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Irreducible Representations of Space Groups

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Abstract

In this seminar, we examine the space group of a crystal and its irreducible representations. We review the basic properties of representations, describe the concepts of Bravais and reciprocal lattice and introduce the Bloch functions as irreducible representations of translational subgroup. In the end, we investigate the behavior of the Bloch functions under space group symmetry operations and develop the rules for construction of the basis of the irreducible representations of space groups.

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1 Introduction

The space group of a crystal is the set of symmetry operations that leave the crystal lattice invariant. The symmetry of a crystal is based on its spatial periodicity – the property of being unchanged by the translations through certain distances in certain directions. All translations are included in translational subgroup T and can be represented by lattice vectors \mathbf{t} which are integral linear combination of the basic lattice vectors \mathbf{x} , \mathbf{y} , \mathbf{z} :

$$\mathbf{t} = l\mathbf{x} + m\mathbf{y} + n\mathbf{z}; \quad l, m, n \text{ integers.} \quad (1)$$

The parallelepiped formed by the basic lattice vectors is called a unit cell and the whole crystal lattice can be described as an assembly of such parallelepipeds. Vertices of every unit cell are equivalent lattice points and each can be mapped into another by a translation through some lattice vector. The set of all such points forms a Bravais lattice of the crystal. In addition, a crystal lattice can also be symmetrical under certain rotations and reflections or their combinations with parallel translations. In general, we can represent every symmetry operation of the crystal lattice as a combination of translation \mathbf{t} and point group operation p (a point group is a set of symmetry operations which leave at least one point invariant, for example rotations and reflections). In solid-state physics we traditionally denote such operations with so-called Seitz operator $\{p|\mathbf{t}\}$ (Fig. 1) defined as:

$$\{p|\mathbf{t}\}\mathbf{r} = p\mathbf{r} + \mathbf{w}. \quad (2)$$

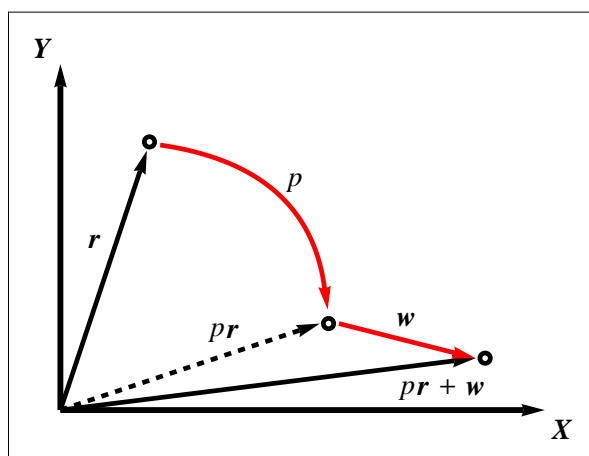


Figure 1: Schematic representation of the Seitz space group operator.

There are 14 possible types of the Bravais lattice, arranged into 7 crystal systems (triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal and cubic system.) Combining 14 Bravais lattices with 32 possible crystallographic point groups produces 230 space groups; 73 of them are symmorphic (without screw axis or glide planes) and 157 are non-symmorphic [1].

Group theory: a short revision

2 Group theory: a short revision

A set G is a group with respect to a given group operation \circ if the following properties are satisfied:

- The result of a product $g_i \circ g_j$ is always an element of the set: $g_i \circ g_j = g_k$.
- The product is associative: $(g_i \circ g_j) \circ g_k = g_i \circ (g_j \circ g_k)$.
- There exists the identity element e : $g_i \circ e = e \circ g_i = g_i$.
- There exists the inverse element g_i^{-1} : $g_i \circ g_i^{-1} = g_i^{-1} \circ g_i = e$.

The product $g \circ g_i \circ g^{-1}$ can be formed for any operation g of the group G and is called the conjugate element of g_i by g . For any given g_i the set of all its conjugates is defined as a class $C(g_i)$. No two classes can have any element in common and as result every group G can be partitioned as a sum of classes [2].

2.1 Schrödinger group

The Schrödinger group is defined as a set of operations g that leave the Hamiltonian H invariant:

$$gHg^{-1} = H. \quad (3)$$

From Eq. (3) it follows that Hamiltonian commute with all Schrödinger group operations and that eigenstates of H are degenerate:

$$gHg^{-1} = H \Rightarrow gH = Hg, \quad (4)$$

$$g(H\varphi) = g(E\varphi) \Rightarrow H(g\varphi) = E(g\varphi). \quad (5)$$

Eq. (5) shows that the states φ and $g\varphi$ are both the eigenstates of the Hamiltonian with the same eigenvalue E . This applies perfectly to symmetry operations which by the definition cannot affect energy eigenvalues. We say that eigenstates are n -fold degenerate if there are exactly n linearly independent eigenstates $g\varphi$ that all belong to the same eigenvalue.

