Group Theory in Materials Science, Applications

R Dirl and P Weinberger, Vienna University of Technology, Vienna, Austria

Applications in Materials Science

The potential applications of group-theoretical methods in solid-state physics – synonymous for materials science – depend on the various groups that are specific for this field. For instance, the compact continuous groups SU(2) or its homomorphic image $SO(3,\mathbb{R})$ are widely used in multiple scattering theory. Proper point groups as specific finite subgroups of $SO(3,\mathbb{R})$ are employed when investigating macroscopic properties of materials that are described by tensors of certain ranks. Crystallographic space groups containing Bravais vector lattices as countable subgroups are taken into account when describing bulk properties of materials. Moreover, sectional layer groups might turn out to be of decisive importance when discussing surface properties of materials, since they describe the symmetries of crystallographic planes. Finally, penetration rod groups may eventually become important when investigating one-dimensional defects in some materials.

Point Groups – Macroscopic Properties

Proper crystallographic point groups $\mathscr{P}(\mathscr{T}(\mathscr{L}))$ are, by definition, intersection groups of the type $SO(3,\mathbb{R}) \cap SL(3,\mathbb{Z})$ where the symbol $SL(3,\mathbb{Z})$ denotes the group of all integral 3×3 matrices with $\det \mathbb{Z}(z) = +1$ such that, in addition, a certain Bravais lattice $\mathscr{T}(\mathscr{L})$ is mapped by these matrices onto itself. Proper noncrystallographic point groups $\mathscr{P}$ are, by definition, finite subgroups of the proper rotation group $SO(3,\mathbb{R})$ which are not constrained by the invariance condition of Bravais vector lattices. Macroscopic properties of materials, such as stress or conductivity, are described by tensors of certain ranks which in the presence of symmetry are invariant with respect to the symmetry group G in question. For instance, the invariance condition implies, for a second rank tensor $\{T_{jk} \mid j,k = 1,2,3\}$,

$$\sum_{j,k=1}^{3} T_{jk} R_{jm}(R)\, R_{kn}(R) = T_{mn} \qquad \forall R \in \mathscr{P} \tag{1}$$

that, depending on the symmetry group $\mathscr{P}$, certain tensor components vanish for symmetry reasons. For instance, in cubic symmetry tensors of rank two are proportional to the three-dimensional unit matrix.

Crystallographic Space Groups

A proper description of bulk properties in solids requires the introduction of three-dimensional crystallographic space groups which, loosely speaking, can be seen as the invariance groups of three-dimensional periodic structures. The basic constituents of space groups are their underlying Bravais vector lattices $\mathscr{T}(\mathscr{L})$ and admissible crystallographic point groups $\mathscr{P}$ that leave the Bravais vector lattice $\mathscr{T}(\mathscr{L})$ invariant. Possible structures of space groups and their classification schemes are discussed later.

Bravais vector lattices Let $\{t_1, t_2, t_3\}$ be a set of three linearly independent (noncoplanar) vectors of the Euclidean vector space $E^3_{\mathbb{R}}$ where the latter is regarded as the vector space component of the underlying Euclidean point space $\mathrm{E}^3_{\mathbb{R}}$. To simplify the notation, let $\boldsymbol{t} = (t_1, t_2, t_3)$ be formally denoted as row vector and $\underline{n} \in \mathbb{Z}^3$ as column vectors with integral coefficients. Then, by definition,

$$\mathcal{T}(\mathcal{L}) = \{t = \boldsymbol{t} \cdot \underline{n} \mid \underline{n} \in \mathbb{Z}^3\} \qquad [2]$$

$$\boldsymbol{t} = \boldsymbol{e}\, \mathbb{D}(\mathcal{L}) \qquad [3]$$

where the countable set of vectors denoted by $\mathcal{T}(\mathcal{L})$ determines uniquely a Bravais vector lattice which can be traced back by means of an appropriate three-dimensional nonsingular matrix $\mathbb{D}(\mathcal{L}) \in \mathrm{SL}(3, \mathbb{R})$ with $\det \mathbb{D}(\mathcal{L}) > 0$ to an orthonormalized basis $\boldsymbol{e}$ of the associated Euclidean vector space $E^3_{\mathbb{R}}$. It is worth noting that the positive sign of the determinant guarantees the right-handedness of the associated coordinate system. Apart from this, the symbol $\boldsymbol{t} \cdot \underline{n}$ should be seen as formal scalar product and likewise $\boldsymbol{e}\, \mathbb{D}(\mathcal{L})$ are the formal multiplication of a row vector times a 3×3 matrix. Moreover, one can define

$$\boldsymbol{t}(z) = \boldsymbol{t}\mathbb{Z}(z) \quad \forall \mathbb{Z}(z) \in \mathrm{SL}(3, \mathbb{Z}) \qquad [4]$$

countable infinitely many vector bases for one and the same Bravais vector lattice $\mathcal{T}(\mathcal{L})$, since the group $\mathrm{SL}(3, \mathbb{Z})$ is countably infinite. Accordingly, the corresponding vector bases $\boldsymbol{t}(z)$ are equally well suited to describe one and the same Bravais vector lattice. Hence, the choice of standardized vector bases, such as vectors of the shortest lengths, is subject to certain conventions to achieve this goal.

Automorphisms of vector lattices – point groups To understand the structure of crystallographic space groups, one first has to understand the structure of crystallographic point groups $\mathcal{P}(\mathcal{T})$ that leave a certain Bravais vector lattice $\mathcal{T}(\mathcal{L})$ invariant. Obviously,

$$\mathrm{Aut}(\mathcal{T}) = \mathrm{GL}(3, \mathbb{Z}) \qquad [5]$$

which implies that the "automorphism group" $\mathrm{Aut}(\mathcal{T})$ is the most general group that leaves the Bravais vector lattice $\mathcal{T}$ invariant, where $\mathrm{GL}(3, \mathbb{Z})$ contains $\mathrm{SL}(3, \mathbb{Z})$ as normal subgroup of index two. To assure that the point group $\mathcal{P}(\mathcal{T})$ contains only orthogonal transformations, one demands the restricting condition

$$\mathcal{P}(\mathcal{T}) = \mathrm{O}(3, \mathbb{R}) \cap \mathrm{GL}(3, \mathbb{Z}) \qquad [6]$$

in order to guarantee a maximal set of orthogonal symmetry operations that leave the Bravais vector lattice $\mathcal{T}$ invariant. The action of the point group operations $R \in \mathcal{P}(\mathcal{T})$ onto the elements of the primitive vector basis $\boldsymbol{t}$ is given by

$$Rt_j = \sum_{k=1}^{3} Z_{kj}(R) t_k \qquad [7]$$

where the additional condition $Z(R) \in \mathrm{GL}(3, \mathbb{Z})$ must be satisfied for all group elements $R \in \mathcal{P}(\mathcal{T})$ of the crystallographic point group. The actual form of the matrix representation $\{Z(R)\}$ is characteristic of the corresponding crystal class, once the associated crystal system has been determined for the Bravais vector lattice $\mathcal{T}$ in question.

Space groups – gross classification The easiest access to crystallographic space groups is to start from the locally compact continuous "Euclidean group" $E(3, \mathbb{R})$ which is composed of the locally compacts three-dimensional continuous translation group $T(3, \mathbb{R})$ and the full rotation group $O(3, \mathbb{R})$:

$$E(3, \mathbb{R}) = T(3, \mathbb{R}) \circledS O(3, \mathbb{R}) \qquad [8]$$

which symbolizes a semidirect product group between the translation group and the full rotation group. The Euclidean group $E(3, \mathbb{R})$ is the most general motion group whose corresponding transformations map the Euclidean vector space $E^3_{\mathbb{R}}$ onto itself, such that not only the distance between two vectors, but also the angle between them remains invariant. The nonsingular transformations $\mathcal{M}(S \mid v)$ that are uniquely assigned to the groups elements $(S \mid v), (X \mid w) \in E(3, \mathbb{R})$ are given by the following expressions:

$$\mathcal{M}(S \mid v)x = Sx + v = x' \in E^3_{\mathbb{R}} \qquad [9]$$

$$\mathcal{M}(S \mid v)\mathcal{M}(X \mid w) = \mathcal{M}(SX \mid v + Sw) \qquad [10]$$

where the so-called Wigner–Seitz symbols are used to denote the group elements of the Euclidean group. In order to combine consistently the various notations, one may express an arbitrary element of the Euclidean vector space $E^3_{\mathbb{R}}$ as follows $x = \boldsymbol{e} \cdot \underline{x}$, where $\underline{x} \in \mathbb{R}^3$ are the corresponding column vectors with real-valued components. Finally, the composition law of the Euclidean group $E(3, \mathbb{R})$ is given by [10] in terms of the nonsingular transformations.

By definition, space groups (hereafter sometimes denoted by the shorthand notation $\mathcal{G}$) are countable subgroups of the Euclidean group $E(3, \mathbb{R})$ where the locally compact continuous translation group $T(3, \mathbb{R})$ is reduced to one of the noncountable infinitely many Bravais vector lattices $\mathcal{T}$ and where the full rotation group $O(3, \mathbb{R})$ is reduced to the utmost maximal crystallographic point group $\mathcal{P}(\mathcal{T})$ that leaves the underlying Bravais vector lattice $\mathcal{T}$ by its orthogonal transformations invariant. In mathematical terms, one writes

$$\mathscr{G} = \{\mathscr{T}, \mathscr{P} \mid \mathcal{O}, \boldsymbol{w}_{\mathscr{P}}\} \qquad [11]$$

to symbolize space groups. Here, the entry $\mathscr{T}$ denotes the Bravais vector lattice and $\mathscr{P}$ its corresponding crystallographic point group which satisfies the group–subgroup relation $\mathscr{P}_{\min} \subseteq \mathscr{P} \subseteq \mathscr{P}_{\max}$, where $\mathscr{P}_{\min}$ and its corresponding counterpart $\mathscr{P}_{\max}$ are determined by the associated arithmetic class of space group types. Moreover, the symbol $\mathcal{O}$ denotes the chosen origin of the associated coordinate system and $\boldsymbol{w}_{\mathscr{P}} \in E^3_{\mathbb{R}}$, the set of nonprimitive translations which are likewise called "fractional translations." They are uniquely assigned to the point group elements $R \in \mathscr{P}$. Accordingly,

