}\,'$ are still given by Equations (13) and (16), respectively. The matrices $\mathbf{D}(\alpha) = [D_{ij}(\alpha)]$ in Equation (83) are again unitary generalized permutation matrices, and the subscripts i and j denote the number of the atoms at position $\vec{T}$ and $\vec{T}\,'$, respectively; see Definition 6.

The operators $P(a)$ now act additionally on the spin coordinate t of a function $f(\vec{r}, t)$,

$$P(a)f(\vec{r}, t) = f(\alpha^{-1}\vec{r} - \alpha^{-1}\vec{t}_\alpha, \alpha^{-1}t), \tag{85}$$

where the effect of a point group operation on the spin coordinate t of the spin function $u_s(t)$ is given by the equation [32]:

$$u_s(\alpha^{-1}t) = \sum_{s'} d_{s's}(\alpha)u_{s'}(t) \text{ for } \alpha \in H_0^d. \tag{86}$$

The matrix

$$\mathbf{d}_{1/2}(\alpha) = [d_{ss'}(\alpha)] \tag{87}$$

denotes the representative of α in the two-dimensional double-valued representation $\boldsymbol{d}_{1/2}$ of $O(3)$, as listed, e.g., in Table 6.1 of [32].

We have to take into consideration that the double-valued representations of a group g are not really representations of g, but of the abstract "double group" g^d of order $2|g|$, while the single-valued representations are representations of both g and g^d [32].

Definition 17 (double-valued)**.** *Though we use the familiar expression "double-valued" representation of a group g, we consider the double-valued representations as ordinary single-valued representations of the related abstract double group g^d, denoted by a superscript "d".*

Since the index m of the spin-dependent Wannier functions is interpreted as spin quantum number, we demand that the term:

$$\sum_{m'=-\frac{1}{2}}^{\frac{1}{2}} d_{m'm}(\alpha)w_{\vec{T}',m'}(\vec{r}, t)$$

in Equation (83) describes a rotation or reflection of the crystal spin. Thus, we demand that also the matrices $[d_{mm'}(\alpha)]$ are the representatives of the two-dimensional double-valued representation $\boldsymbol{d}_{1/2}$,

$$[d_{mm'}(\alpha)] = \mathbf{d}_{1/2}(\alpha) \quad \text{for } \alpha \in H_0^d. \tag{88}$$

Definition 18 (symmetry-adapted)**.** *We call the spin-dependent Wannier functions "symmetry-adapted to the double group H^d related to space group H" if they satisfy Equation (83) for $a \in H^d$, where the matrices $[d_{mm'}(\alpha)]$ are the representatives of the two-dimensional double-valued representation $\boldsymbol{d}_{1/2}$ of $O(3)$.*

Consequently, symmetry-adapted spin-dependent Wannier functions are basis functions for the double-valued representation:

$$\boldsymbol{D}^d = \boldsymbol{D} \otimes \boldsymbol{d}_{1/2} \tag{89}$$

of H_0^d which is the inner Kronecker product of the single-valued representation $\boldsymbol{D}$ defined by Equation (83) and the double-valued representation $\boldsymbol{d}_{1/2}$. Thus, the 2μ-dimensional matrix representatives $\mathbf{D}^d(\alpha)$ of $\boldsymbol{D}^d$ may be written as Kronecker products,

$$\mathbf{D}^d(\alpha) = \mathbf{D}(\alpha) \times \mathbf{d}_{1/2}(\alpha). \tag{90}$$

Definition 19 (representation defining spin-dependent Wannier functions)**.** *The single-valued representation* $\boldsymbol{D}$ *of* H_0 *defined by Equation (83) shall be referred to in short as "the representation defining the spin-dependent Wannier functions" and its matrix: representatives*

$$\mathbf{D}(\alpha) = [D_{ij}(\alpha)]$$

as "the matrices defining the spin-dependent Wannier functions".

While usual (spin-independent) Wannier functions are basis functions for the representation $\boldsymbol{D}$ *defining the Wannier functions, spin-dependent Wannier functions are basis functions for the double-valued representation:*

$$\boldsymbol{D}^d = \boldsymbol{D} \otimes \boldsymbol{d}_{1/2}$$

in Equation (89).

Furthermore, the representation $\boldsymbol{D}$ defining the spin-dependent Wannier functions has to meet the conditions given in Section 3, as shall be summarized in:

Theorem 8. *The two spin-dependent Wannier function* $w_{i,\frac{1}{2}}(\vec{r} - \vec{R} - \vec{\rho}_i, t)$ *and* $w_{i,-\frac{1}{2}}(\vec{r} - \vec{R} - \vec{\rho}_i, t)$ *at the position* $\vec{\rho}_i$ *are basis functions for the two-dimensional representation:*

$$\boldsymbol{d}_i^d = \boldsymbol{d}_i \otimes \boldsymbol{d}_{1/2} \tag{91}$$

of the double group G_{0p}^d *related to the point group of position* G_{0p}*. The one-dimensional representations* $\boldsymbol{d}_i$ *in Equation (91) fix the (generally reducible) representation* $\boldsymbol{D}$ *of* H_0 *defining the spin-dependent Wannier functions (Definition 19). The matrix representatives* $\mathbf{D}(\alpha)$ *of* $\boldsymbol{D}$ *still are unitary generalized permutation matrices, which must be chosen in such a way that they form a representation of* H_0*. We again distinguish between the two cases, (i) and (ii), defined in Theorem 3.*

In addition, Theorem 4 must be noted.

Theorem 5 does not distinguish between usual and spin-dependent Wannier functions, but uses only the special representations of the Bloch functions or Bloch spinors, respectively, at the points $\vec{k}$ of symmetry. Thus, Theorem 5 applies to both usual and spin-dependent Wannier functions, if in the case of spin-dependent Wannier functions, we replace the little groups $H_{\vec{k}}$ by the double groups $H_{\vec{k}}^d$. Just as the groups $H_{\vec{k}}$, the groups $H_{\vec{k}}^d$ are finite groups in Herrings sense, as denoted in [32] by ${}^H G^{\dagger\vec{k}}$, and, fortunately, are explicitly given in Table 6.13 *ibidem*.