There are two important properties of degeneracy to consider. First, any linear combination of degenerate eigenstates $g\varphi$ with eigenvalue E is eigenstate of H with the same energy eigenvalue. Second, any eigenstate of H with eigenvalue E is linear combination of n -fold degenerate eigenstates $g\varphi$ [2].

2.2 Representations

Let us now consider n -fold degenerate energy eigenvalue E :

$$H\varphi_i = E\varphi_i; \quad i = 1, 2, \dots, n. \quad (6)$$

Group theory: a short revision

As mentioned before, any other eigenfunction belonging to the same eigenvalue must be a linear combination of φ_i :

$$H \sum_i^n \varphi_i c_i = E \sum_i^n \varphi_i c_i. \quad (7)$$

If a symmetry operation g_k belongs to the Schrödinger group (from now on denoted by G) then the state $g_k \varphi_j$ must be degenerate by φ_j and therefore can be expressed as a linear combination of the eigenstates φ_i :

$$g_k \varphi_j = \sum_i^n \varphi_i c_{ij}. \quad (8)$$

We added index j to the coefficients c_i because they depend on particular eigenstate φ_j that is being transformed. The coefficients c_{ij} form a matrix $G(g_k)$ which corresponds to the operation g_k of the group G so Eq. (8) can be more compactly rewritten as:

$$g_k \langle \varphi_1, \varphi_2, \dots, \varphi_n | = \langle \varphi_1, \varphi_2, \dots, \varphi_n | G(g_k). \quad (9)$$

For every operation g_i of the group G a matrix $G(g_i)$ can be given so that multiplication rules of G are preserved:

$$g_i \circ g_j = g_k \Rightarrow G(g_i)G(g_j) = G(g_k). \quad (10)$$

The set of matrices $G(g_i)$ is called a representation of the group G and the set of functions $\langle \varphi_1, \varphi_2, \dots, \varphi_n | = \langle \varphi |$ is called the basis of the representation. Matrices $G(g_i)$ depend on our selection of a basis so additional index must be used to label the selected basis and Eq. (9) can be rewritten as:

$$g_k \langle \varphi | = \langle \varphi | G_\varphi(g_k). \quad (11)$$

Suppose that we have a single-degenerate basis $\langle \varphi |$ and doubly-degenerate basis $\langle \psi |$ with representations $G_\varphi(g)$ and $G_\psi(g)$:

$$g \langle \varphi_1 | = \langle \varphi_1 | G_\varphi(g)_{11}, \quad (12)$$

$$g \langle \psi_1 \psi_2 | = \langle \psi_1 \psi_2 | \begin{vmatrix} G_\psi(g)_{11} & G_\psi(g)_{12} \\ G_\psi(g)_{21} & G_\psi(g)_{22} \end{vmatrix}. \quad (13)$$

If we combine the basis $\langle \varphi |$ and $\langle \psi_1 \psi_2 |$ into a three-dimensional basis $\langle \varphi_1 \psi_1 \psi_2 | = \langle \vartheta |$, the corresponding matrix $G_\vartheta(g)$ can be written as:

$$G_\vartheta(g) = \begin{vmatrix} G_\varphi(g)_{11} & 0 & 0 \\ 0 & G_\psi(g)_{11} & G_\psi(g)_{12} \\ 0 & G_\psi(g)_{21} & G_\psi(g)_{22} \end{vmatrix}. \quad (14)$$

Space group representations

The matrix $G_{\vartheta}(g)$ has so-called block-diagonal form, where the diagonal elements of a matrix are square matrices of any size. Representations of this form are said to be reducible. The most important property of reducible representations is that we can divide their basis into smaller degenerate parts and then obtain representations of lower dimensions. In general, the basis of irreducible representations are formed by sets of degenerate energy eigenstates. Group theory provides us with ways to reduce representations or tells us that such task is impossible, in which case the representation is said to be irreducible. As a result, we can routinely obtain irreducible representations and classify energy levels and their degeneracies by only knowing the symmetry group of a system.

2.3 Irreducible representations

The number of irreducible representations of the group equals the number of classes. The dimensionality of the irreducible representations can be determined by a simple rule which states that the sum of the squares of the dimensions of representations equals the order of the group (order of a group is the number of its elements) [2].