$$\boldsymbol{w}_{\mathscr{P}} = \{\boldsymbol{w}_R = \boldsymbol{t} \cdot \boldsymbol{w}_R \mid R \in \mathscr{P}\} \qquad [12]$$

where the components $\boldsymbol{w}_R \in \mathbb{Q}^3$ of the fractional translations become rational numbers if the origin $\mathcal{O}$ of the space group G is suitably chosen. The corresponding space group elements are denoted by $(R \mid \boldsymbol{w}_R + \boldsymbol{t}) \in \mathscr{G}$, where again the Wigner–Seitz notation is employed. The composition law of each space group $\mathscr{G}$ must follow automatically from the composition law [10] the Euclidean group $E(3, \mathbb{R})$ due to their group–subgroup relation. To be more specific

$$\begin{aligned}(R \mid \boldsymbol{w}_R + \boldsymbol{t}) * (S \mid \boldsymbol{w}_S + \boldsymbol{v}) \\ = (RS \mid \boldsymbol{w}_{RS} + \boldsymbol{t}_{R,S} + \boldsymbol{t} + R\boldsymbol{v})\end{aligned} \qquad [13]$$

$$\boldsymbol{t}_{R,S} = \boldsymbol{w}_R + R\boldsymbol{w}_S - \boldsymbol{w}_{RS} \qquad [14]$$

where the closure relation for the space group $\mathscr{G}$ implies $\boldsymbol{t}_{R,S} \in \mathscr{T}$ for all point group elements $R, S \in \mathscr{P}$. This allows one to classify the space groups into two significantly different types, namely "symmorphic" and "nonsymmorphic" space group types. The criterion reads

$$\text{Symmorphic } \mathscr{G}: \quad \boldsymbol{t}_{R,S} = 0 \quad \forall R, S \in \mathscr{P} \qquad [15]$$

$$\text{Nonsymmorphic } \mathscr{G}: \quad \boldsymbol{t}_{R,S} \neq 0 \quad \exists R, S \in \mathscr{P} \qquad [16]$$

which simply shows that symmorphic space groups can be seen as semidirect product groups, whereas nonsymmorphic space groups are more general extensions. As a matter of fact, there exist 230 space group types which split into 73 mutually disjoint arithmetic classes, where each arithmetic class is led by a symmorphic space group type.

$\mathscr{G}$-Invariant atomic arrangements The simplest model for a crystal is the static arrangement of atoms (molecules, clusters, etc.) where it suffices to fix some atomic positions within one primitive cell $\mathscr{P}(\mathscr{T})$ and to exploit its space group symmetry to obtain an infinitely extended periodic structure. Here the symbol $\mathscr{P}(\mathscr{T})$ denotes the primitive cell of the Bravais vector lattice $\mathscr{T}$ that is nothing but the parallelepiped spanned by the primitive basis vectors $\boldsymbol{t}$. Atomic positions in $\mathscr{P}(\mathscr{T})$ are denoted by $\boldsymbol{x} \in \mathscr{P}(\mathscr{T})$ and are classified by the so-called "Wyckoff positions." Here, for simplicity $G = (R \mid \boldsymbol{w}_R + \boldsymbol{t}) \in \mathscr{G}$ a shorthand notation for the space group elements is introduced as

$$\mathscr{G}(\boldsymbol{x}_j) = \{G \in \mathscr{G} \mid \mathscr{M}(G)\boldsymbol{x}_j = \boldsymbol{x}_j\} \qquad [17]$$

$$\{\boldsymbol{x}_j(\mathscr{G})\} = \{\boldsymbol{x}_j(G) = \mathscr{M}(G)\boldsymbol{x}_j \mid G \in \mathscr{G} : \mathscr{G}(\boldsymbol{x}_j)\} \qquad [18]$$

Groups of the type $\mathscr{G}(\boldsymbol{x}_j)$ defined by [17] are called site groups. Infinite sets $\{(\boldsymbol{x}_j)\mathscr{G}\}$ defined by [18] are called single site atomic arrangements. Two positions, say $\boldsymbol{x}_j$ and $\boldsymbol{x}_k$, are called $\mathscr{G}$ equivalent if and only if, there exists at least one space group element $G \in \mathscr{G}$ such that $\mathscr{M}(G)\boldsymbol{x}_j = \boldsymbol{x}_k$. Their site groups are then conjugate subgroups with respect to the space group $\mathscr{G}$ in question. However, if one cannot find a space group element $G \in \mathscr{G}$ such that the previous condition holds, then the two positions are called $\mathscr{G}$ inequivalent. The union of mutually disjoint single site atomic arrangements defined by

$$\begin{aligned}&\{\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_n, \mathscr{G}\} \\ &= \{\boldsymbol{x}_1(\mathscr{G})\} \cup \{\boldsymbol{x}_2(\mathscr{G})\} \cup \cdots \{\boldsymbol{x}_n(\mathscr{G})\}\end{aligned} \qquad [19]$$

is regarded as a multiple-site atomic arrangement which describes a periodic structure that possesses the space group $\mathscr{G}$ as its symmetry group. The notion of Wyckoff position is synonymous for connected subsets of the primitive cell $\mathscr{P}(\mathscr{T})$, whose points (vectors) possess image groups $\mathscr{P}(\boldsymbol{x}_j) \sim \mathscr{G}(\boldsymbol{x}_j)$ that are conjugated subgroups with respect to its crystallographic point group $\mathscr{P}$. Wyckoff positions may consist of isolated points, lines, planes, or compact subsets of $\mathscr{P}(\mathscr{T})$. This specific classification of points $\boldsymbol{x} \in \mathscr{P}(\mathscr{T})$ is of importance in physical applications. Since different elements or any fixed Wyckoff position must have the same point group symmetry, it may or may not lead to a change of energy when the atoms vary their positions within one Wyckoff position.

Space group–subgroup relations Group–subgroup relations between crystallographic space groups play a decisive role in structural phase transitions which are accompanied by changes in the symmetry. Usually, one assumes that the space group $\mathscr{H}$ of the distorted phase is a proper subgroup (of finite index) of the space group $\mathscr{G}$ of the parent phase which implies that $\mathscr{H} \subset \mathscr{G}$. Due to the reduction of the symmetry at the phase transition, the distorted phase can appear in several homogeneous simultaneously coexisting states which have the same structure but different orientations and/or locations in space. Let $\mathscr{G} = \{\mathscr{T}, \mathscr{P} \,|\, \mathscr{O}, \boldsymbol{w}_{\mathscr{P}}\}$ be the superspace group and $\mathscr{H} = \{\mathscr{S}, \mathscr{Q} \,|\, \mathscr{O}', \boldsymbol{w}_{\mathscr{Q}}\}$ be the subspace group of the former. In fact, three significant different types of group–subgroup relations are possible, namely

$$\text{translationsgleiche}: \quad \mathscr{S} = \mathscr{T}, \ \mathscr{Q} \subset \mathscr{P} \qquad [20]$$

$$\text{klassengleiche}: \quad \mathscr{S} \subset \mathscr{T}, \ \mathscr{Q} = \mathscr{P} \qquad [21]$$

$$\text{general}: \quad \mathscr{S} \subset \mathscr{T}, \ \mathscr{Q} \subset \mathscr{P} \qquad [22]$$

where by means of "Hermann's theorem," it can be shown that every general group–subgroup relation between space groups can be traced back to various chains of maximal *translationsgleiche* or *klassengleiche* subspace groups. Group–subgroup relations of infinite index are given by V Kopsky and D B Litvin in 2002 in the International Tables for Crystallography, Volume E, Subperiodic Groups, where sectional layer groups and penetration rod groups are discussed as subgroups of three-dimensional crystallographic space groups.

Space Group Unirreps

This section focuses on the representation theory of space groups with special emphasis on their unirreps. It is well known that space group unirreps can be constructed systematically by applying Mackey's induction procedure, which is exhaustively discussed by C J Bradley and A P Cracknell in 1972 in The Mathematical Theory of Symmetry in Solids. Mackey's induction procedure relies, among others, on the assumption that the given group G possesses a normal subgroup N whose unirreps are known. Specifying these assumptions to space groups, it implies that one should start from the well-known one-dimensional $\mathscr{F}$ unirreps, since every crystallographic space group $\mathscr{G}$ contains a Bravais vector lattice $\mathscr{T}$ as its natural normal subgroup.

Reciprocal vector lattices In order to be able to define the $\mathscr{T}$ unirreps, one has to define first the corresponding reciprocal vector lattice $\mathscr{T}^{\star}$ together with its corresponding "Brillouin zone" $\mathscr{B}(\mathscr{T}^{\star})$

$$\mathscr{T}^{\star} = \{\boldsymbol{K} = \boldsymbol{K} \cdot \underline{n} \,|\, \underline{n} \in \mathbb{Z}^3\} \qquad [23]$$

$$\boldsymbol{t}_j \cdot \boldsymbol{K}_l = 2\pi\delta_{jl} \qquad [24]$$

By definition, the vectors $\boldsymbol{K} = \{\boldsymbol{K}_1, \boldsymbol{K}_2, \boldsymbol{K}_3\}$, formally written as row vectors, form the basis of the corresponding reciprocal lattice $\mathscr{T}^{\star}$, where $\mathscr{T}$ is the underlying direct vector lattice. The Brillouin zone $\mathscr{B}(\mathscr{T}^{\star})$ is the counterpart of the Wigner–Seitz cell of the underlying direct vector lattice. The primitive cell $\mathscr{P}(\mathscr{T}^{\star})$ is spanned as parallelepiped by the basis vectors $\boldsymbol{K}$. Recall that $\mathscr{P}(\mathscr{T}^{\star})$ and its symmetrical counterpart $\mathscr{B}(\mathscr{T}^{\star})$ are equally well suited to describe the basic domains of the reciprocal vector lattice $\mathscr{T}^{\star}$.

$\mathscr{T}$ Unirreps Since $\mathscr{T}$ forms an abelian group, its unirreps over the field $\mathbb{C}$ of complex numbers are one-dimensional, which implies that they are unimodular numbers. In fact,

$$D^{k}(E|\boldsymbol{t}) = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{t}} \qquad [25]$$

$$\boldsymbol{k} = \alpha\boldsymbol{K}_1 + \beta\boldsymbol{K}_2 + \gamma\boldsymbol{K}_3 \qquad [26]$$

where not only $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^{\star})$ but also $\boldsymbol{t} \in \mathscr{T}$ should be taken into account. It is to be noted that the $\mathscr{T}$ irrep label $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^{\star})$ varies continuously over the Brillouin zone. For instance, in the case of primitive cubic Bravais vector lattices, the corresponding continuous parameters have $-1/2 < \alpha, \beta, \gamma \leqslant +1/2$ their domains of definitions to avoid double counting of eventually superfluous $\mathscr{T}$ irrep labels.