When we consider single-valued representations, then the sum on the right-hand side of Equation (38) runs over the μ diagonal elements $\widehat{d}_i(a)$ of the matrices $\overline{\widehat{\mathbf{D}}}_{\vec{k}}(a)$ in Equation (51). When we consider double-valued representations, on the other hand, this sum runs over 2μ diagonal elements $\widehat{d}_{i,m}^d(a)$ of the corresponding matrices:

$$\overline{\widehat{\mathbf{D}}}_{\vec{k}}^d(a) = \overline{\mathbf{S}}^{d*}(\vec{K}_\alpha)\mathbf{D}^d(\alpha)e^{-i\alpha k\cdot\vec{t}_\alpha} \tag{92}$$

where

$$\overline{\mathbf{S}}^{d*}(\vec{K}_\alpha) = \overline{\mathbf{S}}^{*}(\vec{K}_\alpha) \times \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{93}$$

(where $\overline{\mathbf{S}}^{*}(\vec{K}_\alpha)$ is given in Equation (48)) because also $\overline{\mathbf{S}}^{d*}(\vec{K}_\alpha)$ is diagonal, and now, there are two Wannier functions $w_{i,m}(\vec{r} - \vec{R} - \vec{\rho}_i, t)$ with $m = \pm\frac{1}{2}$ at each position $\vec{\rho}_i$.

We need not to solve Equation (38) directly, but we may determine the representations $\boldsymbol{D}^d_{\vec{k}}$ complying with Equation (38) in a quicker way. Equation (93) shows that we may write the matrices $\overline{\widehat{\mathbf{D}}}^d_{\vec{k}}(a)$ simply as Kronecker products,

$$\overline{\widehat{\mathbf{D}}}^d_{\vec{k}}(a) = \overline{\widehat{\mathbf{D}}}_{\vec{k}}(a) \times \mathbf{d}_{1/2}(\alpha), \tag{94}$$

where $\overline{\widehat{\mathbf{D}}}_{\vec{k}}(a)$ is given in Equation (51).

Now, assume that we have already determined according to Theorem 5 the single-valued representations $\boldsymbol{D}^{\text{aff}}_{\vec{k}}$ in the closed band under consideration. Then, the representations $\overline{\widehat{\boldsymbol{D}}}_{\vec{k}}$ and $\boldsymbol{D}^{\text{aff}}_{\vec{k}}$ are equivalent (see Equation (41)), and consequently, also the representations:

$$\overline{\widehat{\boldsymbol{D}}}^d_{\vec{k}} = \overline{\widehat{\boldsymbol{D}}}_{\vec{k}} \otimes \boldsymbol{d}_{1/2} \tag{95}$$

and

$$\boldsymbol{D}^d_{\vec{k}} = \boldsymbol{D}^{\text{aff}}_{\vec{k}} \otimes \boldsymbol{d}_{1/2} \tag{96}$$

are equivalent. Hence (Section 5.1), the double-valued representations $\boldsymbol{D}^d_{\vec{k}}$ comply with Theorem 5 in the same way as the single-valued representations $\boldsymbol{D}^{\text{aff}}_{\vec{k}}$ do.

Definition 20 (affiliated single-valued band)**.** *In this context, we call the band defined by the double-valued representations $\boldsymbol{D}^d_{\vec{k}}$ in Equation (96) the "double-valued band" and the band defined by the single-valued representations $\boldsymbol{D}^{aff}_{\vec{k}}$ an "affiliated single-valued band".*

While a double-valued band may possess several affiliated single-valued bands, any single-valued band is affiliated with exactly one double-valued band.

The affiliated single-valued band is a closed band that, generally, does not exist in the band structure of the considered material. That means that the Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ of the closed band under consideration band generally do not form a basis for the representations $\boldsymbol{D}^{aff}_{\vec{k}}$, even if Equation (80) is valid; see, e.g., the single-valued band affiliated with the superconducting band (Definition 22) of niobium as given in Equation (150).

We may summarize the result of this section in:

Theorem 9. *Remember that we consider a closed energy band of μ branches, and let a representation $\boldsymbol{D}$ be given defining the spin-dependent Wannier functions, which was determined according to Theorem 8. The band may only be closed after the spin-dependent perturbation $\mathcal{H}_s$ was activated.*

Let $\vec{k}$ be a point of symmetry in the first domain of the Brillouin zone for the considered material, and let $H^d_{\vec{k}}$ be the little double group of $\vec{k}$ in Herrings sense. That means, $H^d_{\vec{k}}$ is the finite group denoted in [32] *by ${}^{H}G^{\dagger\vec{k}}$ and explicitly given in Table 6.13 ibidem. Furthermore, let $\boldsymbol{D}^d_{\vec{k}}$ be the 2μ-dimensional representation of $H^d_{\vec{k}}$, whose basis functions are the 2μ Bloch spinors $\psi_{\vec{k},q,s}(\vec{r},t)$ with wave vector $\vec{k}$. $\boldsymbol{D}^d_{\vec{k}}$ either is irreducible or the direct sum over double-valued irreducible representations of $H^d_{\vec{k}}$. The representations $\boldsymbol{D}^d_{\vec{k}}$ follow Equation (96),*

$$\boldsymbol{D}^d_{\vec{k}} = \boldsymbol{D}^{aff}_{\vec{k}} \otimes \boldsymbol{d}_{1/2}, \tag{97}$$

where the μ-dimensional representations $\boldsymbol{D}^{\text{aff}}_{\vec{k}}$ define the affiliated single-valued band. Thus, also, each $\boldsymbol{D}^{aff}_{\vec{k}}$ is the direct sum over single-valued irreducible representations of H_0.

We may choose the coefficients $g_{iq}(\vec{k})$ and $f_{ms}(q,\vec{k})$ in Equations (73) and (72), respectively, in such a way that the spin-dependent Wannier functions are optimally-localized (Definition 5) and symmetry-adapted to the double group H^d (Definition 18) if the characters $\chi_{\vec{k}}(a)$ of the single-valued representations $\boldsymbol{D}^{aff}_{\vec{k}}$ satisfy Equation (38).

The complex numbers $d_i(\alpha)$ in Equation (39) stand for the elements of the one-dimensional representations $\boldsymbol{d}_i$ of G_{0p} fixing the given representation $\boldsymbol{D}$ defining the spin-dependent Wannier functions (according to Definition 19).