When matrices $G(g)$ are given, it is useful to be able to recognize whether the representation is reducible or not. The representation is irreducible if following conditions is satisfied:

$$\sum_g \chi(G(g))^* \chi(G(g)) = n \quad (15)$$

where $\chi(G(g))$ is the character of the group element g [trace of the matrix $G(g)$]. Elements g belonging to the same class all have the same character. Irreducible representations also satisfy two orthogonality relations:

$$\sum_g \chi(G_i(g))^* \chi(G_j(g)) = n \delta_{ij}, \quad (16)$$

$$\sum_i \chi(G_i(g_j))^* \chi(G_i(g_k)) = n \delta_{jk}. \quad (17)$$

The basis of the representation G_i can be constructed by using the so-called projection operator:

$$\sum_g \chi(G_i(g))^* g_j \phi = \text{function of the basis of } G_i \quad (18)$$

where ϕ is an arbitrary function.

3 Space group representations

In this section we investigate the behavior of the electrons moving in the potential field of a crystal and try to find the energy eigenstates which forms the basis for the irreducible

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representations of the crystal space group (each irreducible basis must correspond to single energy eigenvalue). Space group operation can be expressed as a combination of point group operation and translation through a Bravais vector. All translations form the translational subgroup T and its irreducible representations are a good place to start.

3.1 The translational group

The translational group T is a subgroup of the space group G . Elements of the group T are translation operators $\{E|\mathbf{t}\}$ where \mathbf{t} are lattice vectors defined by Eq. (1) and E is identity point operation. Clearly, all translations along the x axis (x axis is parallel to basis lattice vectors \mathbf{x}) form a subgroup T_x and similarly for the other two axis. Since elements of subgroups T_x , T_y and T_z commute (all translations commute!), group T is Abelian and a direct product of the three subgroups:

$$T = T_x \otimes T_y \otimes T_z. \quad (19)$$

When defining translations we must assume that the crystal is infinite which means that we also have infinite number of translations. This inconvenience is solved by the Born-von Kármán boundary condition [3]. Let us assume that that crystal has N_x primitive cells along x axis. Using Seitz operators we can express Born-von Kármán condition with following equation:

$$\{E|N_x\mathbf{x}\} = \{E|\mathbf{0}\}. \quad (20)$$

By using periodic boundary condition we limited the number of translations along x axis to N_x and the same procedure can be used for the other two axis. The total number of elements in group T is therefore $N_x N_y N_z = N$. Since group T is Abelian, every group element is in a class of its own. Following the two rules from Section 2.3 we can finally determine that group T has N one-dimensional irreducible representations. When searching for representations of group T , we can limit ourselves to one of its subgroups and then construct the representations of T as a product of representations of T_x , T_y and T_z [4]. We will denote the representation corresponding to operator $\{E|l\mathbf{x}\}$ as $T_{l\mathbf{x}}^{k_x}$ where k_x is index labeling one of the N_x possible representations of subgroup T_x . Translation representations must obey the same multiplication rules as operators:

$$\{E|l_1\mathbf{x}\}\{E|l_2\mathbf{x}\} = \{E|(l_1 + l_2)\mathbf{x}\} \Rightarrow T_{l_1\mathbf{x}}^{k_x} T_{l_2\mathbf{x}}^{k_x} = T_{(l_1+l_2)\mathbf{x}}^{k_x}. \quad (21)$$

Exponential function in l satisfies multiplication rules in Eq. (21) and we multiply it with constant related to label k_x :

$$T_{l\mathbf{x}}^{k_x} = \exp(-i2\pi l k_x). \quad (22)$$

The same holds for irreducible representations of T_y and T_z :

$$T_{m\mathbf{y}}^{k_y} = \exp(-i2\pi m k_y), \quad (23)$$

$$T_{n\mathbf{z}}^{k_z} = \exp(-i2\pi n k_z). \quad (24)$$

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The direct product of representations of groups T_x , T_y and T_z can be written as:

$$T_{lx}^{k_x} T_{my}^{k_y} T_{nz}^{k_z} = \exp [- i2\pi(k_x l + k_y m + k_z n)] . \quad (25)$$

The choice of constant $i2\pi$ will be justified in following subsection.