Periodic boundary conditions Once the so-called "periodic boundary conditions" are imposed to any given Bravais vector lattice $\mathscr{T}$, it implies that only finite homomorphic image of the originally countable Bravais vector lattice are considered. This reduces the originally compact continuous Brillouin zone $\mathscr{B}(\mathscr{T}^{\star})$ to a finite set of vectors. Hence, the original continuous parameters α, β, γ become discrete and lose their continuity properties. Usually, periodic boundary conditions are introduced to avoid mathematical difficulties that arise from the fact that the $\mathscr{T}$ unnirreps (see eqn [25]) are normalized to delta functions. On the other hand, they reduce to ordinary Kronecker delta functions if periodic boundary conditions are imposed. Closely related to these difficulties is the fact that Bloch functions, which are associated with infinitely extended crystals, cannot be normalized to unity, since their ℓ_2 norms do not exist for fundamental reasons.

Little group unirreps The next step in Mackey's induction procedure consists of determining the corresponding little group $\mathscr{G}(\boldsymbol{k}) \subseteq \mathscr{G}$ for each $\mathscr{T}$ irrep label $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^{\star})$. Once this is done, the corresponding

$\mathcal{G}(\mathbf{k})$ unirreps are computed. To summarize,

$$\mathcal{G}(\mathbf{k}) = \{G \in \mathcal{G} \mid D^{\mathbf{k}}(G^{-1}(E|\mathbf{t})G) = D^{\mathbf{k}}(E|\mathbf{t})\} \qquad [27]$$

$$\mathcal{P}(\mathbf{k}) \sim \mathcal{G}(\mathbf{k})/\mathcal{T} \subseteq \mathcal{P} \qquad [28]$$

$$\mathcal{P}(\mathbf{k}) = \{R \in \mathcal{P} \mid R\,\mathbf{k} = \mathbf{k} + \mathbf{K}(\mathbf{k}, R)\} \qquad [29]$$

where, in particular, it is assumed that $\mathbf{K}(\mathbf{k}, R) \in \mathcal{T}^{\star}$ for all point group elements $R \in \mathcal{P}$. The homomorphic images $\mathcal{P}(\mathbf{k})$ of the little groups $\mathcal{G}(\mathbf{k})$ are usually called "little co-groups." It is to be noted that

$$\mathbf{K}(\mathbf{k}, RS) = \mathbf{K}(\mathbf{k}, R) + R\mathbf{K}(\mathbf{k}, S) \qquad [30]$$

must be valid for all point group elements $R, S \in \mathcal{P}(\mathbf{k})$ as, otherwise, the closure condition for the little co-group $\mathcal{P}(\mathbf{k})$ would be violated. The closure condition [30] plays an important role when symmetrizing plane waves or any other type of wave functions. It is seen in this context that the reciprocal lattice vectors $\mathbf{K}(\mathbf{k}, R) \in \mathcal{T}^{\star}$ may only occur if and only if, the associated $\mathbf{k} \in \mathcal{B}(\mathcal{T}^{\star})$ belongs to the surface of the Brillouin zone $\mathcal{B}(\mathcal{T}^{\star})$ as otherwise they are zero.

Apart from this, corresponding $\mathcal{G}(\mathbf{k})$ unirreps are usually obtained by computing suitable $\mathcal{P}(\mathbf{k})$ unirreps. Provided the underlying space group G is symmorphic, suitable $\mathcal{P}(\mathbf{k})$ unirreps have to be ordinary vector unirreps. However, if the underlying space group $\mathcal{G}$ is nonsymmorphic, suitable $\mathcal{P}(\mathbf{k})$ unirreps are the so-called projective $\mathcal{P}(\mathbf{k})$ unnirreps. Nevertheless, the use of projective representations is merely an auxiliary tool which simplifies the construction of $\mathcal{P}(\mathbf{k})$ unirreps significantly. Accordingly, suitable $\mathcal{P}(\mathbf{k})$ unirreps are constrained by the following condition:

$$D^{\xi}(R)D^{\xi}(R) = \mathcal{F}^{\mathbf{k}}(R, S)D^{\xi}(RS) \qquad [31]$$

$$\mathcal{F}^{\mathbf{k}}(R, S) = \exp(-i\mathbf{k} \cdot \mathbf{t}_{R,S}) \qquad [32]$$

for all point group elements $R, S \in \mathcal{P}(\mathbf{k})$ and where the special translations $\mathbf{t}_{R,S} \in \mathcal{T}$ are defined by [14]. As previously noted, these vectors vanish, if the space group $\mathcal{G}$ is symmorphic, and hence the corresponding $\mathcal{P}(\mathbf{k})$ unirreps are ordinary vector representations. However, if the space group $\mathcal{G}$ is nonsymmorphic, the corresponding $\mathcal{P}(\mathbf{k})$ unirreps may be projective representations, since some $\mathbf{t}_{R,S} \in \mathcal{T}$ may be nonzero. By definition, the constructions

$$D^{\xi,\mathbf{k}}(R|\boldsymbol{w}_R + \mathbf{t}) = \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{t}}D^{\xi}(R) \qquad [33]$$

$$\dim D^{\xi,\mathbf{k}}(\mathcal{G}(\mathbf{k})) = n(\xi) \qquad [34]$$

$$\begin{aligned} &D^{\xi,\mathbf{k}}(R|\boldsymbol{w}_R + \mathbf{t})D^{\xi,\mathbf{k}}(S|\boldsymbol{w}_S + \mathbf{v}) \\ &\quad = D^{\xi,\mathbf{k}}(RS|\boldsymbol{w}_{RS} + \mathbf{t}_{R,S} + \mathbf{t} + R\mathbf{v}) \end{aligned} \qquad [35]$$

define ordinary vector $\mathcal{G}(\mathbf{k})$ unirreps, provided that suitable $\mathcal{P}(\mathbf{k})$ unirreps are constructed. Note in particular that $\xi \in \mathcal{A}(\mathcal{P}(\mathbf{k}))$ define the complete sets of all $\mathcal{P}(\mathbf{k})$ irrep labels. In summary, the set of ordered pairs

$$\mathcal{A}(\mathcal{G}(\mathbf{k})) = \{(\mathbf{k}, \xi) | \xi \in \mathcal{A}(\mathcal{P}(\mathbf{k}))\} \qquad [36]$$

define complete sets of $\mathcal{G}(\mathbf{k})$ unirreps for each $\mathbf{k} \in \mathcal{B}(\mathcal{T}^{\star})$.

Full space group unirreps The final step is, among others, to restrict the Brillouin zone $\mathcal{B}(\mathcal{T}^{\star})$ to a suitable subset, sometimes called "representation domain," $\Delta\mathcal{B}(\mathcal{T}^{\star}, \mathcal{P})$, in order to avoid double counting of equivalent $\mathcal{G}$ unirreps. This is done by taking only one representative (arm) from each $\mathbf{k}$-vector star $S(\mathbf{k})$ defined by

$$S(\mathbf{k}) = \{\mathbf{k}_R \in \mathcal{B}(\mathcal{T}^{\star}, \mathcal{P}) \mid \mathbf{k}_R = R\mathbf{k};\ R \in \mathcal{P}\} \qquad [37]$$

$$|S(\mathbf{k})| = |\mathcal{P} : \mathcal{P}(\mathbf{k})| \qquad [38]$$

It is worth noting that the order $|S(\mathbf{k})|$ of any star is a divisor of the order $|\mathcal{P}|$ of the corresponding crystallographic point group $\mathcal{P}$. The union set of all these representative $\mathbf{k}$ vectors defines the representation domain $\Delta\mathcal{B}(\mathcal{T}^{\star}, \mathcal{P})$. As commonly accepted in physics, one takes a simply connected continuous subset $\Delta\mathcal{B}(\mathcal{T}^{\star}, \mathcal{P})$ of the original Brillouin zone $\mathcal{B}(\mathcal{T}^{\star})$ in order to avoid unnecessary difficulties when dealing, for instance, with the so-called "compatibility relations," whichever have been discussed for the first time by L P Bouckaert *et al.*, in 1936.

The actual final step in Mackey's induction procedure consists in inducing the full $\mathcal{G}$ representations from the $\mathcal{G}(\mathbf{k})$ unirreps given by [33]. A general theorem guarantees that the corresponding induced $\mathcal{G}$ representations are automatically irreducible. The induction formulas read

$$D^{(\mathbf{k},\xi)\uparrow\mathcal{G}}_{\underline{R},\underline{S}}(G) = \delta_{\underline{R}\mathcal{P}(\mathbf{k}),R\underline{S}\mathcal{P}(\mathbf{k})}D^{\mathbf{k},\xi}(\underline{A}^{-1}G\underline{B}) \qquad [39]$$

$$G = (R \mid \boldsymbol{w}_R + \mathbf{t}) \qquad [40]$$

$$\underline{A} = (\underline{R}|\boldsymbol{w}_{\underline{R}}) \qquad [41]$$

$$\underline{B} = (\underline{S}|\boldsymbol{w}_{\underline{S}}) \qquad [42]$$

$$\delta_{\underline{R}\mathcal{P}(\mathbf{k}),R\underline{S}\mathcal{P}(\mathbf{k})} = \begin{cases} 1, & \underline{R}^{-1}R\underline{S} \in \mathcal{P}(\mathbf{k}) \\ 0, & \text{otherwise} \end{cases} \qquad [43]$$

$$\dim D^{(\mathbf{k},\xi)\uparrow\mathcal{G}}(\mathcal{G}) = |\mathcal{P} : \mathcal{P}(\mathbf{k})| \cdot n(\xi) \qquad [44]$$

where the specific space group elements $\underline{A} = (\underline{R}|\boldsymbol{w}_{\underline{R}})$ and $\underline{B} = (\underline{S}|\boldsymbol{w}_{\underline{S}})$ are coset representatives of the space group $\mathcal{G}$ with respect to the corresponding little group $\mathcal{G}(\boldsymbol{k})$. Specifying the conjugation $\underline{A}^{-1}G\underline{B} \in \mathcal{G}$ by taking into account [33] and [43], one immediately arrives at the following final formulas for $\mathcal{G}$ unirreps:

$$D^{(\boldsymbol{k},\xi)\uparrow\mathcal{G}}_{\underline{R}a,\underline{S}b}((R|\boldsymbol{w}_R + \boldsymbol{t})) = \delta_{\underline{R}\mathcal{P}(\boldsymbol{k}),R\underline{S}\mathcal{P}(\boldsymbol{k})} \mathrm{e}^{-\mathrm{i}\underline{R}\boldsymbol{k}\cdot\boldsymbol{t}} \Phi^{\boldsymbol{k}}_{\underline{R},\underline{S}}(R) D^{\xi}_{ab}(\underline{R}^{-1}R\underline{S}) \quad [45]$$

$$\Phi^{\boldsymbol{k}}_{\underline{R},\underline{S}}(R) = \exp\left(-\mathrm{i}\boldsymbol{k}\cdot \boldsymbol{t}_{\underline{R},\underline{S}}(R)\right) \quad [46]$$

$$\boldsymbol{t}_{\underline{R},\underline{S}}(R) = \boldsymbol{t}_{\underline{R}^{-1},R} + \boldsymbol{t}_{\underline{R}^{-1}R,\underline{S}} - \underline{R}^{-1}\boldsymbol{t}_{\underline{R},\underline{R}^{-1}} \in \mathcal{T} \quad [47]$$