7.3. Time Inversion

7.3.1. Time-Inversion Symmetry of the Spin-Dependent Wannier Functions

Within the nonadiabatic Heisenberg model, we are not interested in spin-dependent Wannier functions that are symmetry-adapted to a general magnetic group, as given in Equation (57), but we only demand that they are adapted to the "grey" [32] magnetic group:

$$M^d = H^d + KH^d, \tag{98}$$

or, in brief, we demand that they are adapted to the time-inversion symmetry. K still denotes the operator of time inversion acting on a function of position $f(\vec{r})$ according to Equation (59) and on Pauli's spin functions $u_s(t)$ according to:

$$Ku_s(t) = \pm u_{-s}(t) \tag{99}$$

(see, e.g., Table 7.15 of [32]), where we may define the plus to belong to $s = +\frac{1}{2}$ and the minus to $s = -\frac{1}{2}$.

The index m of the spin-dependent Wannier functions we still interpret as the quantum number of the crystal spin. Consequently, we demand that K acts on m in the same way as it act on s,

$$Kw_{\vec{T},m}(\vec{r},t) = \pm w_{\vec{T},-m}(\vec{r},t) \tag{100}$$

where, again, we define the plus to belong to $m = +\frac{1}{2}$ and the minus to $m = -\frac{1}{2}$.

Definition 21 (symmetry-adapted to a magnetic group)**.** *We call the spin-dependent Wannier functions "symmetry-adapted to the magnetic group M^d" as given in Equation (98) if they are symmetry-adapted to H^d (Definition 18), and if, in addition, Equation (100) is satisfied.*

In analogy to Equation (83), Equation (100) may be written as:

$$Kw_{\vec{T},m}(\vec{r},t) = N_{ii} \sum_{m'=-\frac{1}{2}}^{\frac{1}{2}} n_{m'm} w_{\vec{T},m'}(\vec{r},t) \tag{101}$$

where $\mathbf{N} = [N_{ij}]$ denotes the μ-dimensional identity matrix:

$$\mathbf{N} = \begin{pmatrix} 1 & 0 & \dots & 0 \\ 0 & 1 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & 1 \end{pmatrix} = \mathbf{1} \tag{102}$$

and

$$\mathbf{n} = [n_{mm'}] = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}. \tag{103}$$

Equation (101) shows that the 2μ-dimensional matrix:

$$\mathbf{N}^d = \mathbf{N} \times \mathbf{n} \tag{104}$$

is the matrix representative of the operator K of time inversion in the co-representation of the magnetic point group:

$$M_0^d = H_0^d + KH_0^d \tag{105}$$

derived from the representation $\boldsymbol{D}^d$ in Equation (89). Thus, the matrix $\mathbf{N}^d$ has to comply (Section 6) with the three equations, (65), (66) and (69), which now may be written as:

$$\mathbf{N}^d\mathbf{N}^{d*} = \mathbf{D}^d(K^2) = -\mathbf{1}, \tag{106}$$

$$\mathbf{D}^d(\alpha) = \mathbf{N}^d\mathbf{D}^{d*}(\alpha)\mathbf{N}^{d-1} \text{ for } \alpha \in H_0^d, \tag{107}$$

and

$$\overline{\mathbf{S}}^{d*}(\vec{K}) = \mathbf{N}^{d*}\overline{\mathbf{S}}^{d*}(\vec{K})\mathbf{N}^{d*-1}, \tag{108}$$

respectively.

The first Equation (106) is true because:

$$\mathbf{n}\mathbf{n}^* \ (= \mathbf{n}\mathbf{n}) = -\mathbf{1} \tag{109}$$

and the second Equation (107) is satisfied if $\mathbf{n}$ and $\mathbf{N}$ in Equation (104) follow two conditions,

$$\mathbf{d}_{1/2}(\alpha) = \mathbf{n}\mathbf{d}_{1/2}^*(\alpha)\mathbf{n}^{-1} \text{ for } \alpha \in H_0^d, \tag{110}$$

and

$$\mathbf{D}(\alpha) = \mathbf{N}\mathbf{D}^*(\alpha)\mathbf{N}^{-1} \text{ for } \alpha \in H_0. \tag{111}$$

The first condition (110) is always valid (see, e.g., Table 7.15 (q) of [32]), and the second condition (111) is satisfied if the representation $\boldsymbol{D}$ defining the spin-dependent Wannier functions is real.

In the third Equation (108), the diagonal matrix $\overline{\mathbf{S}}^{d*}(\vec{K})$ has the form:

$$\overline{\mathbf{S}}^{d*}(\vec{K}) = \overline{\mathbf{S}}^{*}(\vec{K}) \times \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{112}$$

(*cf.* Equation(93)), where $\overline{\mathbf{S}}^{*}(\vec{K})$ is given in Equation (54). Thus, Equation (108) decomposes into two parts,

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{n}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\mathbf{n}^{-1} \tag{113}$$

and

$$\overline{\mathbf{S}}^{*}(\vec{K}) = \mathbf{N}^{*}\overline{\mathbf{S}}^{*}(\vec{K})\mathbf{N}^{*-1} \tag{114}$$

both of which are evidently satisfied.

We summarize our results in this Section 7.3.1 in:

Theorem 10. *The coefficients $g_{iq}(\vec{k})$ and $f_{ms}(q,\vec{k})$ in Equations (73) and (72), respectively, may be chosen in such a way that the spin-dependent Wannier functions are optimally-localized (Definition 5) and even symmetry-adapted to the magnetic group M^d in Equation (98) (Definition 21) if, according to Theorem 9, they may be chosen symmetry-adapted to H^d and if, in addition, the representation $\boldsymbol{D}$ defining the spin-dependent Wannier functions used in Theorem 9 is real.*

Definition 22 (superconducting band)**.** *If, according to Theorem 10, the unitary transformation in Equation (74) may be chosen in such a way that the spin-dependent Wannier functions are optimally-localized and symmetry-adapted to the magnetic group M^d in Equation (98), we call the band under consideration (as defined by the double-valued representations $\boldsymbol{D}^d_{\vec{k}}$ in Equation (97)) a superconducting band.*

Within the nonadiabatic Heisenberg model, the existence of a narrow, roughly half-filled superconducting band in the band structure of a material is a precondition for the stability of a superconducting state in this material.

7.3.2. Time-Inversion Symmetry of the Matrices $\mathbf{f}(q,\vec{k})$

In this section, we derive the time-inversion symmetry of the matrices $\mathbf{f}(q,\vec{k})$ defined in Equation (72) and shall give the result in Theorem 11. Though evidence for this important theorem was already provided in [11] and later papers [16,35], we repeat the proof with the notations used in the present paper.