3.2 The reciprocal lattice

Physical properties of a crystal (charge density due to the electrons, probability of finding the atom at particular point in the lattice etc.) have the same periodicity as the lattice itself [1]. Let the $U(\mathbf{r})$ be such function. Due to periodicity following relation holds:

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{t}) \quad (26)$$

where \mathbf{t} is an arbitrary lattice vector. If function $U(\mathbf{r})$ is expanded as a Fourier series:

$$U = \sum_{\mathbf{g}} U_{\mathbf{g}} e^{i\mathbf{g}\mathbf{r}} \quad (27)$$

it still must satisfy Eq. (26) which means that exponential factors must be invariant under $\mathbf{r} \rightarrow \mathbf{r} + \mathbf{t}$ transformation. To meet this requirement the scalar product $\mathbf{g}\mathbf{t}$ must be an integral multiple of 2π . Vectors \mathbf{g} that produce function $U(\mathbf{r})$ with desired periodicity are called vectors of the reciprocal lattice and are given by [3]:

$$\mathbf{g} = g_1 \mathbf{a} + g_2 \mathbf{b} + g_3 \mathbf{c}; \quad g_1, g_2, g_3 \text{ integers.} \quad (28)$$

Vectors \mathbf{a} , \mathbf{b} and \mathbf{c} are called the reciprocal basis vectors and are defined as:

$$\mathbf{a} = \frac{2\pi}{V} \mathbf{y} \times \mathbf{z}, \quad (29)$$

$$\mathbf{b} = \frac{2\pi}{V} \mathbf{z} \times \mathbf{x}, \quad (30)$$

$$\mathbf{c} = \frac{2\pi}{V} \mathbf{x} \times \mathbf{y}, \quad (31)$$

where $V = \mathbf{x}(\mathbf{y} \times \mathbf{z})$ is the volume of unit cell. Just like we constructed a Bravais lattice with vectors \mathbf{x} , \mathbf{y} and \mathbf{z} , we can construct the so-called reciprocal lattice using vectors \mathbf{a} , \mathbf{b} and \mathbf{c} . Let us now calculate the scalar product $\mathbf{g}\mathbf{t}$:

$$\mathbf{g}\mathbf{t} = (g_1 \mathbf{a} + g_2 \mathbf{b} + g_3 \mathbf{c})(l \mathbf{x} + m \mathbf{y} + n \mathbf{z}) = 2\pi(g_1 l + g_2 m + g_3 n). \quad (32)$$

We encountered similar term in Eq. (25). It is therefore convenient to include the representation labels k_x , k_y and k_z into vector \mathbf{k} :

$$\mathbf{k} = (k_x, k_y, k_z) = k_x \mathbf{a} + k_y \mathbf{b} + k_z \mathbf{c}; \quad k_x, k_y, k_z \text{ reals.} \quad (33)$$

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and rewrite the irreducible representation of group T from Eq. (25) into a more convenient form:

$$T_{lx}^{k_x} T_{my}^{k_y} T_{nz}^{k_z} = T_{\mathbf{t}}^{\mathbf{k}} = \exp[-i2\pi(k_x l + k_y m + k_z n)] = \exp(-i\mathbf{k}\mathbf{t}). \quad (34)$$

The label \mathbf{k} can be any general reciprocal vector (k_x, k_y and k_z are real!) which is clearly in conflict with demand to have exactly N irreducible representations. In the following section we shall therefore include a few restrictions that will narrow the number of irreducible representations.

3.3 Brillouin zone

Two vectors are defined as equivalent if they differ only by a vector \mathbf{g} of the reciprocal lattice given by Eq. (28) [1]. It is easy to show that equivalent vectors belong to the same representation:

$$T_{\mathbf{t}}^{\mathbf{k}} = \exp(-i\mathbf{k}\mathbf{t}), \quad (35)$$

$$T_{\mathbf{t}}^{\mathbf{k} + \mathbf{g}} = \exp[-i(\mathbf{k} + \mathbf{g})\mathbf{t}] = \exp(-i\mathbf{k}\mathbf{t}) \exp(-i\mathbf{g}\mathbf{t}). \quad (36)$$

From Eq. (32) we get:

$$\begin{aligned} \mathbf{g}\mathbf{t} &= 2\pi(g_1 l + g_2 m + g_3 n) = 2\pi\mu \\ g_1, g_2, g_3, l, m, n \text{ integers} &\Rightarrow \mu \text{ integer} \end{aligned} \quad (37)$$

and

$$T_{\mathbf{t}}^{\mathbf{k} + \mathbf{g}} = \exp(-i\mathbf{k}\mathbf{t}) \exp(-i\mathbf{g}\mathbf{t}) = \exp(-i\mathbf{k}\mathbf{t}) \underbrace{\exp(-i2\pi\mu)}_{=1} = \exp(-i\mathbf{k}\mathbf{t}) = T_{\mathbf{t}}^{\mathbf{k}}. \quad (38)$$

