Symmetry and Analyticity of Energy Bands in Solids

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We show that pairs of simple energy bands exist that have identical symmetries for their Bloch functions, but different symmetries for the corresponding Wannier functions. For finite crystals such pairs of bands belong to equivalent band representations. In the case of infinite crystals, we use the analyticity of simple bands to prove the inequivalence of their band representations. This means that the energies of such pairs of bands cannot coincide despite the identical symmetries of their Bloch functions.

It is customary for one to apply Born–von Karman or cyclic boundary conditions in solid-state theory both in solving dynamical problems[1] and in symmetry applications of group theory.[2] This is a very useful approach, and experience gained over many years shows that, for solutions of Schrödinger's equation in a periodic potential, the replacement of the infinite crystal by a finite one does not change the physics. A similar situation prevails concerning the irreducible representations of space groups which are used for specification of the symmetry of Bloch functions. The reason for this is that these representations are finite dimensional (independent of the size of the crystal) and because the Bloch functions of a finite crystal coincide with those of an infinite one at special discrete values of the **k** vector. There are, however, other types of representations of space groups which are used for connecting the symmetries of Bloch and Wannier functions. These are the so-called band representations[3] which specify symmetries of whole energy bands via the symmetries of their Wannier functions.[4-7] For them, finite and infinite crystals are very different because for the latter convergence and continuity properties of the basis functions have to be taken into account.

In this Letter we investigate the symmetry correspondence between Bloch and Wannier functions by using the concept of band representations. We show that there are pairs of simple energy bands with identical symmetries for their Bloch functions, but whose Wannier functions have different symmetries. By invoking Nenciu's theorem about analyticity and periodicity of Bloch functions for simple bands,[8] we prove that these energy bands are equivalent for a finite crystal (their Bloch functions differ by a phase factor), but are inequivalent for an infinite crystal (no continuous phase transformation can

connect their Bloch functions).

For one-dimensional crystals there is a one-to-one correspondence between the symmetries of Bloch and Wannier functions.[9] Despite the interest in the subject for many years,[10] it seems that the only case where a one-to-one symmetry correspondence was rigorously established between Bloch and Wannier functions in three dimensions is the case of simple bands in crystals with inversion symmetry.[5] By using band representation theory, we have recently shown that for the overwhelming majority of simple bands there is a rule that different symmetries of Wannier functions determine different symmetries of Bloch functions.[11] The exceptions to this rule appear only in the space groups $F222$ (No. 22) and $F23$ (No. 196).

In proving the existence of the exceptional pairs of simple bands, we use the notion of band representations[3,5,6] which are labeled by two indices (q,ρ), where q is the Wyckoff position[12] and ρ is the index of an irreducible representation of the isotropy group G_q of q. (q,ρ) is an induced representation of the space group G from the representation ρ of G_q. Band representations have recently attracted attention in various applications.[7]

Consider the band representations $(a,1)$ and $(b,1)$ of space group No. 22 ($F222$). a and b denote the Wyckoff positions, $a = (0,0,0)$ and $b = (0,0,c/2)$, and the index 1 denotes the trivial representation of the corresponding isotropy groups G_a and G_b. We shall first discuss the finite-crystal case when the Born–von Karman boundary conditions are applied. What we know is that for the finite crystal the characters of the band representations $(a,1)$ and $(b,1)$ are the same.[11]

In the particular case of the band representation $(a,1)$, the basis is given by the set [the set is similar

for $(b,1)$]

$$\psi^{(a,1)}(\mathbf{r}-\mathbf{R}_n), \tag{1}$$

where $\mathbf{R}_n$ runs over all the Bravais lattice vectors in the Born–von Karman crystal [in an infinite crystal, Eq. (1) contains an infinite number of functions]. Thus, for the condition

$$\psi(\mathbf{r}+N\mathbf{a}_i)=\psi(\mathbf{r}), \tag{2}$$

where the $\mathbf{a}_i (i=1,2,3)$ are unit-cell vectors and N is an integer, the set in Eq. (1) contains N^3 functions. Let $\psi^{(a,1)}(\mathbf{r}-\mathbf{R}_n)$ and $\psi^{(b,1)}(\mathbf{r}-\mathbf{R}_n)$ [see relation (1)] form bases for the band representations $(a,1)$ and $(b,1)$. This means that $\psi^{(a,1)}(\mathbf{r})$ and $\psi^{(b,1)}(\mathbf{r})$ are the bases for the trivial representations of the isotropy groups G_a and G_b. The latter are[12] (C_2^x is a rotation by π, the superscript gives the rotation axis)