Combining Equations (73) and (74), we may write the spin-dependent Wannier functions as:

$$w_{i,m}(\vec{r}-\vec{R}-\vec{\rho}_i,t)=\frac{1}{\sqrt{N}}\sum_{\vec{k}}^{BZ}\sum_{q=1}^{\mu}e^{-i\vec{k}(\vec{R}+\vec{\rho}_i)}g_{iq}(\vec{k})\varphi_{\vec{k},q,m}(\vec{r},t). \tag{115}$$

By application of the operator K of time-inversion on Equation (115), we receive:

$$Kw_{i,m}(\vec{r}-\vec{R}-\vec{\rho}_i,t)=\frac{1}{\sqrt{N}}\sum_{\vec{k}}^{BZ}\sum_{q=1}^{\mu}e^{i\vec{k}(\vec{R}+\vec{\rho}_i)}g^*_{iq}(\vec{k})K\varphi_{\vec{k},q,m}(\vec{r},t). \tag{116}$$

Equation (100), on the other hand, may be written as:

$$Kw_{i,m}(\vec{r}-\vec{R}-\vec{\rho}_i,t)=\frac{1}{\sqrt{N}}\sum_{\vec{k}}^{BZ}\sum_{q=1}^{\mu}e^{-i\vec{k}(\vec{R}+\vec{\rho}_i)}g_{iq}(\vec{k})\nu(m)\varphi_{\vec{k},q,-m}(\vec{r},t) \tag{117}$$

or, by replacing under the sum $\vec{k}$ by $-\vec{k}$,

$$Kw_{i,m}(\vec{r}-\vec{R}-\vec{\rho}_i,t)=\frac{1}{\sqrt{N}}\sum_{\vec{k}}^{BZ}\sum_{q=1}^{\mu}e^{i\vec{k}(\vec{R}+\vec{\rho}_i)}g_{iq}(-\vec{k})\nu(m)\varphi_{-\vec{k},q,-m}(\vec{r},t), \tag{118}$$

where

$$\nu\big(\pm\frac{1}{2}\big)=\pm 1. \tag{119}$$

Comparing Equation (118) with Equation (116), we receive the two equations:

$$g^*_{iq}(\vec{k})=g_{iq}(-\vec{k}) \tag{120}$$

and

$$K\varphi_{\vec{k},q,m}(\vec{r},t) = \nu(m)\varphi_{-\vec{k},q,-m}(\vec{r},t). \tag{121}$$

While the first Equation (120) is relatively meaningless, from the second Equation (121), we may derive the important Equation (125):

Equation (72) yields the two equations:

$$\varphi_{-\vec{k},q,-m}(\vec{r},t) = \sum_{s=-\frac{1}{2}}^{+\frac{1}{2}} f_{-m,-s}(q,-\vec{k})\psi_{-\vec{k},q,-s}(\vec{r},t) \tag{122}$$

where now, the sum runs over $-s$, and:

$$K\varphi_{\vec{k},q,m}(\vec{r},t) = \sum_{s=-\frac{1}{2}}^{+\frac{1}{2}} f^*_{ms}(q,\vec{k})\nu(s)\psi_{-\vec{k},q,-s}(\vec{r},t) \tag{123}$$

because [32]:

$$K\psi_{\vec{k},q,s}(\vec{r},t) = \nu(s)\psi_{-\vec{k},q,-s}(\vec{r},t). \tag{124}$$

Theorem 11. *Substituting Equations (122) and (123) into Equation (121), we obtain the fundamental condition:*

$$f^*_{ms}(q,-\vec{k}) = \pm f_{-m,-s}(q,\vec{k}), \tag{125}$$

where the plus sign holds for $m = s$ *and the minus for* $m = -s$.

Within the nonadiabatic Heisenberg model, the validity of this condition is the cause of the formation of symmetrized Cooper pairs in superconducting bands [16,35,36].

This Equation (125) may evidently be written in the more compact form:

$$\mathbf{f}^*(q,-\vec{k}) = \mathbf{nf}(q,\vec{k})\mathbf{n}^{-1} \tag{126}$$

where $\mathbf{n}$ is given in Equation (103).

7.4. $\vec{k}$-Dependence of the Matrices $\mathbf{f}(q,\vec{k})$

Only those bands are of physical relevance in the theory of superconductivity which are closed not before the spin-dependent perturbation $\mathcal{H}_s$ is activated. In this section, we derive the essential property of such bands and shall give the result in Theorem 12.

Let $\vec{k}$ be a point lying on the surface of the first domain in the Brillouin zone for the space group H, and let $H_{\vec{k}}$ be the little group of $\vec{k}$. In this section, $\vec{k}$ need not be a point of symmetry (according to Definition 13), but also may lie in a line or a plane of symmetry. However, we only consider wave vectors $\vec{k}$ for which Equation (80) is valid. Hence, in general, the Bloch functions $\varphi_{\vec{k},q}(\vec{r})$ are basis functions for a one-dimensional (single-valued) representation of $H_{\vec{k}}$. Nevertheless, in very rare cases, the Bloch function $\varphi_{\vec{k},q}(\vec{r})$ can be a basis function for a degenerate (single-valued) representation. Both cases shall be examined separately.

Just as in Equation (3.1) of [28] we arrange the 2μ Bloch spinors $u_s(t)\varphi_{\vec{k},q}(\vec{r})$ in Equation (80) as a column vector:

$$\Phi_{\vec{k}}(\vec{r},t) = \begin{pmatrix} u_{+\frac{1}{2}}(t)\varphi_{\vec{k},\mu}(\vec{r}) \\ u_{-\frac{1}{2}}(t)\varphi_{\vec{k},\mu}(\vec{r}) \\ \vdots \\ u_{+\frac{1}{2}}(t)\varphi_{\vec{k},2}(\vec{r}) \\ u_{-\frac{1}{2}}(t)\varphi_{\vec{k},2}(\vec{r}) \\ u_{+\frac{1}{2}}(t)\varphi_{\vec{k},1}(\vec{r}) \\ u_{-\frac{1}{2}}(t)\varphi_{\vec{k},1}(\vec{r}) \end{pmatrix} \tag{127}$$

with increasing energy,

$$E_{\vec{k},q-1} \leq E_{\vec{k},q} \leq E_{\vec{k},q+1}. \tag{128}$$

Then, the analogous column vector $\widetilde{\Phi}_{\vec{k}}(\vec{r},t)$ consisting of the Bloch spinors $\widetilde{\varphi}_{\vec{k},i,m}(\vec{r},t)$ in Equation (73) may be written as:

$$\widetilde{\Phi}_{\vec{k}}(\vec{r},t) = \mathbf{g}^d(\vec{k}) \cdot \mathbf{f}^d(\vec{k}) \cdot \Phi_{\vec{k}}(\vec{r},t) \tag{129}$$

where

$$\mathbf{g}^d(\vec{k}) = \mathbf{g}(\vec{k}) \times \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{130}$$

and

$$\mathbf{f}^d(\vec{k}) = \begin{pmatrix} \mathbf{f}(\mu,\vec{k}) & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \vdots & \ddots & \vdots & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{f}(2,\vec{k}) & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{f}(1,\vec{k}) \end{pmatrix}. \tag{131}$$