As a consequence, we can always replace general reciprocal vector \mathbf{k} with an equivalent vector inside the primitive cell of a reciprocal lattice when labeling representations:

$$T_{\mathbf{t}}^{\mathbf{k}} = \exp(-i\mathbf{k}\mathbf{t}); \quad k_x, k_y, k_z \text{ real and } \in (0, 1]. \quad (39)$$

Open interval border at 0 is necessary because vector $\mathbf{0}$ is equivalent of all basis lattice vectors! For practical reasons, the primitive cell is usually replaced with centered primitive cell called the Brillouin zone or the first Brillouin zone which better reflects symmetry of the reciprocal lattice. To further reduce the number of representations we now use Born-von Kármán boundary condition:

$$\{E|N_x \mathbf{x}\} = \{E|\mathbf{0}\} \Rightarrow T_{N_x \mathbf{x}}^{k_x} = T_{\mathbf{0}}^{k_x} \Rightarrow \exp(-i2\pi N_x k_x) = 1 \Rightarrow k_x N_x \text{ integer}. \quad (40)$$

Since k_x must lie on the interval $(0, 1]$, all its possible values can be written as:

$$k_x = \frac{\epsilon}{N_x}; \quad \epsilon = 1, 2, \dots, N_x \quad (41)$$

Space group representations

and similarly for k_y and k_z :

$$k_y = \frac{\rho}{N_y}; \quad \rho = 1, 2, \dots, N_y, \quad (42)$$

$$k_z = \frac{\sigma}{N_z}; \quad \sigma = 1, 2, \dots, N_z. \quad (43)$$

By limiting \mathbf{k} to Brillouin zone and taking into account the Born-von Kármán boundary condition we finally obtain the total of $N_x N_y N_z = N$ irreducible representations that correspond to N classes of translational group T .

3.4 Bloch functions

After finding N irreducible representations of translational group T we must now find their basis functions. From the definition of the representations follows:

$$T_{\mathbf{t}}^{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) = \lambda_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}) = \exp(-i\mathbf{k}\mathbf{t}) \psi_{\mathbf{k}}(\mathbf{r}) \quad (44)$$

where $\psi_{\mathbf{k}}(\mathbf{r})$ are basis functions of \mathbf{k} representation. We assume that the functions $\psi_{\mathbf{k}}(\mathbf{r})$ vary continuously over the Brillouin zone [5] and all N possible functions form what is in solid-state physics called the band. Translational group T is a subgroup of Schrödinger group so operators $T_{\mathbf{t}}^{\mathbf{k}}$ commute with Hamiltonian H :

$$H(T_{\mathbf{t}}^{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r})) = T_{\mathbf{t}}^{\mathbf{k}}(H\psi_{\mathbf{k}}(\mathbf{r})) = \lambda_{\mathbf{k}}(H\psi_{\mathbf{k}}(\mathbf{r})). \quad (45)$$

Since eigenvalues $\lambda_{\mathbf{k}}$ are all distinct, we can conclude that they are not degenerate as long as we stay in the same band so function $H\psi_{\mathbf{k}}(\mathbf{r})$ must be linearly dependent on $\psi_{\mathbf{k}}(\mathbf{r})$:

$$H\psi_{\mathbf{k}}(\mathbf{r}) = \epsilon_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{r}). \quad (46)$$

Eigenstates of translational group are clearly the eigenstates of the Hamiltonian and their label \mathbf{k} also labels the energy eigenvalues $\epsilon_{\mathbf{k}}$. In general, eigenvalues $\epsilon_{\mathbf{k}}$ are not all different because degeneracies could appear when symmetry operations of space group G other than translations are applied.

Functions that satisfy Eq. (44) are known since late twenties of the 20th century and are called Bloch functions. General form of Bloch function is given by [3, 5]:

$$\Psi_{\mathbf{k}}^j(\mathbf{r}) = u_{\mathbf{k}}^j(\mathbf{r}) \exp(i\mathbf{k}\mathbf{r}) \quad (47)$$

where $u_{\mathbf{k}}^j(\mathbf{r})$ has periodicity of the crystal lattice:

$$u_{\mathbf{k}}^j(\mathbf{r}) = u_{\mathbf{k}}^j(\mathbf{r} + \mathbf{t}); \quad \forall \mathbf{t}. \quad (48)$$

Additional index j is necessary because in limiting case of separated atoms reciprocal space collapses into $\mathbf{k} = \mathbf{0}$, exponential part of Bloch functions vanishes and $u_{\mathbf{k}}^j(\mathbf{r})$ would

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become one of the manifold atomic orbitals ϕ^j ($j = 1s, 2s, 1p$, etc.). The physical meaning of a band is now clear: If crystal atoms are separated, all states from the band would reduce into the same atomic orbital.