$$G_a{:}g_a \equiv E, \ C_2^x, \ C_2^y, \ C_2^z, \tag{3}$$

$$G_b{:}g_b \equiv E, \ (C_2^x|00c), \ (C_2^y|00c), \ C_2^z, \tag{4}$$

where g_a and g_b denote a general element of the group and where, in relation (4), $00c$ is a translation by the vector $(0,0,c)$. By definition of the band representation $(a,1)$ and $(b,1)$, we have

$$g_a\psi^{(a,1)}(\mathbf{r})=\psi^{(a,1)}(\mathbf{r}); \ \ g_b\psi^{(b,1)}(\mathbf{r})=\psi^{(b,1)}(\mathbf{r}), \tag{5}$$

for all g_a and g_b in relations (3) and (4). As was proven in Ref. 11, the band representations $(a,1)$ and $(b,1)$ for a finite crystal are equivalent and there is therefore a unitary matrix $A(\mathbf{R}_n)$ [we assume orthonormality of the basis in relation (1) and similarly for $(b,1)$] connecting their bases,

$$\psi^{(b,1)}(\mathbf{r})=\sum_n A(\mathbf{R}_n)\psi^{(a,1)}(\mathbf{r}-\mathbf{R}_n). \tag{6}$$

In the language of the corresponding Bloch functions,[3] relation (6) assumes the form

$$\psi_k^{(b,1)}(\mathbf{r})=T(\mathbf{k})\psi_k^{(a,1)}(\mathbf{r}), \tag{7}$$

where $T(\mathbf{k})$ is a sum of exponentials with the coefficients $A(\mathbf{R}_n)$ from relation (6),

$$T(\mathbf{k})=\frac{1}{\sqrt{N^3}}\sum_n A(\mathbf{R}_n)\exp(-i\mathbf{k}\cdot\mathbf{R}_n). \tag{8}$$

The function $T(\mathbf{k})$ in Eq. (7) is, by definition, periodic in $\mathbf{k}$ with the periods of the Brillouin zone.[13] (These periods are the reciprocal-lattice vectors $\mathbf{K}_1$, $\mathbf{K}_2$, and $\mathbf{K}_3$ which are given in Ref. 12, p. 54, in their Cartesian coordinates.) Let us now use the fact that $\psi^{(a,1)}(\mathbf{r})$ is an eigenfunction with eigenvalue 1 of all the elements of G_a and similarly for $\psi^{(b,1)}(\mathbf{r})$ [relation (5)]. Thus, by applying the elements of G_b to both sides of relation (6) and by using relations (5) and (7), we find

$$(C_2^x|00c){:}T(k_x,k_y,k_z)$$
$$=\exp(-ik_zc)T(k_x,-k_y,-k_z), \tag{9}$$

$$(C_2^y|00c){:}T(k_x,k_y,k_z)$$
$$=\exp(-ik_zc)T(-k_x,k_y,-k_z), \tag{10}$$

$$C_2^z{:}T(k_x,k_y,k_z)=T(-k_x,-k_y,k_z). \tag{11}$$

To these restrictions on $T(\mathbf{k})$ we have to add the unitarity of $T(\mathbf{k})$, and the assumption that the orbitals $\psi^{(a,1)}(\mathbf{r})$ and $\psi^{(b,1)}(\mathbf{r})$ are real. The latter can always be done for real representations of G_a and G_b.[5,9] We then have

$$T(\mathbf{k})T(-\mathbf{k})=1. \tag{12}$$

For explicit calculations of the relations between different components of $T(\mathbf{k})$ that follow from relations (9)–(12), it is more convenient to use the components along the unit vectors $\mathbf{K}_1$, $\mathbf{K}_2$, and $\mathbf{K}_3$ of the reciprocal lattice rather than the Cartesian components as in Eqs. (9)–(11). The components of $\mathbf{k}$ along the $\mathbf{K}_1$, $\mathbf{K}_2$, and $\mathbf{K}_3$ vectors, m_1, m_2, and m_3, are independent and each of them can assume an arbitrary value. We shall denote by $T(m_1, m_2, m_3)$ the T matrix in m_1, m_2, m_3. Equations (9)–(11) will become, correspondingly,