The matrices $\mathbf{g}(\vec{k})$ and $\mathbf{f}(q,\vec{k})$ are defined by Equations (75) and (76) and still follow Equations (8) and (77), respectively, and:

$$\mathbf{0} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}. \tag{132}$$

The matrices $\mathbf{g}^d(\vec{k}) \cdot \mathbf{f}^d(\vec{k})$ must satisfy Equations (4.8) and (4.29) of [28] in order that the Wannier functions are symmetry-adapted and optimally-localized. (We shall consider only Equation (4.29) of [28], because this equation comprises Equation (4.8) *ibidem*).

Using the notations of the present paper, Equation (4.29) of [28] may be written as:

$$\mathbf{D}^d_{\vec{k}}(a) \;=\; \left(\mathbf{g}^{d*}(\vec{k}) \cdot \mathbf{f}^{d*}(\vec{k})\right)^{-1} \cdot \overline{\widehat{\mathbf{D}}}^d_{\vec{k}}(a) \cdot \left(\mathbf{g}^{d*}(\vec{k}) \cdot \mathbf{f}^{d*}(\vec{k})\right) \text{for } a \in H^d_{\vec{k}}, \tag{133}$$

where the matrices $\mathbf{D}^d_{\vec{k}}(a)$ and $\overline{\widehat{\mathbf{D}}}^d_{\vec{k}}(a)$ denote the representatives of the the representations $\boldsymbol{D}^d_{\vec{k}}$ and $\overline{\widehat{\boldsymbol{D}}}^d_{\vec{k}}$ given in Equations (97) and (95), respectively. Assume that the representations $\boldsymbol{D}^d_{\vec{k}}$ are determined according to Theorem 9. Then, the representations $\boldsymbol{D}^{\text{aff}}_{\vec{k}}$ and $\overline{\widehat{\boldsymbol{D}}}_{\vec{k}}$, as well as the representations $\boldsymbol{D}^d_{\vec{k}}$ and $\overline{\widehat{\boldsymbol{D}}}^d_{\vec{k}}$ are equivalent for the points $\vec{k}$ of symmetry. Consequently, these representations are even equivalent

in any point $\vec{k}$ of the Brillouin zone, because the compatibility relations are valid in a closed band [28]. First, from the equivalence of $\boldsymbol{D}^{\text{aff}}_{\vec{k}}$ and $\overline{\widehat{\boldsymbol{D}}}_{\vec{k}}$, it follows that the equation:

$$\mathbf{D}^{\text{aff}}_{\vec{k}}(a) = \mathbf{g}^{*-1}(\vec{k}) \cdot \overline{\widehat{\mathbf{D}}}_{\vec{k}}(a) \cdot \mathbf{g}^{*}(\vec{k}) \text{ for } a \in H_{\vec{k}} \tag{134}$$

is solvable for any $\vec{k}$.

7.4.1. The Bloch Functions $\varphi_{\vec{k},q}(\vec{r})$ Are Basis Functions for a Non-Degenerate Representation

In this subsection, we assume that the Bloch states $\varphi_{\vec{k},q}(\vec{r})$ are basis functions for a one-dimensional (single-valued) representation of $H_{\vec{k}}$.

The representations $\boldsymbol{D}^{d}_{\vec{k}}$ are the direct sum over the double-valued representations of the Bloch spinors in the considered band, as arranged in the column vector given in Equation (127). Hence, the matrices $\mathbf{D}^{d}_{\vec{k}}(a)$ on the left-hand side of Equation (133) may be written as:

$$\mathbf{D}^{d}_{\vec{k}}(a) = \begin{pmatrix} \mathbf{d}_{\vec{k},\mu}(a) & 0 & 0 & 0 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \mathbf{d}_{\vec{k},2}(a) & 0 \\ 0 & 0 & 0 & \mathbf{d}_{\vec{k},1}(a) \end{pmatrix} \times \mathbf{d}_{1/2}(\alpha) \tag{135}$$

(for $a = \{\alpha|\vec{t}_{\alpha}\} \in H^{d}_{\vec{k}}$), where the Bloch state $\varphi_{\vec{k},q}(\vec{r})$ is the basis function for the single-valued representations $\boldsymbol{d}_{\vec{k},q}$.

The matrices on the right-hand side of Equation (133) may be written as:

$$\begin{gathered} \left(\mathbf{g}^{d*}(\vec{k}) \cdot \mathbf{f}^{d*}(\vec{k})\right)^{-1} \cdot \overline{\widehat{\mathbf{D}}}^{d}_{\vec{k}}(a) \cdot \left(\mathbf{g}^{d*}(\vec{k}) \cdot \mathbf{f}^{d*}(\vec{k})\right) = \\ \left(\mathbf{f}^{d*}(\vec{k})\right)^{-1} \cdot \left[\left(\mathbf{g}^{d*}(\vec{k})\right)^{-1} \cdot \overline{\widehat{\mathbf{D}}}^{d}_{\vec{k}}(a) \cdot \mathbf{g}^{d*}(\vec{k})\right] \cdot \mathbf{f}^{d*}(\vec{k}). \end{gathered} \tag{136}$$