The proof that Bloch functions really are eigenstates of the translational group is trivial:

$$\begin{aligned}
 T_{\mathbf{t}}^{\mathbf{k}} \Psi_{\mathbf{k}}^j(\mathbf{r}) &= \Psi_{\mathbf{k}}^j(\mathbf{r} - \mathbf{t}) \\
 &= u_{\mathbf{k}}^j(\mathbf{r} - \mathbf{t}) \exp [i\mathbf{k}(\mathbf{r} - \mathbf{t})] \\
 &= u_{\mathbf{k}}^j(\mathbf{r}) \exp(i\mathbf{k}\mathbf{r}) \exp(-i\mathbf{k}\mathbf{t}) \\
 &= \exp(-i\mathbf{k}\mathbf{t}) \Psi_{\mathbf{k}}^j(\mathbf{r}).
 \end{aligned} \tag{49}$$

3.5 Irreducible representations of the space group

In previous subsections we obtained the irreducible representations of translational group T and Bloch functions as their eigenstates. We must now investigate how the Bloch functions transforms under the space group operations. Using following operator product [4]:

$$\{E|\mathbf{t}\}\{p|\mathbf{w}\} = \{p|\mathbf{w}\}\{E|p^{-1}\mathbf{t}\} \tag{50}$$

we obtain:

$$\{E|\mathbf{t}\} [\{p|\mathbf{w}\}\Psi_{\mathbf{k}}] = \{p|\mathbf{w}\} [\{E|p^{-1}\mathbf{t}\}\Psi_{\mathbf{k}}] = \{p|\mathbf{w}\} \exp [-i\mathbf{k}(p^{-1}\mathbf{t})] \Psi_{\mathbf{k}}. \tag{51}$$

Scalar product is invariant under point group symmetry operation ($\mathbf{k} \cdot \mathbf{t} = p\mathbf{k} \cdot p\mathbf{t}$) so Eq. (51) can be rewritten as:

$$\begin{aligned}
 \{E|\mathbf{t}\} [\{p|\mathbf{w}\}\Psi_{\mathbf{k}}] &= \{p|\mathbf{w}\} \exp [-i\mathbf{k}(p^{-1}\mathbf{t})] \Psi_{\mathbf{k}} \\
 &= \{p|\mathbf{w}\} \exp [-i(p\mathbf{k})(pp^{-1}\mathbf{t})] \Psi_{\mathbf{k}} \\
 &= \exp [-i(p\mathbf{k})\mathbf{t}] [\{p|\mathbf{w}\}\Psi_{\mathbf{k}}].
 \end{aligned} \tag{52}$$

Function $\{p|\mathbf{w}\}\Psi_{\mathbf{k}}$ clearly transforms as $\Psi_{p\mathbf{k}}$ under arbitrary space group operation $\{p|\mathbf{w}\}$:

$$\{p|\mathbf{w}\}\Psi_{\mathbf{k}} = \Psi_{p\mathbf{k}}. \tag{53}$$

By definition, basis functions transforms into each other under symmetry operations. Basis of the representation can therefore be constructed using following rule:

$$\langle \Psi_{\mathbf{k}} | = \langle \Psi_{p\mathbf{k}} |; \quad \forall p \in P \text{ and } \forall p\mathbf{k} \in \text{Brillouin zone}. \tag{54}$$

Because point group P is closed, the same set is generated by any of the functions of the set. At the end, we must prove that the same state $\Psi_{p\mathbf{k}}$ cannot appear in two different basis. We start with point group operations p_1 and p_2 and two sets of basis functions:

$$\Psi_{p_1\mathbf{k}_1} \in \langle \Psi_{\mathbf{k}_1} | \text{ and } \Psi_{p_2\mathbf{k}_2} \in \langle \Psi_{\mathbf{k}_2} |. \tag{55}$$

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If $p_1 \mathbf{k}_1$ and $p_2 \mathbf{k}_2$ are equal we have:

$$\mathbf{k}_1 = p_1^{-1} p_2 \mathbf{k}_2. \quad (56)$$

$p_1^{-1} p_2$ is clearly the element of the point group P so vector $\mathbf{k}_1 = p_1^{-1} p_2 \mathbf{k}_2$ must, by definition in Eq. (54), belong to basis $\langle \Psi_{\mathbf{k}_2} |$ and consequently basis $\langle \Psi_{\mathbf{k}_1} |$ and $\langle \Psi_{\mathbf{k}_2} |$ are exactly the same. The bases are therefore either equal or have no state $\Psi_{\mathbf{k}}$ in common so N eigenstates of the translational group are separated into disjoint bases of space group G . Such basis are not necessary irreducible as we will now demonstrate.