Clearly, if $\mathcal{G}$ defines a symmorphic space group, then the corresponding phase factors $\Phi^{\boldsymbol{k}}_{\underline{R},\underline{S}}(R)$ defined by [45] reduce to 1, since the special translation vectors $\boldsymbol{t}_{R,S}$ are zero-vectors. However, if $\mathcal{G}$ defines a nonsymmorphic space group, then some of the phase factors defined by [45] are nontrivial and lead to quite different expressions for its corresponding $\mathcal{G}$ unirreps.

Operator Representations of Space Groups

Usually, space group symmetry and space group representations are applied in the one-particle approximation to Hamiltonians that describe the motion of an electron in periodic structures quantum mechanically. The first step consists of defining a homomorphism $\varepsilon : \mathcal{G} \to U(\mathcal{G})$ of the given space group $\mathcal{G}$ into a group of unitary operators $U(\mathcal{G})$ that map the underlying Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$ onto itself (here the spin degree of freedom has been neglected):

$$U(\mathcal{G}) = \{U(G) | G \in \mathcal{G}\} \quad [48]$$

$$[U(G)\Phi](x) = \phi(\mathcal{M}(G^{-1})x) \quad [49]$$

$$U(G)U(G') = U(GG') \quad [50]$$

In this context, it is worth noting that every mapping $\mathcal{M}(G) : \mathbb{R}^3 \to \mathbb{R}^3$ is nonsingular but likewise nonlinear, if and only if the translational part $\boldsymbol{t} \in \mathcal{T}$ contained in $G = (R|\boldsymbol{w}_R + \boldsymbol{t})$ is nonzero, whereas the uniquely associated unitary operator representation is linear with respect to the Hilbert space $L^2(\mathbb{R}^3)$ in any case. The one-particle Hamiltonian reads

$$H = \frac{1}{2m}P^2 + V(X) \quad [51]$$

where the potential is responsible for the symmetry of the problem. Apart from this, space groups and their representation theory are likewise utilized in order to simplify systematically the diagonalization of the force matrix in the "harmonic approximation" when dealing with lattice vibrations in classical point mechanics.

Bloch Theorem – Energy Bands

The eigenvalue problem of periodic one-particle Hamiltonians, where the spin degree of freedom is neglected, presents one of the most popular examples where group-theoretical methods are applied. Taking into account that every space group $\mathcal{G}$, whether $\mathcal{G}$ is symmorphic or nonsymmorphic, contains a countable translational group $\mathcal{T}$ as a normal subgroup, one may use, as a first step, the translational symmetry of the Hamiltonian represented by the vanishing commutators

$$[H, U(E|\boldsymbol{t})] = 0 \quad \forall \boldsymbol{t} \in \mathcal{T} \quad [52]$$

to simplify the eigenvalue problem. According to a general theorem of functional analysis, the countable set $U(\mathcal{T}) = \{U(E|\boldsymbol{t}) | \boldsymbol{t} \in \mathcal{T}\}$ of mutually commuting unitary operators and the Hamiltonian H can be diagonalized simultaneously.

Bloch theorem Bloch's theorem predicts partly the form of the common eigenfunctions of the periodic Hamiltonian. It leads to the following well-known and extensively used statement:

$$\Psi^{\boldsymbol{k}}(x) = \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot x} w(\boldsymbol{k}, x) \quad [53]$$

$$w(\boldsymbol{k}, x) = w(\boldsymbol{k}, x + \boldsymbol{t}) \quad \forall \boldsymbol{t} \in \mathcal{T} \quad [54]$$

These eigenfunctions are called "Bloch functions," of the Hamiltonian, and the unitary translational operators have the form given by [53] and [54]. The translational symmetry has been utilized for this factorization. The eigenvalue problem reads

$$H\Psi^{\boldsymbol{k}} = E(\boldsymbol{k})\Psi^{\boldsymbol{k}} \quad [55]$$

where the eigenfunctions are assumed to be Bloch functions. What remains to be done in practical applications is the determination of the periodic Bloch factors

$$w(\boldsymbol{k}) : \mathcal{P}(\mathcal{T}) \to \mathbb{C} \quad [56]$$

for every $\boldsymbol{k} \in \mathcal{B}(\mathcal{T}^{\star})$, which is a problem in its own right. Simple manipulations yield the following noncountable infinite set of decoupled partial differential equations for the unknown Bloch factors:

$$H(\boldsymbol{k}) = \frac{1}{2m}(Q + \hbar\boldsymbol{k})^2 + V(X) \quad [57]$$

$$H(\boldsymbol{k})w(\boldsymbol{k}) = E(\boldsymbol{k})w(\boldsymbol{k}) \quad [58]$$

for all $\boldsymbol{k} \in \mathcal{B}(\mathcal{T}^{\star})$ where, in particular, the operator $Q = -\mathrm{i}\hbar\nabla$ is the usual differential operator but its domain of definition is the Hilbert space $L^2(\mathcal{P}(\mathcal{T}))$

group $\mathcal{G}(\boldsymbol{k})$. Specifying the conjugation $\underline{A}^{-1}G\underline{B}\in\mathcal{G}$ by taking into account [33] and [43], one immediately arrives at the following final formulas for $\mathcal{G}$ unirreps:

$$\begin{aligned} &D^{(\boldsymbol{k},\xi)\uparrow\mathcal{G}}_{\underline{R}a,\underline{S}b}((R|\boldsymbol{w}_R+\boldsymbol{t})) \\ &\quad = \delta_{\underline{R}\mathcal{P}(\boldsymbol{k}),R\underline{S}\mathcal{P}(\boldsymbol{k})}\mathrm{e}^{-\mathrm{i}\underline{R}\boldsymbol{k}\cdot\boldsymbol{t}}\Phi^{\boldsymbol{k}}_{\underline{R},\underline{S}}(R)D^{\xi}_{ab}(\underline{R}^{-1}R\underline{S}) \end{aligned} \qquad [45]$$

$$\Phi^{\boldsymbol{k}}_{\underline{R},\underline{S}}(R)=\exp\big(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{t}_{\underline{R},\underline{S}}(R)\big) \qquad [46]$$

$$\boldsymbol{t}_{\underline{R},\underline{S}}(R)=\boldsymbol{t}_{\underline{R}^{-1},R}+\boldsymbol{t}_{\underline{R}^{-1}R,\underline{S}}-\underline{R}^{-1}\boldsymbol{t}_{\underline{R},\underline{R}^{-1}}\in\mathcal{T} \qquad [47]$$

Clearly, if $\mathcal{G}$ defines a symmorphic space group, then the corresponding phase factors $\Phi^{\boldsymbol{k}}_{\underline{R},\underline{S}}(R)$ defined by [45] reduce to 1, since the special translation vectors $\boldsymbol{t}_{R,S}$ are zero-vectors. However, if $\mathcal{G}$ defines a nonsymmorphic space group, then some of the phase factors defined by [45] are nontrivial and lead to quite different expressions for its corresponding $\mathcal{G}$ unirreps.

Operator Representations of Space Groups

Usually, space group symmetry and space group representations are applied in the one-particle approximation to Hamiltonians that describe the motion of an electron in periodic structures quantum mechanically. The first step consists of defining a homomorphism $\varepsilon:\mathcal{G}\to U(\mathcal{G})$ of the given space group $\mathcal{G}$ into a group of unitary operators $U(\mathcal{G})$ that map the underlying Hilbert space $\mathcal{H}=L^2(\mathbb{R}^3)$ onto itself (here the spin degree of freedom has been neglected):

$$U(\mathcal{G})=\{U(G)|G\in\mathcal{G}\} \qquad [48]$$

$$[U(G)\Phi](x)=\phi(\mathcal{M}(G^{-1})x) \qquad [49]$$

$$U(G)U(G')=U(GG') \qquad [50]$$

In this context, it is worth noting that every mapping $\mathcal{M}(G):\mathbb{R}^3\to\mathbb{R}^3$ is nonsingular but likewise nonlinear, if and only if the translational part $\boldsymbol{t}\in\mathcal{T}$ contained in $G=(R|\boldsymbol{w}_R+\boldsymbol{t})$ is nonzero, whereas the uniquely associated unitary operator representation is linear with respect to the Hilbert space $L^2(\mathbb{R}^3)$ in any case. The one-particle Hamiltonian reads

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together with periodic boundary conditions which give rise to a pure point spectrum of the operator Q in contrast to $P = -i\hbar\nabla$ that possesses a continuous spectrum with respect to $L^2(\mathbb{R}^3)$. To recapitulate, if one does not introduce periodic boundary conditions for the original eigenvalue problem, admissible vectors $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^\star)$ vary continuously over the Brillouin zone, whereas the spectrum of the momentum operator Q is discrete and coincides with the corresponding reciprocal lattice $K \in \mathscr{T}^\star$. Assuming that [58] has been solved for all $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^\star)$, then [55] reads

$$H\Psi_s^{\boldsymbol{k},n} = E_n(\boldsymbol{k})\Psi_s^{\boldsymbol{k},n} \qquad [59]$$

where $n \in \mathbb{N}$ is usually called the "band index," where $s = 1, 2, \ldots, \deg E_n(\boldsymbol{k})$ describes possible degeneracies of the eigenvalues $E_n(\boldsymbol{k})$. The band index n is a countable index, since the Hamiltonians $H(\boldsymbol{k})$ given by [57] possess pure point spectra for fixed $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^\star)$.