Using Equations (130), (94) and (134), we may write the matrices between the square brackets as:

$$\begin{aligned} \left(\mathbf{g}^{d*}(\vec{k})\right)^{-1} \cdot \overline{\widehat{\mathbf{D}}}^{d}_{\vec{k}}(a) \cdot \mathbf{g}^{d*}(\vec{k}) &= \left(\mathbf{g}^{*-1}(\vec{k}) \cdot \overline{\widehat{\mathbf{D}}}_{\vec{k}}(a) \cdot \mathbf{g}^{*}(\vec{k})\right) \times \mathbf{d}_{1/2}(\alpha) \\ &= \mathbf{D}^{\text{aff}}_{\vec{k}}(a) \times \mathbf{d}_{1/2}(\alpha) \\ &= \begin{pmatrix} \mathbf{d}^{\text{aff}}_{\vec{k},\mu}(a) & 0 & 0 & 0 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \mathbf{d}^{\text{aff}}_{\vec{k},2}(a) & 0 \\ 0 & 0 & 0 & \mathbf{d}^{\text{aff}}_{\vec{k},1}(a) \end{pmatrix} \times \mathbf{d}_{1/2}(\alpha), \end{aligned} \tag{137}$$

where, again, the matrices $\mathbf{d}^{\text{aff}}_{\vec{k},q}(a)$ form single-valued one-dimensional representations $\boldsymbol{d}^{\text{aff}}_{\vec{k},q}$. Remember that (Definition 20) the single-valued representations $\boldsymbol{d}^{\text{aff}}_{\vec{k},q}$ are not associated with the Bloch functions of the considered band, but are fixed by the representation $\boldsymbol{D}$ defining the spin-dependent Wannier functions.

Equation (137) shows that also the matrices between the square brackets form a representation being the direct sum over double-valued representations, and hence, Equation (133) splits into the μ equations:

$$\boldsymbol{d}_{\vec{k},q} \otimes \boldsymbol{d}_{1/2} = \mathbf{f}^{*-1}(q,\vec{k}) \cdot \left(\boldsymbol{d}^{\text{aff}}_{\vec{k},q} \otimes \boldsymbol{d}_{1/2}\right) \cdot \mathbf{f}^{*}(q,\vec{k}), \tag{138}$$

($1 \leq q \leq \mu$), which are solvable because the representations $\boldsymbol{D}^{d}_{\vec{k}}$ and $\overline{\widehat{D}}^{d}_{\vec{k}}$ and, hence, also, the representations $\boldsymbol{d}_{\vec{k},q} \otimes \boldsymbol{d}_{1/2}$ and $\boldsymbol{d}^{\text{aff}}_{\vec{k},q} \otimes \boldsymbol{d}_{1/2}$ are equivalent.

We now distinguish between two possibilities:

– If the considered energy band was already closed before the spin-dependent perturbation $\mathcal{H}_s$ was activated, then the affiliated single-valued band actually exists as a closed band in the band structure of the material under consideration, and thus, the representations $\boldsymbol{d}_{\vec{k},q}$ and $\boldsymbol{d}^{\text{aff}}_{\vec{k},q}$ are equal,

$$\boldsymbol{d}_{\vec{k},q} = \boldsymbol{d}^{\text{aff}}_{\vec{k},q}. \tag{139}$$

Hence, all of the μ equations (138) are solved by:

$$\mathbf{f}(q,\vec{k}) \equiv \mathbf{1}, \tag{140}$$

with the consequence that the Wannier functions are, in fact, not spin-dependent, but are usual Wannier functions, as defined in Equation (6).

– If the considered energy band was not closed before the spin-dependent perturbation $\mathcal{H}_s$ was activated, then not all of the representations $\boldsymbol{d}_{\vec{k},q}$ are equal to $\boldsymbol{d}^{\text{aff}}_{\vec{k},q}$. Evidently, the q-th equation is not solved by $\mathbf{f}(q,\vec{k}) \equiv \mathbf{1}$ when $\boldsymbol{d}_{\vec{k},q} \neq \boldsymbol{d}^{\text{aff}}_{\vec{k},q}$, and consequently, the Wannier function actually are spin-dependent.

We summarize this result in Theorem 12.

Theorem 12. *If the considered energy band were not closed before the spin-dependent perturbation $\mathcal{H}_s$ was activated, the matrices $\mathbf{f}(q,\vec{k})$ in Equation (72) cannot be chosen independent of $\vec{k}$.*

In the Section 7.5, the matrix $\mathbf{f}(q,\vec{k})$ shall by determined for some points in the Brillouin zone of niobium.

7.4.2. The Bloch Functions $\varphi_{\vec{k},q}(\vec{r})$ Are Basis Functions for a Degenerate Representation

In rare cases, it can happen that at a special point $\vec{k}$, some of the Bloch states $\varphi_{\vec{k},q}(\vec{r})$ are basis functions for a degenerate (single-valued) representation and that this degeneracy is not removed by the perturbation $\mathcal{H}_s$. For example, each of the two superconducting bands in the space group $P4/nmm = \Gamma_q D^7_{4h}$ (129) listed in Table 3(b) of [13] consist of two branches degenerate at points M and A. The single-valued Bands 1 and 2 in Table 3(a) of [13] are affiliated with the superconducting Band 1 in Table 3(b) *ibidem*; Bands 3 and 4 in Table 3(a) are affiliated with Band 2 in Table 3(b).

It is crucial for the localization of the spin-dependent Wannier functions that also in this case, Equation (133) is solvable. We reveal the solubility of this equation for the example of the bands listed in Table 3 of [13].

At point M in each of these bands, Equation (138) may be written as:

$$\boldsymbol{d}_{\vec{k}_M} \otimes \boldsymbol{d}_{1/2} = \left(\mathbf{f}^{d*}(\vec{k}_M)\right)^{-1} \cdot \left(\boldsymbol{d}^{\text{aff}}_{\vec{k}_M} \otimes \boldsymbol{d}_{1/2}\right) \cdot \mathbf{f}^{d*}(\vec{k}_M), \tag{141}$$

where $\boldsymbol{d}_{\vec{k}_M}$ and $\boldsymbol{d}^{\text{aff}}_{\vec{k}_M}$ now are two-dimensional (single-valued) representations, and the matrix $\mathbf{f}^d(\vec{k}_M)$ now is four-dimensional,

$$\mathbf{f}^d(\vec{k}_M) = \begin{pmatrix} \mathbf{f}(2,\vec{k}_M) & \mathbf{0} \\ \mathbf{0} & \mathbf{f}(1,\vec{k}_M) \end{pmatrix}, \tag{142}$$

see Equation (131).