Consider a two-dimensional square lattice with side a and the C_{4v} point symmetry. The corresponding Brillouin zone is centered square lattice of length $2\pi/a$ with basis vectors \mathbf{a} and \mathbf{b} . Vector \mathbf{K}_1 is chosen inside the Brillouin zone and then translated by 8 elements of the C_{4v} group ($E, C_2, C_4^+, C_4^-, \sigma_{v1}, \sigma_{v2}, \sigma_{d1}, \sigma_{d2}$). The resulting set of vectors ($\mathbf{K}_1, \mathbf{K}_2, \dots, \mathbf{K}_8$) is shown in Fig. 2.

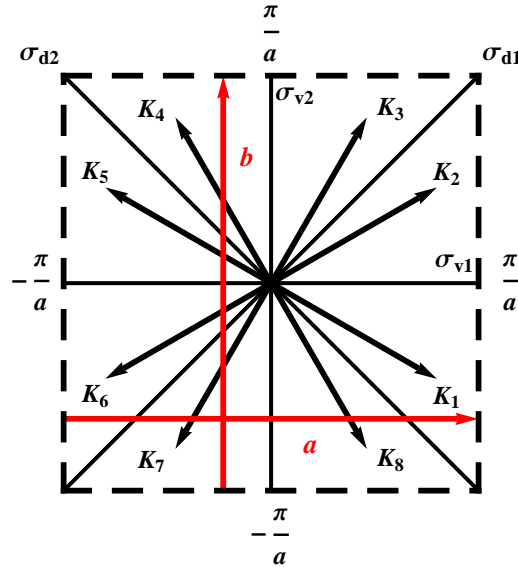


Figure 2: Set of vectors \mathbf{K} , obtained when vector \mathbf{K}_1 is transformed by all elements of group C_{4v} . Brillouin zone is denoted with black dashed line and basis vectors \mathbf{a} and \mathbf{b} are denoted with red arrows.

Since no pair of vectors \mathbf{K} is equivalent, Bloch functions corresponding to vectors \mathbf{K} are linearly independent and they form a basis of irreducible representation. Set of such non-equivalent vectors of the form $p\mathbf{K}$, where p goes over all elements of point group P is called the star of vector \mathbf{K} .

By lengthening vectors \mathbf{K} until they touch the edge of the Brillouin zone we construct the set of vectors \mathbf{H} depicted in Fig. 3. As seen on Fig. 3, vectors \mathbf{H}_4 and \mathbf{H}_7 differ only by the vector \mathbf{b} of the reciprocal lattice and are hence equivalent. Bloch functions corresponding to equivalent vectors transforms under the same representation so such basis is clearly reducible. To construct the irreducible representation we only need vectors $\mathbf{H}_1, \mathbf{H}_2, \mathbf{H}_3$ and \mathbf{H}_4 while the rest of them are redundant.

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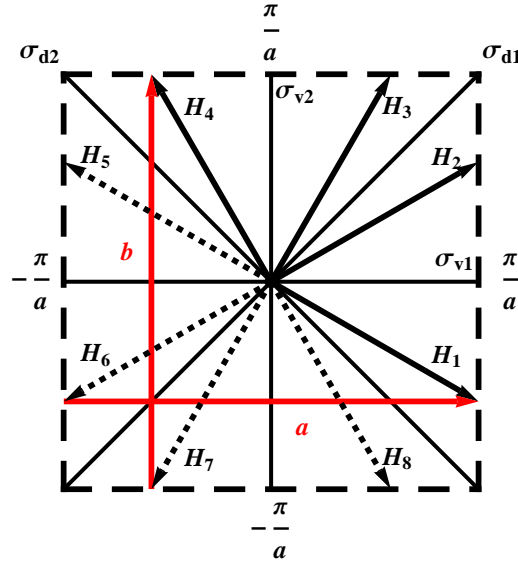


Figure 3: Set of vectors \mathbf{H} , obtained by lengthening vectors \mathbf{K} until they touch the edge of Brillouin zone. Vectors \mathbf{H}_1 \mathbf{H}_2 \mathbf{H}_3 and \mathbf{H}_4 (black arrows) form the base of irreducible representation while other vectors (dashed arrows) are all their equivalents.