$$T(m_1,m_2,m_3)=\exp[-i(2\pi/N)(-m_1+m_2+m_3)]T(m_2-m_3,m_1-m_3,-m_3), \tag{13}$$

$$T(m_1,m_2,m_3)=\exp[-i(2\pi/N)(-m_1+m_2+m_3)]T(m_3-m_2,-m_2,m_1-m_2), \tag{14}$$

$$T(m_1,m_2,m_3)=T(m_1,m_3-m_1,m_2-m_1). \tag{15}$$

We subdivide the additional conditions on $T(\mathbf{k})$ [following from Eq. (12)] into two kinds [Eqs. (16) and (17)]:

$$T(-m_1,-m_2,-m_3)\neq T(m_1,m_2,m_3), \tag{16}$$

$$T(-m_1,-m_2,-m_3)=T(m_1,m_2,m_3). \tag{17}$$

When Eq. (16) holds, the orthogonality condition [Eq.

(12)] leads to additional relations between different $T(m_1,m_2,m_3)$

$$T(-m_1,-m_2,-m_3)=\frac{1}{T(m_1,m_2,m_3)}. \tag{18}$$

On the other hand, when Eq. (17) is satisfied, we find conditions on the values of $T(m_1,m_2,m_3)$. Thus, from

Eqs. (13)-(15) and (17) we have, correspondingly,

$$T^2(m_1,m_2,m_1+m_2)=\exp[-i(2\pi/N)2m_2],\qquad(19)$$

$$T^2(m_1,m_1+m_3,m_3)=\exp[-i(2\pi/N)2m_3],\qquad(20)$$

$$T^2(m_1,m_2,m_1-m_2)=1,\qquad(21)$$

$$T^2(m_1,m_2,m_3)=1,\quad m_1,m_2,m_3=0,N/2.\qquad(22)$$

These equations determine the T matrix (at the corresponding values of k) up to a sign. The question arises as to whether all the Eqs. (19)-(22) lead to the same values of $T(m_1,m_2,m_3)$. In order to answer this question one has to find which values of k appear in more than one line of these equations. For this let us consider in more detail Eqs. (19) and (20). By equating the components in T, we find that for the k vectors in these equations to be equal, the following relation has to hold

$$m_2=m_3+m_1,\quad m_1=0,N/2.\qquad(23)$$

We can choose arbitrarily the plus sign as a solution for T from Eq. (19) [as was already mentioned above, Eq. (19) determines T up to a sign],

$$T(m_1,m_2,m_1+m_2)=\exp[-i(2\pi/N)m_2].\qquad(24)$$

Having fixed the sign in Eq. (19), we shall consider separately the plus and minus signs for the solution of T from Eq. (20). Choose first the plus sign. We have

$$T(m_1,m_1+m_3,m_3)=\exp[-i(2\pi/N)m_3].\qquad(25)$$

For $m_1=0$, Eqs. (24) and (25) become

$$T(0,m_3,m_3)=\exp[-i(2\pi/N)m_3]\qquad(26)$$

[both Eqs. (24) and (25) give the same result]. However, for $m_1=N/2$ in Eq. (23), we find different results for the T matrix depending on whether we use Eq. (24) or Eq. (25). Thus, for (24), it follows

$$T(N/2,m_3+N/2,m_3)=-\exp[-i(2\pi/N)m_3],\qquad(27)$$

while from (25) we find

$$T(N/2,m_3+N/2,m_3)=\exp[-i(2\pi/N)m_3].\qquad(28)$$

Equations (27) and (28) have opposite signs. For a finite crystal, the k vector is discrete (m_1,m_2,m_3 are discrete) and consequently the incompatibility in sign of Eqs. (27) and (28) does not lead to a contradiction. The reason for this is that there is no continuous path connecting Eqs. (27) and (28) when k is discrete [see, however, Eqs. (31)-(35) for continuous k]. Thus, in Table I we present one such possible choice of $T(m_1,m_2,m_3)$, which is a unitary matrix. It satisfies Eqs. (12)-(15) and therefore intertwines the orthogonal bases of the band representations $(a,1)$ and $(b,1)$.

For an infinite crystal the situation is very different and, as will be shown below, because of continuity of $T(k)$ it is no longer possible to choose the signs in Eqs.

TABLE I. Values of the unitary intertwining matrix $T(m_1,m_2,m_3)$ for $N=4$.