Though $\boldsymbol{d}_{\vec{k}_M} \otimes \boldsymbol{d}_{1/2}$ and $\boldsymbol{d}^{\text{aff}}_{\vec{k}_M} \otimes \boldsymbol{d}_{1/2}$ again are equivalent, it is not immediately evident that Equation (141) is solvable, because $\mathbf{f}^d(\vec{k}_M)$ is not a general 4×4 matrix. However, also, the representations $\boldsymbol{d}_{\vec{k}_M} \otimes \boldsymbol{d}_{1/2}$ and $\boldsymbol{d}^{\text{aff}}_{\vec{k}_M} \otimes \boldsymbol{d}_{1/2}$ have a very special form, since they may be written simply as Kronecker products. Equation (141) indeed is solvable, since it expresses the most general unitary transformation between these special representations.

For instance, consider the point M of one of the bands in Table 3b of [13], and let $\boldsymbol{d}_{\vec{k}_M} = M_3$ be given by the calculated band structure of the material under consideration. In addition, let us choose Band 1 in Table 3a of [13] as the affiliated single-valued band. Thus, we have $\boldsymbol{d}^{\text{aff}}_{\vec{k}_M} = M_2$, and Equation (141) is solved by:

$$\mathbf{f}^d(\vec{k}_M) = \begin{pmatrix} \begin{pmatrix} 0 & -i \\ 1 & 0 \end{pmatrix} & \mathbf{0} \\ \mathbf{0} & \begin{pmatrix} 0 & 1 \\ -i & 0 \end{pmatrix} \end{pmatrix}, \tag{143}$$

as may be determined by means of the tables given in [32].

Though both Band 1 and Band 2 in Table 3b of [13] are mathematically correct superconducting bands, they cannot be occupied in undoped LaFeAsO [13], which, consequently, is not superconducting.

7.4.3. Additions

In this subsection, we show that neither Equation (120) nor Equation (126) is inconsistent with Equation (133). Remember that in this section, we only consider points $\vec{k}$ for which Equation (80) is valid.

First, taking the complex conjugate of Equation (134), we receive with $\boldsymbol{D}^{\text{aff}*}_{\vec{k}} = \boldsymbol{D}^{\text{aff}}_{-\vec{k}}$ and $\overline{\widehat{\boldsymbol{D}}}^{*}_{\vec{k}} = \overline{\widehat{\boldsymbol{D}}}_{-\vec{k}}$ the condition:

$$\boldsymbol{D}^{\text{aff}}_{-\vec{k}} = \mathbf{g}^{-1}(\vec{k}) \cdot \overline{\widehat{\boldsymbol{D}}}_{-\vec{k}} \cdot \mathbf{g}(\vec{k}) \tag{144}$$

showing that we may choose:

$$\mathbf{g}^*(-\vec{k}) = \mathbf{g}(\vec{k}) \tag{145}$$

and hence, Equation (120) is consistent with Equation (144) and, consequently, with Equation (133).

Secondly, transforming the complex conjugate of Equation (138) with the matrix $\mathbf{n}$ in Equation (103) and using $\boldsymbol{d}^*_{\vec{k},q} = \boldsymbol{d}_{-\vec{k},q}$, $\boldsymbol{d}^{\text{aff}*}_{\vec{k},q} = \boldsymbol{d}^{\text{aff}}_{-\vec{k},q}$ and:

$$\boldsymbol{d}^*_{1/2} = \mathbf{n}^{-1}\boldsymbol{d}_{1/2}\mathbf{n} \tag{146}$$

(see Equation (110)), we obtain the equation:

$$\boldsymbol{d}_{-\vec{k},q} \otimes \boldsymbol{d}_{1/2} = \left(\mathbf{nf}(q,\vec{k})\mathbf{n}^{-1}\right)^{-1} \cdot (\boldsymbol{d}^{\text{aff}}_{-\vec{k},q} \otimes \boldsymbol{d}_{1/2}) \cdot \left(\mathbf{nf}(q,\vec{k})\mathbf{n}^{-1}\right) \tag{147}$$

showing that, in fact, we may choose:

$$\mathbf{f}^{*}(q,-\vec{k}) = \mathbf{nf}(q,\vec{k})\mathbf{n}^{-1}.$$

Hence, Equation (126) is consistent with Equation (133).

7.5. Example: Band Structure of Niobium

Consider the superconducting band (Definition 22) of niobium in Figure 1, as denoted by the dotted line. At the four points of symmetry Γ, H, N and P in the Brillouin zone for the space group O_h^9 of niobium, this band is characterized by the representations:

$$\Gamma'_{25},\ H'_{25},\ N_2 \text{ and } P_4$$

of O_h^9 in the familiar notation of Bouckaert, Smoluchowski and Wigner [29], which may be written as:

$$\Gamma_5^+,\ H_5^+,\ N_4^+, \text{ and } P_5, \tag{148}$$

respectively, in the notation of Bradley and Cracknell [32] (see Tables 5.7 and 5.8 *ibidem*), which is consistently used in our papers. When we take into account that the electrons possess a spin, we receive:

$$\begin{array}{lllllll}
\Gamma_5^+ & \otimes & d_{1/2} & = & \Gamma_7^+ & \oplus & \Gamma_8^+, \\
H_5^+ & \otimes & d_{1/2} & = & H_7^+ & \oplus & H_8^+, \\
P_5 & \otimes & d_{1/2} & = & P_7 & \oplus & P_8, \\
N_4^+ & \otimes & d_{1/2} & = & N_5^+. & &
\end{array}$$

Hence, at the points Γ, H, P and N, the Bloch spinors can be transformed in such a way that at each of the four points Γ, H, N and P, two spinors form basis functions for the double-valued representations:

$$\Gamma_7^+,\ H_7^+,\ P_7, \text{ and } N_5^+, \tag{149}$$

respectively. We may unitarily transform the Bloch spinors $\psi_{\vec{k},q,s}(\vec{r},t)$ of this single energy band characterized by the representations (149) into optimally-localized and symmetry-adapted spin-dependent Wannier functions, because Theorem 9 yields with $H_0 = O_h$, $\mu = 1$, $\vec{\rho}_1 = \vec{0}$, $G_{0p} = H_0 = O_h$ and $\boldsymbol{d}_1 = \Gamma_2^+$ first the single-valued representations:

$$\boldsymbol{D}^{\text{aff}}_{\Gamma} = \Gamma_2^+,\ \boldsymbol{D}^{\text{aff}}_{H} = H_2^+,\ \boldsymbol{D}^{\text{aff}}_{P} = P_2, \text{ and } \boldsymbol{D}^{\text{aff}}_{N} = N_3^+ \tag{150}$$

and then, with Equation (97), the double-valued representations (149).