To fully utilize the concept of the star we must introduce so-called group of the vector \mathbf{k} defined as the set of symmetry operations that leave the chosen vector \mathbf{k} invariant or transform it into equivalent vector. Irreducible representations of the group of the vector are called small representations. For example, group of vector \mathbf{H}_1 (Fig. 3) is point group C_s which includes elements E and reflection over the σ_{v2} plane. Group C_s is Abelian and includes two irreducible representations: A^+ which is symmetrical with respect to the plane σ_{v2} and A^- which is antisymmetrical. Representations and corresponding bases are shown in Table 1.

representation	E	σ	base
A^+	1	1	y
A^-	1	-1	x

Table 1: Irreducible representations A^+ and A^- of the group C_s . Plane σ is perpendicular to the x axis.

Let us now arrange the Bloch functions corresponding to vectors \mathbf{H} into set $\langle \Psi_1, \Psi_2, \dots, \Psi_8 |$. None of the functions Ψ is either symmetrical or antisymmetrical under the reflection σ_{v2} but linear combinations $\Psi_1 + \Psi_6$ and $\Psi_1 - \Psi_6$ are:

$$\{\sigma_{v2}|\mathbf{0}\}\mathbf{H}_1 = \mathbf{H}_6 \Rightarrow \{\sigma_{v2}|\mathbf{0}\}\Psi_1 = \Psi_6, \quad (57)$$

$$\{\sigma_{v2}|\mathbf{0}\}\mathbf{H}_6 = \mathbf{H}_1 \Rightarrow \{\sigma_{v2}|\mathbf{0}\}\Psi_6 = \Psi_1, \quad (58)$$

$$\Rightarrow \{\sigma_{v2}|\mathbf{0}\}(\Psi_1 + \Psi_6) = (+1) \cdot (\Psi_1 + \Psi_6), \quad (59)$$

$$\Rightarrow \{\sigma_{v2}|\mathbf{0}\}(\Psi_1 - \Psi_6) = (-1) \cdot (\Psi_1 - \Psi_6). \quad (60)$$

Space group representations

Combination $\Psi_1 + \Psi_6$ is symmetrical and transforms under representation A^+ while combination $\Psi_1 - \Psi_6$ is antisymmetrical and transforms under representation A^- . As mentioned before, vectors \mathbf{H}_1 and \mathbf{H}_6 are equivalent so their symmetric and antisymmetric combinations can be labeled as Ψ_1^+ and Ψ_1^- . The same hold for pairs of Bloch functions (Ψ_2, Ψ_5) , (Ψ_3, Ψ_8) and (Ψ_4, Ψ_7) so set of basis states can be rewritten as:

$$\langle \Psi_1^+, \Psi_2^+, \Psi_3^+, \Psi_4^+, \Psi_1^-, \Psi_2^-, \Psi_3^-, \Psi_4^- |. \quad (61)$$

Symmetric function cannot be transformed into antisymmetric so above basis reduces into two new basis:

$$\langle \Psi_1^+, \Psi_2^+, \Psi_3^+, \Psi_4^+ | \quad \text{and} \quad \langle \Psi_1^-, \Psi_2^-, \Psi_3^-, \Psi_4^- |. \quad (62)$$

Basis functions in $\langle \Psi^+ |$ are orthogonal because they belong to the non-equivalent vectors $\mathbf{H}_1, \mathbf{H}_2, \mathbf{H}_3$ and \mathbf{H}_4 . They are also orthogonal to the functions in set $\langle \Psi^- |$ because either they belong to the non-equivalent vectors $(\Psi_1^+$ and $\Psi_2^-)$ or have been symmetrized with respect to the small representations of vector \mathbf{H}_1 (Ψ_1^+ and Ψ_1^-). Both new bases are therefore irreducible.

Although the reduction of the base $\langle \Psi_i |$ was done for a specific example of vector \mathbf{H}_1 the procedure is quite general. The star of a arbitrary vector \mathbf{k} determines the irreducible basis when corresponding functions are symmetrized with respect to the small representations of the vector \mathbf{k} . Accordingly, each irreducible representation of the space group is completely determined by the star of corresponding reciprocal vector and its small representation.

Conclusion

4 Conclusion

We have examined the space group of a crystal and its irreducible representations. We have reviewed the basic properties of groups, their representations and describe the concepts of Bravais and reciprocal lattice. We focused on translational subgroup and developed the Bloch functions as its irreducible representations. By investigating the behavior of the Bloch functions under space group symmetry operations and by introducing the concepts of the star of the vector and small representation we have developed the rules for generating the irreducible representations of the space group.

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