Energy bands To define energy bands in terms of functions of the following type $E_n : \mathscr{B}(\mathscr{T}^\star) \to \mathbb{R}$, one has, in principle, two different possibilities. Either one defines these functions by assuming the strict ordering

$$1. \quad E_1(\boldsymbol{k}) < E_2(\boldsymbol{k}) < \cdots < E_n(\boldsymbol{k}) < E_{n+1}(\boldsymbol{k}) < \cdots \qquad [60]$$

$$2. \quad E_n(\boldsymbol{k}) = \text{analytic functions} \qquad [61]$$

or one demands that these functions be analytic functions. The second possibility is usually preferred, since it leads to smooth functions with respect to the variable $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^\star)$, whereas the first possibility may lead to cusps with band contacts and hence accidental degeneracies. Obviously, the second possibility may likewise lead to band crossings, which indicate the same type of accidental degeneracies.

Wannier functions Assume that the eigenfunctions $\{\Psi_s^{\boldsymbol{k},n}\}$ are orthonormal with respect to the scalar product of the underlying Hilbert space $\mathscr{H}$:

$$\langle \Psi_s^{\boldsymbol{k},n}, \Psi_{s'}^{\boldsymbol{k}',n'} \rangle_{\mathscr{H}} = \delta(\boldsymbol{k} - \boldsymbol{k}')\delta_{nn'}\delta_{ss'} \qquad [62]$$

where the entries $\delta(\boldsymbol{k} - \boldsymbol{k}')$ define the delta functions. This implies that for the infinite system, that is, system without periodic boundary conditions, Bloch functions cannot be normalized to unity. This is one of the main reasons for the introduction of periodic boundary conditions, since then the delta-functions reduce to ordinary Kronecker deltas, which means that the corresponding Bloch functions become square-integrable functions. In the case of infinite systems, Wannier functions are defined as

$$\Omega_s^{n,\boldsymbol{t}} = \frac{1}{\sqrt{|\mathscr{B}(\mathscr{T}^\star)|}} \int_{\mathscr{B}(\mathscr{T}^\star)} \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{t}} \Psi_s^{\boldsymbol{k},n} \qquad [63]$$

$$\langle \Omega_s^{n,\boldsymbol{t}}, \Omega_{s'}^{n',\boldsymbol{t}'} \rangle_{\mathscr{H}} = \delta_{\boldsymbol{t},\boldsymbol{t}'}\delta_{nn'}\delta_{ss'} \qquad [64]$$

which are square integrable and orthonormal with respect to all labels $\boldsymbol{t}$, n, s respectively. These functions are localized around the positions $\boldsymbol{t} \in \mathscr{T}$ but have infinitely many oscillations to achieve their mutual orthogonality. Whether the Bloch functions $\Psi_s^{\boldsymbol{k},n}$ are directly taken to construct [63] or specific linear combinations (U matrix approach) of $\{\Psi_s^{\boldsymbol{k},n} \mid s = 1, 2, \ldots, \deg E_n(\boldsymbol{k})\}$ are considered, turns out to be problem of its own right and is sensitively influenced by the physical problem.

Energy bands – full space group symmetry More information is gained regarding the degeneracy of the eigenvalues $E_n(\boldsymbol{k})$ and their corresponding eigenfunctions $\{\Psi_s^{\boldsymbol{k},n}\}$, if the full space group symmetry is exploited. The correspondingly refined eigenvalue equation reads

$$H\Psi_{\underline{R}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n} = E_n^\xi(\boldsymbol{k})\Psi_{\underline{R}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n} \qquad [65]$$

$$E_n^\xi(\boldsymbol{k}) = E_n^\xi(\underline{R}\boldsymbol{k}) \quad \forall \underline{R} \in \mathscr{P} : \mathscr{P}(\boldsymbol{k}) \qquad [66]$$

$$\deg E_n^\xi(\boldsymbol{k}) = |\mathscr{P} : \mathscr{P}(\boldsymbol{k})| \cdot n(\xi) \qquad [67]$$

where the eigenfunctions $\Psi_{\underline{R}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}$ are written as $\mathscr{G}$-symmetry-adapted functions, the eigenvalues $E_n^\xi(\boldsymbol{k})$ are labeled by the band index n and the $\mathscr{G}$ irrep labels. Apart from this, the formula [67] for the degeneracies of the eigenvalues is valid, if and only if there is no accidental degeneracy caused by band crossings. The symmetry properties (see eqn [66]) of the eigenvalues explain why energy band calculations are restricted to subsets of $\boldsymbol{k}$ vectors, namely $\boldsymbol{k} \in \Delta\mathscr{B}(\mathscr{T}^\star, \mathscr{P})$, where the symbol $\Delta\mathscr{B}(\mathscr{T}^\star, \mathscr{P})$ denotes the so-called representation domain of the Brillouin zone $\mathscr{B}(\mathscr{T}^\star)$. Note that $\Delta\mathscr{B}(\mathscr{T}^\star, \mathscr{P})$ presents, loosely speaking, the $|\mathscr{P}|$th part (simply connected subwedge) of the Brillouin zone. The restriction to $\Delta\mathscr{B}(\mathscr{T}^\star, \mathscr{P})$ guarantees the uniqueness and completeness of the corresponding $\mathscr{G}$-irrep label set $\mathscr{A}(\mathscr{G})$:

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Compatibility relations It was in the famous article of L P Bouckaert *et al.* in 1936 where for the first time continuity properties of $\mathscr{G}$-symmetry-adapted eigenfunctions were discussed. The basic idea was together with periodic boundary conditions which give rise to a pure point spectrum of the operator Q in contrast to $P = -i\hbar\nabla$ that possesses a continuous spectrum with respect to $L^2(\mathbb{R}^3)$. To recapitulate, if one does not introduce periodic boundary conditions for the original eigenvalue problem, admissible vectors $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^\star)$ vary continuously over the Brillouin zone, whereas the spectrum of the momentum operator Q is discrete and coincides with the corresponding reciprocal lattice $K \in \mathscr{T}^\star$. Assuming that [58] has been solved for all $\boldsymbol{k} \in \mathscr{B}(\mathscr{T}^\star)$, then [55] reads

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Compatibility relations It was in the famous article of L P Bouckaert *et al.* in 1936 where for the first time continuity properties of $\mathscr{G}$-symmetry-adapted eigenfunctions were discussed. The basic idea was to change smoothly the continuous parameters $\boldsymbol{k}\in\Delta\mathscr{B}(\mathscr{T}^\star,\mathscr{P})$ in the vicinity of some $\boldsymbol{k}$-vectors and study the transformation properties of the corresponding $\mathscr{G}$-symmetry-adapted eigenfunctions $\Psi_{\underline{R}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}$ at different $\boldsymbol{k}$-positions, say $\boldsymbol{k}$ and $\boldsymbol{k}'=\boldsymbol{k}+\varepsilon$. In addition, the authors studied whether the assigned eigenvalues, say $E_n^\xi(\boldsymbol{k})$ and $E_n^\xi(\boldsymbol{k}+\varepsilon)$ may or may not split, depending on the relationship of the associated little co-groups $\mathscr{P}(\boldsymbol{k})$ and $\mathscr{P}(\boldsymbol{k}+\varepsilon)$. The important result culminated in the so-called compatibility relations which allow one to make some predictions on the splitting of energy bands. To summarize, if and only if $\mathscr{P}(\boldsymbol{k})=\mathscr{P}(\boldsymbol{k}+\varepsilon)$, then, because of $D^{\boldsymbol{k},\xi}(\mathscr{P}(\boldsymbol{k}))\downarrow\mathscr{P}(\boldsymbol{k}+\varepsilon)=D^{\boldsymbol{k},\xi}(\mathscr{P}(\boldsymbol{k}))$ it follows that $E_n^\xi(\boldsymbol{k}+\varepsilon)$ must not split. Conversely, if and only if, $\mathscr{P}(\boldsymbol{k})\subset\mathscr{P}(\boldsymbol{k}+\varepsilon)$, and if, in addition, $D^{\boldsymbol{k},\xi}(\mathscr{P}(\boldsymbol{k}))\downarrow\mathscr{P}(\boldsymbol{k}+\varepsilon)$ becomes reducible, then the corresponding eigenvalue $E_n^\xi(\boldsymbol{k}+\varepsilon)$ may split, unless accidental degeneracies occur. The compatibility relations are an indispensable tool when calculating energy bands or phonon dispersion relations, since in many situations the numerical accuracy may be insufficient to decide whether eigenvalues degenerate or not.