The representations in Equation (150) define (the only) single-valued band affiliated with the superconducting band defined by the representations in Equation (149) (Definition 20). The representation $\boldsymbol{D}$ defining the spin-dependent Wannier functions (Definition 19) is equal to Γ_2^+,

$$\boldsymbol{D} = \Gamma_2^+. \tag{151}$$

$\boldsymbol{D}$ is one-dimensional, since we have one Nb atom in the unit cell. The spin-dependent Wannier functions may be chosen symmetry-adapted to the magnetic group in Equation (98), because Γ_2^+ is real.

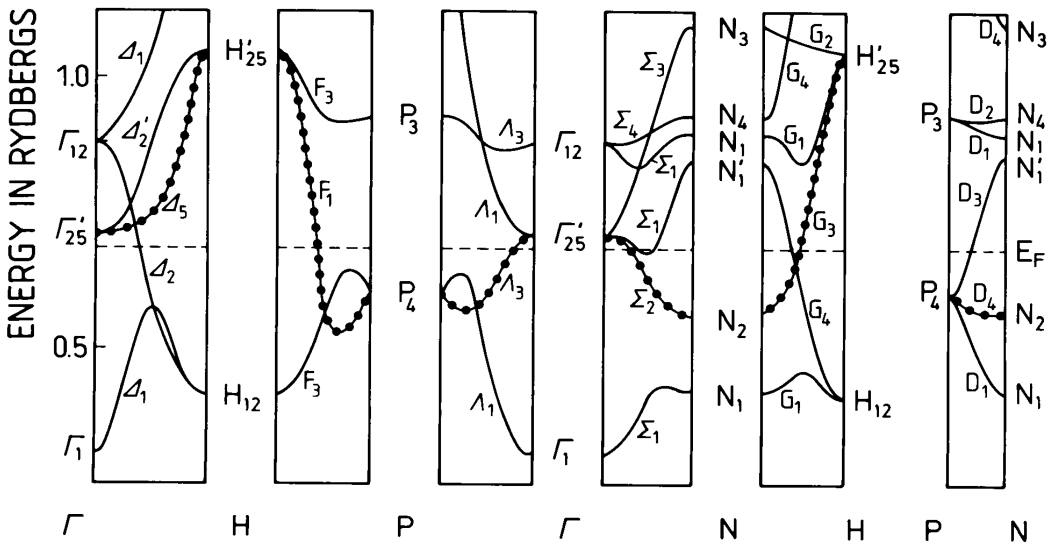

Figure 1. Band structure of Nb after Mattheis [37]. The dotted line denotes the superconducting band.

The Bloch functions of the superconducting band cannot be unitarily transformed into usual Wannier functions, which are optimally-localized and symmetry-adapted to O_h^9, since it was not closed before the spin-dependent perturbation $\mathcal{H}_s$ was activated. Thus (Theorem 12), we cannot choose the matrix $\mathbf{f}(1,\vec{k})$ in Equation (72) (with $q = 1$, since we only have one branch in the superconducting band of Nb) independent of $\vec{k}$ when we demand that the Wannier functions are optimally-localized and symmetry-adapted. This important statement shall be demonstrated by an example:

Consider the point N with the wave vector $\vec{k}_N$ in the first domain of the Brillouin zone for O_h^9. The representations $\boldsymbol{d}^{\text{aff}}_{\vec{k}_N,1}$ and $\boldsymbol{d}_{\vec{k}_N,1}$ in Equation (138) are given by Equations (150) and (148),

$$\boldsymbol{d}^{\text{aff}}_{\vec{k}_N,1} = N_3^+ \tag{152}$$

and

$$\boldsymbol{d}_{\vec{k}_N,1} = N_4^+. \tag{153}$$

Thus, Equation (138) may be written as

$$N_4^+ \otimes \boldsymbol{d}_{1/2} = (\mathbf{f}^*(1,\vec{k}_N))^{-1} \cdot (N_3^+ \otimes \boldsymbol{d}_{1/2}) \cdot \mathbf{f}^*(1,\vec{k}_N). \tag{154}$$

This equation is solvable, since both representations $N_4^+ \otimes \boldsymbol{d}_{1/2}$ and $N_3^+ \otimes \boldsymbol{d}_{1/2}$ are equivalent, but it is evidently not solved by $\mathbf{f}(1,\vec{k}_N) = \mathbf{1}$. In fact, we receive:

$$\mathbf{f}(1,\vec{k}_N) = \begin{pmatrix} 0 & 1 \\ -i & 0 \end{pmatrix} \tag{155}$$

by means of Tables 5.7 and 6.1 of [32]. This is the value of $\mathbf{f}(1,\vec{k})$ also on the planes of symmetry intersecting at N in the neighborhood of N. Further away from N, however, $\mathbf{f}(1,\vec{k})$ may change, since it is $\vec{k}$ dependent.

In the same way, we find:

$$\mathbf{f}(1,\vec{k}_F) = \frac{1}{\sqrt{3}} \begin{pmatrix} -i & -1+i \\ 1+i & i \end{pmatrix} \tag{156}$$

for the points $\vec{k}_F$ on the line F.

Equations (155) and (156) demonstrate that $\mathbf{f}(1,\vec{k})$ cannot be chosen independent of $\vec{k}$ in the superconducting band of niobium.

8. Conclusions

In the present paper, we gave the group theory of optimally-localized and symmetry-adapted Wannier functions with the expectation that it will be helpful to determine the symmetry of the Wannier functions in the band structure of any given material. The paper is written in such a way that it should be possible to create a computer program automating the determination of the symmetry of the Wannier functions.

In this paper, we restricted ourselves to Wannier functions that define magnetic or superconducting bands. That means that we considered only Wannier functions centered at the atomic positions. When other physical phenomena shall be explored, as, e.g., the metallic bond, other Wannier functions may be needed, which are centered at other positions, e.g., between the atoms. It should be noted that [28,30,33] define optimally-localized and symmetry-adapted Wannier functions in general terms, which may be centered at a variety of positions $\vec{\rho}_i$ being different from the positions of the atoms.

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Author Contributions

Ekkehard Krüger wrote the group theory in Sections 2–7; Horst P. Strunk initiated this paper and wrote parts of Section 1, the Introduction.

Conflicts of Interest

The authors declare no conflict of interest.

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