$T(000)=T(101)=T(202)=T(303)=T(110)=T(220)$
$=T(330)=T(022)=T(123)=T(321)=T(132)=T(312)$
$=T(013)=T(211)=T(233)=T(031)=T(020)=T(002)$
$=T(010)=T(001)=T(030)=T(003)=T(021)=T(012)$
$=T(023)=T(032)=T(313)=T(102)=T(131)=T(302)$
$=T(221)=T(230)=T(223)=T(210)=1;$
$T(222)=T(200)=-1;$
$T(011)=T(112)=T(213)=T(121)=T(310)=T(301)$
$=T(100)=T(333)=T(122)=T(311)=T(201)=T(232)$
$=T(113)=T(320)=i;$
$T(033)=T(231)=T(332)=T(130)=T(323)=T(103)$
$=T(300)=T(111)=T(133)=T(322)=T(212)=T(203)$
$=T(120)=T(331)=-i.$

(19)-(22) arbitrarily. From Eqs. (9) and (12), one finds

$$T(-k_x,k_y,k_z)T(k_x,k_y,k_z)=\exp(-ik_zc).\qquad(29)$$

On the other hand, from Eqs. (10) and (12) it follows

$$T(k_x,-k_y,k_z)T(k_x,k_y,k_z)=\exp(-ik_zc).\qquad(30)$$

These equations hold for any value of the k vector. For some particular values of k we find

$$T^2(0,k_y,k_z)=T^2(2\pi/a,k_y,k_z)$$
$$=\exp(-ik_zc),\qquad(31)$$

$$T^2(k_x,0,k_y)=T^2(k_x,2\pi/b,k_z)$$
$$=\exp(-ik_zc).\qquad(32)$$

They are the analog equations to Eqs. (19) and (20) for the finite crystal. In writing Eqs. (31) and (32), we used the periodicity of $T(k)$ with the periods $(4\pi/a,0,0)$ and $(0,4\pi/b,0)$ of k. The T matrix itself is determined from Eqs. (31) and (32) up to a sign. Let us choose arbitrarily the sign of one of the functions, say,

$$T(0,k_y,k_z)=\exp(-\tfrac{1}{2}ik_zc).\qquad(33)$$

This corresponds to Eq. (24) for the finite crystal. However, now, for an infinite crystal, we can use the continuity of $T(k)$ and we then have from Eq. (32),

$$T(k_x,0,k_z)=\exp(-\tfrac{1}{2}ik_zc).\qquad(34)$$

We cannot use the minus sign in Eq. (34), because we want $T(0,0,k_z)$ to have the same sign for both Eqs. (33) and (34). By use of the period $(2\pi/a,2\pi/b,2\pi/c)$ of $T(k)$, Eq. (33) can also be rewritten

$$T(2\pi/a,k_y+2\pi/b,k_z+2\pi/c)=\exp(-ik_zc/2).\qquad(35)$$

From here $T(2\pi/a,0,0)=-1$, while from Eq. (34), $T(2\pi/a,0,0)=1$. This shows that there is no continuous and periodic function $T(k)$ satisfying Eqs. (9)-(12). By using this continuity of T as a function of k, we have

shown that no unitary intertwining matrix $T(\mathbf{k})$ exists for the bases of the band representations $(a,1)$ and $(b,1)$.

We have therefore arrived at a very unusual result for band representations which depends on whether the crystal is finite or infinite. For a finite crystal, the band representations $(a,1)$ and $(b,1)$ are equivalent[1] and in Table I we list the values of the phase factor $T(\mathbf{k})$ [relation (7)], which connects their Bloch functions for $N=4$ [by using relation (8), one can also calculate the coefficients $A(\mathbf{R}_n)$ connecting the Wannier functions in relation (6)]. It should be pointed out that despite their linear dependence [relation (6)], the Wannier functions $\psi^{(a,1)}(\mathbf{r})$ and $\psi^{(b,1)}(\mathbf{r})$ have different symmetries, because it is impossible to require either $\psi^{(a,1)}(\mathbf{r})$ or $\psi^{(b,1)}(\mathbf{r})$ to satisfy both equations in relation (5). Such a requirement, together with relation (6), leads to a contradiction. We have here a situation when Wannier functions $\psi^{(a,1)}(\mathbf{r})$ and $\psi^{(b,1)}(\mathbf{r})$ with different symmetries [relation (5)] lead to Bloch functions with identical symmetries.