Space Group Symmetrized States

As already noted, the $\mathscr{G}$-symmetrized eigenfunctions $\{\Psi_{\underline{R}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}\}$, which are normalized to unity, are mutual orthogonal and, by definition, transform according to the $\mathscr{G}$ unirreps. One simply proves that the eigenfunctions

$$\Psi_{\underline{R}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}(\boldsymbol{x})=\mathrm{e}^{\mathrm{i}\underline{R}\boldsymbol{k}\cdot\boldsymbol{x}}w_a^{\xi,n}(\underline{R}\boldsymbol{k},\boldsymbol{x}) \qquad [69]$$

retain their structure to form Bloch functions, where the lattice periodic Bloch factors carry the transformation properties with respect to the correspondingly conjugated little co-groups $\mathscr{P}(\underline{R}\boldsymbol{k})=\underline{R}\mathscr{P}(\boldsymbol{k})\underline{R}^{-1}$. Turning back to the penultimate step of the induction procedure, one has the forms

$$\Psi_{\underline{E}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}(\boldsymbol{x})=\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}w_a^{\xi,n}(\boldsymbol{k},\boldsymbol{x}) \qquad [70]$$

$$U(R\mid\boldsymbol{w}_R)\Psi_{\underline{E}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}=\sum_{b=1}^{n(\xi)}D_{ba}^{\boldsymbol{k},\xi}(R)\Psi_{\underline{E}b}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n} \qquad [71]$$

which represents the special case $\underline{R}=E$ where, especially, $G=(R|\boldsymbol{w}_R)\in\mathscr{G}(\boldsymbol{k})$ with $R\in\mathscr{P}(\boldsymbol{k})$ and $\boldsymbol{t}=0$. This yields the subset of the eigenfunctions that must transform according to the corresponding $\mathscr{G}(\boldsymbol{k})$ unirreps. Accordingly, one can define

$$\begin{aligned}&[U(R\mid\boldsymbol{w}_R)\Psi_{\underline{E}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}](\boldsymbol{x})\\&\quad=[\Psi_{\underline{E}a}^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}](\mathscr{M}(R\mid\boldsymbol{w}_R)^{-1}\boldsymbol{x}) &&[72]\\&\quad=\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}[V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)w_a^{\xi,n}(\boldsymbol{k})](\boldsymbol{x}) &&[73]\end{aligned}$$

where $R\in\mathscr{P}(\boldsymbol{k})$ is assumed. It is worth noting that definition [72] is used to assign uniquely via definition [73] to each unitary operator $U(R|\boldsymbol{w}_R)$ for every $\boldsymbol{k}$-vector belonging to $\Delta\mathscr{B}(\mathscr{T}^\star,\mathscr{P})$ an isometrical operator $V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)$ where, especially, the constraints $R\in\mathscr{P}(\boldsymbol{k})$ must not be forgotten. To summarize,

$$\begin{aligned}&[V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)w_a^{\xi,n}(\boldsymbol{k})](\boldsymbol{x})\\&\quad=\mathrm{e}^{-\mathrm{i}R\boldsymbol{k}\cdot\boldsymbol{w}_R}\mathrm{e}^{\mathrm{i}\boldsymbol{K}(\boldsymbol{k},R)\cdot\boldsymbol{x}}w_a^{\xi,n}(\boldsymbol{k},R^{-1}(\boldsymbol{x}-\boldsymbol{w}_R)) &&[74]\end{aligned}$$

where every set of operators $V^{\boldsymbol{k}}(\mathscr{P}(\boldsymbol{k}))=\{V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)|R\in\mathscr{P}(\boldsymbol{k})\}$ forms a generalized unitary operator representation with respect to the Hilbert space $L^2(\mathscr{P}(\mathscr{T}))$, since these operators leave the $L^2(\mathscr{P}(\mathscr{T}))$ scalar product invariant. Rather straightforward manipulations yield

$$V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)V^{\boldsymbol{k}}(S|\boldsymbol{w}_S)=\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{t}_{R,S}}V^{\boldsymbol{k}}(RS|\boldsymbol{w}_{RS}) \qquad [75]$$

for all point group elements $R,S\in\mathscr{P}(\boldsymbol{k})$. In fact, the operator representation $V^{\boldsymbol{k}}(\mathscr{P}(\boldsymbol{k}))$ defines the so-called "projective multiplier" representations, since the occurrence of the factor system [32] on the RHS of [75] shows, among others, that they must be projective ones. The notion multiplier representation comes from the extra factor $\mathrm{e}^{-\mathrm{i}\boldsymbol{K}(\boldsymbol{k},R)\cdot\boldsymbol{x}}$ on the RHS of [74], where the special reciprocal vectors $\boldsymbol{K}(\boldsymbol{k},R)\in\mathscr{T}^\star$ may occur, if and only if the vectors $\boldsymbol{k}\in\Delta\mathscr{B}(\mathscr{T}^\star,\mathscr{P})$ belong to the surface of the corresponding Brillouin zone $\mathscr{B}(\mathscr{T}^\star)$. Accordingly,

$$V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)w_a^{\xi,n}(\boldsymbol{k})=\sum_{b=1}^{n(\xi)}D_{ba}^{\boldsymbol{k},\xi}(R)w_b^{\xi,n}(\boldsymbol{k}) \qquad [76]$$

which represents the transformation properties of the lattice-periodic $\mathscr{P}(\boldsymbol{k})$-symmetrized Bloch factors. It is to be noted that even in the case of symmorphic space groups the extra factors $\mathrm{e}^{-\mathrm{i}\boldsymbol{K}(\boldsymbol{k},R)\cdot\boldsymbol{x}}$ on the RHS of [74] occur and hence crucially enter into the discussions when constructing $\mathscr{G}(\boldsymbol{k})$-symmetrized functions as the penultimate step in the induction procedure. Point symmetrized states have been extensively discussed by S L Altmann and P Herzig in 1994.

Symmetrized plane waves A brief comment on the construction of symmetrized plane waves is made here. By virtue of the previous discussions, it is immediately clear that the construction of all $\mathscr{P}(\boldsymbol{k})$-symmetrized bases of the image Hilbert space $L^2(\mathscr{P}(\mathscr{T}))$ is sufficient to obtain symmetrized plane waves, since the last step in the induction procedure consists in inducing from $\mathscr{G}(\boldsymbol{k})$-symmetrized bases, the $\mathscr{G}$-symmetrized bases. As noted before, an orthonormalized basis of the Hilbert space $L^2(\mathscr{P}(\mathscr{T}))$ is defined by the plane wave basis $\{\Phi^K \mid K \in \mathscr{T}^\star\}$:

$$\Phi^K(\boldsymbol{x}) = \frac{1}{\sqrt{|\mathscr{P}(\mathscr{T})|}} \mathrm{e}^{-\mathrm{i}K\cdot \boldsymbol{x}} \qquad [77]$$

$$\langle \Phi^K, \Phi^{K'} \rangle_{L^2(\mathscr{P}(\mathscr{T}))} = \delta_{K,K'} \qquad [78]$$

Now, let Φ^K be a fixed plane wave. To achieve $\mathscr{P}(\boldsymbol{k})$-symmetrization, one must apply for the chosen $\boldsymbol{k} \in \Delta\mathscr{B}(\mathscr{T}^\star, \mathscr{P})$, the corresponding set of unitary operators $V^{\boldsymbol{k}}(\mathscr{P}(\boldsymbol{k}))$ to the fixed plane wave Φ^K which induces a $\mathscr{P}(\boldsymbol{k})$ matrix representation, which in general should be decomposed into a direct sum of its irreducible constituents. The definition [74] yields

$$\begin{aligned}&[V^{\boldsymbol{k}}(R|\boldsymbol{w}_R)\Phi^K](\boldsymbol{x})\\ &\quad = \mathrm{e}^{-\mathrm{i}R\boldsymbol{k}\cdot\boldsymbol{w}_R}\mathrm{e}^{-\mathrm{i}K(\boldsymbol{k},R)\cdot\boldsymbol{x}}\Phi^K(R^{-1}(\boldsymbol{x}-\boldsymbol{w}_R))\\ &\quad = \mathrm{e}^{-\mathrm{i}R(\boldsymbol{k}+K)}\Phi^{RK+K(\boldsymbol{k},R)}(\boldsymbol{x})\end{aligned} \qquad [79]$$

which illustrates among others, the importance of the specific reciprocal lattice vectors $K(\boldsymbol{k}, R) \in \mathscr{T}^\star$, where the latter inevitably occur if the corresponding $\boldsymbol{k}$-vector $\boldsymbol{k} \in \Delta\mathscr{B}(\mathscr{T}^\star, \mathscr{P})$ belongs to the surface of the Brillouin zone $\mathscr{B}(\mathscr{T}^\star)$. To summarize, even in the case of symmorphic space groups, nontrivial multiplier representations may be realized. Once the $\mathscr{P}(\boldsymbol{k})$ matrix representations are decomposed into their irreducible constituents, the last step of the induction procedure consists in passing over from the corresponding $\mathscr{G}(\boldsymbol{k})$ unirreps to $\mathscr{G}$ unirreps in order to construct the correspondingly symmetrized plane waves.

Selection rules for space groups Let $\mathscr{G}$ be a space group and $\{\Psi^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}_{\underline{R}a}\}$ be some $\mathscr{G}$-symmetrized eigenfunctions of the Hamiltonian H in question. Moreover, let $T^{(\boldsymbol{k}_o,\lambda_o)\uparrow\mathscr{G}} = \{T^{(\boldsymbol{k}_o,\lambda_o)\uparrow\mathscr{G}}_{\underline{S}s} \mid \underline{S} \in \mathscr{P} : \mathscr{P}(\boldsymbol{k});\ s = 1, 2, \ldots, n(\lambda_o)\}$, an irreducible $\mathscr{G}$-tensor operator of rank $(\boldsymbol{k}_o, \lambda_o)\uparrow\mathscr{G}$. According to the Wigner–Eckart theorem, one expects

$$\begin{aligned}&\langle \Psi^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}_{\underline{R}a}, T^{(\boldsymbol{k}_o,\lambda_o)\uparrow\mathscr{G}}_{\underline{S}s}\Psi^{(\boldsymbol{k}',\xi')\uparrow\mathscr{G},n'}_{\underline{R}'a'} \rangle\\ &\quad = \sum_{w=1}^{m((\boldsymbol{k}_o,\lambda_o),(\boldsymbol{k}',\xi')|(\boldsymbol{k},\xi))} \left(\begin{array}{cc|c} (\boldsymbol{k}_o, \lambda_o) & (\boldsymbol{k}', \xi') & (\boldsymbol{k}, \xi)w \\ \underline{S}s & \underline{R}'a' & \underline{R}a \end{array} \right)^*\\ &\quad \times \langle \Psi^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n} \| T^{(\boldsymbol{k}_o,\lambda_o)\uparrow\mathscr{G}} \| \Psi^{(\boldsymbol{k}',\xi')\uparrow\mathscr{G},n'} \rangle_w\end{aligned} \qquad [80]$$

where the absolute square of the matrix elements describes, apart from a time dependent factor, "Fermi's golden rule," namely the transition probability from the initial state $\Psi^{(\boldsymbol{k}',\xi')\uparrow\mathscr{G},n'}_{\underline{R}'a'}$ to the final state $\Psi^{(\boldsymbol{k},\xi)\uparrow\mathscr{G},n}_{\underline{R}a}$, provided that the interaction operator is described by the irreducible $\mathscr{G}$ tensor operator component $T^{(\boldsymbol{k}_o,\lambda_o)\uparrow\mathscr{G}}_{\underline{S}s}$. The appearance of nontrivial multiplicities

$$m((\boldsymbol{k}_o, \lambda_o), (\boldsymbol{k}', \xi')|(\boldsymbol{k}, \xi)) > 1$$

causes additional difficulties, since not only the determination of suitable Clebsch–Gordan coefficients becomes more complicated, but also the dependence of the reduced matrix elements causes additional problems. These problems might be the main reason why the application of the Wigner–Eckart theorem in solid-state physics has not been popular. Basic material concerning space group unirreps and Clebsch–Gordan coefficients for space groups were cited by A P Cracknell *et al.*, in 1979 and 1980. Important applications, such as infrared absorptions or Raman spectroscopy, of this topic are discussed by J L Birman and J F Cornwell in 1974 and 1984, respectively.

What Group Theory Provides

Finally, the usefulness of group-theoretical methods, especially in solid state physics, when applied to simplify certain tasks, is summarized. Here, exclusive comments on group-theoretical tools and methods which refer to space groups, subgroups of space groups, and eventually certain homomorphic images of space groups are made. Possible applications of so-called magnetic space groups, spin groups, and other groups to describe the symmetries of more complex periodic, or even quasiperiodic structures, such as the symmetry properties of quasicrystals, are not discussed here.

- *Bravais vector lattices and sublattices*. Group theory presents an effective tool to identify vector lattices and their sublattices, which are useful for determining not only their crystal system and their crystal class, but also their correlations to standardized lattices. Standardized lattices have basis vectors of the shortest length and specific orientation.
- *Deformed and distorted lattices*. By definition, deformed lattices are obtained by continuously varying the lattice parameters, whereas distorted lattices have lattice matrix that is post-multiplied by a nonsingular matrix which describes the distortion. The proper identification of such lattices is of vital importance in practical applications, for instance, in relaxation processes.
- *Subgroups of space groups of finite index*. Group–subgroup relations of space groups of finite index are of interest in structural phase transitions that are accompanied with changes in symmetry. The knowledge of admissible chains of subgroups from the determination of all intermediate groups is vital in such discussions, since they allow one to

predict the preferred chains of admissible structures of the intermediate phases.

- *Coset and double cosets of space groups*. In phase transitions (with changing structures) which are accompanied with the loss of symmetries, it turns out that simultaneously coexisting domain states are generated whose positions and orientations in space are directly related to the coset decomposition of the parent space group with respect to the subspace group (and correspondingly conjugated subspace groups) which describes the symmetry of the domain states. Likewise, double coset decompositions are used to describe the so-called ordered domain states.
- *Sectional layer and penetration rod groups*. The systematic determination of the symmetries of crystallographic planes, which are subsumed under the notion of sectional layer groups, as subgroups of three-dimensional space groups, plays an essential role in the analysis of the physical properties of two-dimensional surfaces. Likewise, the symmetries of crystallographic lines denoted as penetration rod groups are of interest when describing one-dimensional defects.
- *Point group symmetries of tensors*. Macroscopic properties, such as electrical conductivity, are usually described by tensors of certain ranks. In the presence of some symmetries, for example, point group symmetries, the invariance of such tensors with respect to point groups leads to restrictions as regards their nonzero components.
- *Space group unirreps*. The computation of space group unirreps by means of Mackey's induction procedure can be carried out systematically for every space group in question. Likewise, this approach allows one to gain more insight into the constructions of space–group-symmetrized states.
- *Space group Clebsch–Gordan coefficients*. Knowledge of sets of space group Clebsch–Gordan coefficients allows one not only to study selection rules when calculating transition probabilities, but also to construct systematically product states that transform according to the Kronecker product of the space group in question.
- *Bloch theorem*. One of the most prominent applications of group-theoretical methods in solid-state physics is presented by the Bloch theorem. This theorem allows one to predict the functional form of the common eigenfunctions of the mutually commuting translational operators which represent the Bravais vector lattice and the periodic Hamiltonian, where the latter is assumed to commute with the translational group.
- *Spectral properties of periodic Hamiltonians*. Once, the entire space group symmetry of the periodic Hamiltonian is taken into account, more information gained not only as regards the point group symmetries of the energy eigenvalues, but also systematic construction of the corresponding eigenstates.
- *Compatibility relations*. The continuity behavior of the energy eigenvalues and their associated eigenfunctions in the vicinity of some $\boldsymbol{k}$-vectors can be described by some specific subduction rules of the corresponding $\mathcal{P}(\boldsymbol{k})$ unirreps when passing over continuously to some adjacent $\boldsymbol{k}$-vectors with lower symmetry. Thus, group theory provides a necessary condition which decides whether the eigenvalues do not split or alternatively may eventually split.
- *Transformation properties of states*. An important task in applications, for instance energy band calculations, concerns determining according to which representation the lattice periodic Bloch factors transform. Every careful treatment of this problem inevitably leads to multiplier or even projective multiplier representations of the corresponding little co-groups provided that in the latter case the underlying space group is nonsymmorphic.
- *Symmetrized states*. The systematic construction of space group symmetry-adapted functions follows closely along the lines of Mackey's induction procedure for space group unirreps. For instance, symmetrized plane waves may be useful when calculating matrix elements of some interaction operators.
- *Symmetrized operation*. In order to apply the Wigner–Eckart theorem to space groups, irreducible space group tensors are required. However, in many cases the interaction operators do not represent irreducible space group tensors. Nevertheless, group theory allows one to decompose any operator into a sum of its irreducible space group tensor components. The corresponding method closely resembles the symmetry adaptation of states, apart from some minor modifications.
- *Wigner–Eckart theorem*. The application of the Wigner–Eckart theorem to problems which possess space group symmetry requires not only the, knowledge of space group symmetry adapted states and irreducible space group tensors, but also the corresponding space group Clebsch–Gordan coefficients. Due to the fact that space groups are nonsimple reducible groups, additional difficulties may arise because of the occurrence of nontrivial multiplicities.
- *Magnetic groups – co-representations*. The inclusion of the so-called "antiunitary" operators, for instance, the time reversal operator, requires, substantial extension of the concept of groups to the so-called magnetic groups, and their representations to co-representations.

Applications of Group Theory

Group theory was originally used extensively in evaluating the so-called energy band structures along special symmetry directions, that is for computing the eigenvalues corresponding to a special $\boldsymbol{k}$-vector from the three-dimensional Brillouin zone of a particular bulk system. The reasons were quite clear, namely the dimension of the secular matrix could be reduced substantially and therefore the computing times for inversion or diagonalization procedures were drastically shortened. Furthermore, respective compatibility relations guaranteed an unambiguous classification of energy bands along the rays in the Brillouin zone. The usefulness of such classifications was, in particular, evident in photoemission experiments and studies involving the Fermi surfaces.

With increasing speed of computers, in particular, with the innovation of architectures utilizing vectorizations, efforts at directly deriving the physical properties grew. This implied, for example, in most cases summations over all occupied states, that is, the use of Brillouin zone integrals by means of sophisticated sampling techniques. Thus, no longer were individual $\boldsymbol{k}$-states of interest, but so was the sum over all these states. Consequently, the incentive for using group theory, shifted from projecting particular states to theoretical means of reducing the computational efforts in evaluating Brillouin zone integrals.

Nowadays, most theoretical descriptions of problems in materials science, nanoscience, etc., are based on Kohn's density-functional theory, that is, on the use of effective (single-particle) Hamiltonians (H_{eff}, Kohn–Sham Hamiltonians). In particular, since the interest in solid-state physics shifted to systems with surfaces and interfaces, mostly group-theoretical means for two-dimensional translationally invariant systems are applied. It turned out that in two kinds of applications, namely in Brillouin zone integrations and in reduction of angular momentum coupling constants, the use of group theory is very valuable indeed. These two applications are discussed below and are meant to illustrate the contemporary use of group theory in solid-state physics.

Brillouin Zone Integrations

Taking the density of states as the simplest physical observable,

$$\begin{aligned} n(\varepsilon) &= -\frac{1}{\pi}\operatorname{Im}\mathcal{G}(\boldsymbol{r},\boldsymbol{r},\varepsilon) \\ &= -\frac{1}{\pi}|\mathcal{T}|^{-1}\sum_{\boldsymbol{k}}\operatorname{Im}\mathcal{G}(\boldsymbol{k};\varepsilon) \qquad [81] \\ &= -\frac{1}{\pi}|\mathcal{B}(\mathcal{T}^{\star})|^{-1}\int\operatorname{Im}\mathcal{G}(\boldsymbol{k};\varepsilon)\,\mathrm{d}\boldsymbol{k} \qquad [82] \end{aligned}$$

where the Green's function $\mathcal{G}(\boldsymbol{r},\boldsymbol{r},\varepsilon)$ is the diagonal configuration space representation of the resolvent of H_{eff}, $(z-H_{\text{eff}})^{-1}$ and $\mathcal{G}(\boldsymbol{k};\varepsilon)$ the corresponding lattice Fourier transformed Green's function, and $|\mathcal{T}|$ the order of the translational group. It should be noted that in eqn [81] a symmorphic space group is assumed and $|\mathcal{B}(\mathcal{T}^{\star})|$ refers to the volume of the corresponding Brillouin zone $\mathcal{B}(\mathcal{T}^{\star})$.

Suppose now that an appropriate matrix representation is used for $\mathcal{G}(\boldsymbol{r},\boldsymbol{r},\varepsilon)$ and $\mathcal{G}(\boldsymbol{k};\varepsilon)$, which, of course, depends largely on the applied quantum mechanical approach: Korringa–Kohn–Rostoker method (KKR), linear combination of muffin-tin orbitals (LMTO), or by using directly the effective Hamiltonain in the formulation of $n(\varepsilon)$ by means of a pseudopotential approach, or the linearized augmented plane wave method), then eqn [81] can be rewritten as

$$\begin{aligned} n(\varepsilon) &= -\frac{1}{\pi}|\mathcal{B}(\mathcal{T}^{\star})|^{-1}\int\operatorname{Im}\operatorname{tr}\left[\underline{\mathcal{G}}(\boldsymbol{k};\varepsilon)\,\mathrm{d}\boldsymbol{k}\right] \\ &= -\frac{1}{\pi}|\mathcal{B}(\mathcal{T}^{\star})|^{-1}\operatorname{Im}\operatorname{tr}\left[\int\underline{\mathcal{G}}(\boldsymbol{k};\varepsilon)\,\mathrm{d}\boldsymbol{k}\right] \qquad [83] \end{aligned}$$

where $\underline{\mathcal{G}}(\boldsymbol{k};\varepsilon)$ refers to the matrix representation of the Green's function and tr denotes the trace. In most of the methods mentioned above, the matrix representations are related in essence to angular momentum representations, that is they are expressed in terms of spherical harmonics.