On the other hand, for infinite crystals the situation changes. Relation (5), which determines the symmetry of Wannier functions, holds as it is; however, relations (6)–(8) depend on whether or not the band representations $(a,1)$ and $(b,1)$ are equivalent. As was proven in Ref. 8, Wannier functions of simple bands can be chosen with exponential decay. Let us then assume that the simple bands $(a,1)$ and $(b,1)$ have exponentially decaying Wannier functions and, correspondingly, their Bloch functions $\psi_{\mathbf{k}}^{(b,1)}(\mathbf{r})$ and $\psi_{\mathbf{k}}^{(a,1)}(\mathbf{r})$ are analytic and periodic in $\mathbf{k}$. From our proof that $T(\mathbf{k})$ for an infinite crystal cannot be a continuous function, it follows that relation (7) cannot hold [the Bloch functions on both sides should be analytic, while $T(\mathbf{k})$ is not continuous]. Also, from the discontinuity of $T(\mathbf{k})$, it follows that the coefficients $A(\mathbf{R}_n)$ in relation (8) do not fall off fast enough. They can therefore not appear in relation (6) where on both sides we have exponentially falling off Wannier functions $\psi^{(a,1)}(\mathbf{r})$ and $\psi^{(b,1)}(\mathbf{r})$. From relations (6)–(8), one concludes that in an infinite crystal the band representations $(a,1)$ and $(b,1)$ are inequivalent.

In summary, we have shown that the bands corresponding to $(a,1)$ and $(b,1)$ have Wannier functions with different symmetries, but their Bloch functions have identical continuity *chords* or symmetries (the precise meaning of continuity chords is given in the second paper of Ref. 3). This is correct for finite and infinite crystals. In the former case, however, the band representations

$(a,1)$ and $(b,1)$ are equivalent, while they are inequivalent in the latter case. Similar results hold for the other nine pairs of simple bands: seven in $F222$ (for all the one-dimensional representations of a,b and c,d Wyckoff positions) and two in $F23$ (for the trivial representations of a,b and c,d Wyckoff positions[12]). We have found, therefore, ten pairs of simple energy bands with identical symmetries for their Bloch functions and different symmetries for their Wannier functions. These bands are represented by band representations which are equivalent in finite crystals, but are inequivalent when the crystal is infinite. The physics of these results is very unusual. We have here for the first time an example where only for infinite crystals is it possible to conclude that simple energy bands with identical symmetries for the Bloch functions cannot appear with identical energies.

[1]R. E. Peierls, *Quantum Theory of Solids* (Clarendon, Oxford, 1955).

[2]G. F. Koster, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1957), Vol. 5.

[3]J. Zak Phys. Rev. Lett. **45**, 1025 (1980), and Phys. Rev. B **25**, 1344 (1982), and **26**, 3010 (1982).

[4]I. P. Burneika and I. B. Levinson, Jr., Akad. Nauk Lit. SSR, Ser. B **4**, 21 (1961).

[5]Jacques des Cloizeaux, Phys. Rev. **129**, 554 (1963), and **135**, A685 (1964).

[6]O. V. Kovalev, Fix. Tverd. Tela (Leningrad) **17**, 1700 (1975) [Sov. Phys. Solid State **17**, 1106 (1975)].

[7]R. A. Evarestov and V. P. Smirnov, Phys. Status Solidi (b) **145**, 391 (1988), and references therein; D. M. Hatch, H. T. Stokes, and R. M. Putnam, Phys. Rev. B **35**, 4935 (1987), and references therein.

[8]G. Nenciu, Commun. Math. Phys. **91**, 81 (1983).

[9]W. Kohn, Phys. Rev. **15**, 809 (1959).

[10]G. G. Hall, Proc. Roy. Soc. London A **202**, 306 (1950); G. G. Hall and J. E. Lennard-Jones, Proc. Roy. Soc. London A **202**, 155 (1950); G. F. Koster, Phys. Rev. **89**, 67 (1953); G. Parzen, Phys. Rev. **89**, 237 (1953).

[11]H. Bacry, L. Michel, and J. Zak in Proceedings of the Sixteenth International Colloquium on Group-Theoretical Methods in Physics, Varna, Bulgaria, 1987 (to be published).

[12]*International Tables for Crystallography,* edited by T. Hahn (Reidel, Dordrecht, 1983).

[13]A. Cashev, M. Glück, and Y. Gur, in *The Irreducible Representations of Space Groups,* edited by J. Zak (Benjamin, New York, 1969).