Let $\mathcal{P}$ be the point group of the underlying (three-dimensional) lattice $\mathcal{T}$ and suppose $\underline{\mathbb{D}}(S)$ contains blockwise the irreducible representations of $S\in\mathcal{P}$. If $\Delta\mathcal{B}_E\,(\mathcal{T}^{\star},\mathcal{P})=\Delta\mathcal{B}_E$ as shorthand notation denotes an irreducible wedge of the Brillouin zone of volume $|\Delta\mathcal{B}_E(\mathcal{T}^{\star},\mathcal{P})|=|\Delta\mathcal{B}_E|$, then any other wedge $\Delta\mathcal{B}_S(\mathcal{T}^{\star},\mathcal{P})$ of the Brillouin zone is defined by

$$\Delta\mathcal{B}_S(\mathcal{T}^{\star},\mathcal{P})=\{S\boldsymbol{k}\,|\,\boldsymbol{k}\in\Delta\mathcal{B}_E|\} \qquad [84]$$

where $S\in\mathcal{P}:\mathcal{P}(\boldsymbol{k})$ is sufficient such that the union of the mutually disjoint subsets, (formally written as a sum here) can be written as follows:

$$\mathcal{B}(\mathcal{T}^{\star})=\sum_{S\in\mathcal{P}}\Delta\mathcal{B}_S(\mathcal{T}^{\star},\mathcal{P}) \qquad [85]$$

It is seen from eqn [83] that

$$\underline{\mathcal{G}}(S^{-1}\boldsymbol{k};\varepsilon)=\underline{\mathbb{D}}(S)^{\dagger}\,\underline{\mathcal{G}}(\boldsymbol{k};\varepsilon)\,\underline{\mathbb{D}}(S) \qquad [86]$$

that is for a rotated $\boldsymbol{k}$ vector, the corresponding Green's function matrix is related to the original one by means of a similarly transformation.

The Brillouin zone integral in eqn [83] can, therefore, be expressed as

$$\begin{aligned}&\frac{1}{|\mathscr{B}(\mathscr{T}^{\star})|}\int \underline{\mathscr{G}}(\boldsymbol{k};\varepsilon)\,\mathrm{d}\boldsymbol{k}\\ &\quad=\frac{1}{|\Delta\mathscr{B}_E|}\sum_{S\in\mathscr{P}}\mathbb{D}(S)^{\dagger}\left[\int_{\Delta\mathscr{B}_E}\underline{\mathscr{G}}(\boldsymbol{k};\varepsilon)\,\mathrm{d}\boldsymbol{k}\right]\mathbb{D}(S)\end{aligned} \qquad [87]$$

which, of course, results in a very large reduction of computing time, even if the order of the point group is rather small. In the case of a relativistic description, (Kohn–Sham–Dirac Hamiltonians) in the presence of an effective magnetization, the proper rotational invariance group of the corresponding Hamilton should be used. This is one of the rare cases when antiunitary operators are practically important. Of course, the same type of procedure as in eqn [87] can be applied when only two-dimensional translational symmetry is applied.

Reduction of Angular Momentum Coupling: The Point Group Symmetry of Single-Particle Densities

Let $\bar{\rho}(\boldsymbol{r})$ be the (shape-truncated) charge density in the cell $\mathscr{W}(\mathscr{T})$ (which may denote the corresponding Weigner–Seitz cell or any other type of primitive cell) centered at a particular origin $\boldsymbol{R}_0$ of given lattice or of any particular site in an arbitrary ensemble of scatterers,

$$\bar{\rho}(\boldsymbol{r})=\rho(\boldsymbol{r})\sigma(\boldsymbol{r})=\sum_{L}\bar{\rho}_L(r)Y_L^{*}(\hat{\boldsymbol{r}}) \qquad [88]$$

where $\sigma(\boldsymbol{r})$ is the so-called shape function given by

$$\sigma(\boldsymbol{r})=\left\{\begin{matrix}1, & \boldsymbol{r}\in\mathscr{W}(\mathscr{T})\\ 0, & \boldsymbol{r}\notin\mathscr{W}(\mathscr{T})\end{matrix}\right\} \qquad [89]$$

which usually is expanded into spherical harmonics as

$$\begin{aligned}\sigma(\boldsymbol{r})&=\sum_{L}\sigma_L(r)Y_L(\hat{\boldsymbol{r}})\\ &=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sigma_{lm}(r)Y_{lm}(\hat{\boldsymbol{r}})\end{aligned} \qquad [90]$$

where the expansion coefficients are determined by

$$\sigma_L(r)=\int_{\mathscr{W}(\mathscr{T})}\mathrm{d}\hat{\boldsymbol{r}}\,\sigma(\hat{\boldsymbol{r}})Y_L^{*}(\hat{\boldsymbol{r}}) \qquad [91]$$

It should be noted that the $\bar{\rho}_L(r)$ are the coefficients of the shape-truncated charge density, that is,

$$\bar{\rho}_L(r)=\sum_{L',L''}C^{L'}_{L''L}\rho_{L'}(r)\sigma_{L''}(r) \qquad [92]$$

$$C^{L'}_{L,L''}=\int \mathrm{d}\Omega\, Y_L(\Omega)Y^{*}_{L'}(\Omega)Y_{L''}(\Omega) \qquad [93]$$

Table 1 Table of nonvanishing azimuthal quantum number terms

Plane	*n*	*Two-dimensional lattice*
(1 0 0)	4	Quadratic lattice
(1 1 0)	2	Rectangular lattice
(1 1 1)	3	Hexagonal lattice

Since $\rho(\boldsymbol{r})$ is a real function, in eqn [88] one needs to evaluate only terms $\bar{\rho}_{l,-m}(r)$ for $m\geqslant 0$ and then make use of the relation

$$\bar{\rho}_{l,-m}(r)=(-1)^m\bar{\rho}_{l,m}(r)^{*} \qquad [94]$$

Furthermore, for a system with inversion symmetry with respect to $\boldsymbol{R}_0$,

$$\bar{\rho}_{lm}(r)=0,\quad \forall l=\text{odd} \qquad [95]$$

If the z-axis of the coordinate system is an n-fold rotational symmetry axis, the selection rule

$$m=\ldots,-n,0,n,\ldots \qquad [96]$$

applies, which in turn implies for example, that for simple cubic systems, there are only very few nonvanishing terms, namely those shown in **Table 1**.

Reviewing eqn [93], it is obvious that even very simple group theory can help substantially in reducing the number of terms to be evaluated. This kind of application is a very transparent example of reducing angular momentum coupling constants and is desperately needed whenever the so-called full-potential approaches are applied.

Much more advanced procedures are used whenever spectroscopic intensities are to be calculated, since then 3j-, 6j- or even higher coupling constants occur, depending, of course, on the type of excitation to be investigated.

See also: Group Theory.

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Nomenclature

$\mathcal{B}(\mathcal{T}^\star)$	Brillouin zone
$\Delta\mathcal{B}(\mathcal{T}^\star,\mathcal{P})$	irreducible subwedge of $\mathcal{B}(\mathcal{T}^\star)$
$C^{L'}_{L,L''}$	Gaunt coefficient
$\boldsymbol{D}^{\boldsymbol{k}}(\boldsymbol{E}\vert\boldsymbol{t}) = \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{t}}$	$\mathcal{T}(\mathcal{L})$-unirreps
$\boldsymbol{D}^{(\boldsymbol{k},\mathcal{E})\uparrow\mathcal{G}}(\mathcal{G})$	space group unirrep
$\boldsymbol{D}^{(\boldsymbol{k},\mathcal{E})\uparrow\mathcal{G}}(R\vert w_R + \boldsymbol{t})$	matrix element of space group element of space group unirrep
$\mathcal{G} = \{\mathcal{T},\mathcal{P}\vert o,\boldsymbol{w}_{\mathcal{P}}\}$	shorthand and extended space group symbol
$\mathcal{G}(\boldsymbol{k})\subseteq\mathcal{G}$	little group
$\boldsymbol{H}$	periodic one-particle Hamiltonian
$\mathcal{P}(\boldsymbol{k})\sim\mathcal{G}(\boldsymbol{k})/\mathcal{T}\subseteq\mathcal{P}$	little co-group
$\mathcal{P}(\mathcal{T})$	point group of $\mathcal{T}(\mathcal{I})$
$\mathcal{P}(\mathcal{T})$	primitive cell of $\mathcal{T}(\mathcal{I})$
$(R\vert\boldsymbol{w}_R + \boldsymbol{t})$	Wigner–Seitz symbol for space group element
$\boldsymbol{t} = (t_1, t_2, t_3)$	vector basis of Bravais vector lattice
$\mathcal{T}^\star$	reciprocal vector lattice
$\mathcal{T}(\mathcal{L})$	Bravais vector lattice
$\boldsymbol{w}_{\mathcal{P}} = \{\boldsymbol{w}_R\vert R\in\mathcal{P}\}$	set of fractional translations
$\mathcal{W}(\mathcal{T})$	Wigner–Seitz cell of $\mathcal{T}(\mathcal{L})$
$\mathbb{Z}(z)\in \boldsymbol{SL}(3,\mathbb{Z})$	integral 3 × 3-matrix with determinant 1
$\boldsymbol{\Psi}^k(\boldsymbol{x}) = \mathrm{e}^{\mathrm{i}k\cdot\boldsymbol{x}} w(\boldsymbol{k},\boldsymbol{x})$	Bloch function
$\boldsymbol{\Psi}^{k,n}_s$	Bloch eigenfunction of periodic Hamiltonian
$\boldsymbol{\Psi}^{(k,\xi)\uparrow\mathcal{G},n}_{\underline{R}_a}$	$\mathcal{G}$-symmetrized eigenfunctions of periodic Hamiltonian
$\Phi^k(\boldsymbol{x}) = \dfrac{1}{\sqrt{\vert\mathcal{P}(\mathcal{T})\vert}}\mathrm{e}^{\mathrm{i}K\cdot x}$	plane wave basis of Hilbert space $L^2(\mathcal{P}(\mathcal{T}))$
$\boldsymbol{\Omega}^{n,t}_s$	Wannier functions