Electronic level degeneracy in nonsymmorphic periodic or aperiodic crystals

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The theory of space-group representations is extended to aperiodic crystals by reformulating it as the theory of symmetry-required degeneracies of electronic levels that emerges from the Fourier-space approach to crystal symmetry. As an illustration it is shown that the nonvanishing of a simple linear combination of phase functions belonging to commuting elements from the little group of **q** requires the degeneracy of all levels with generalized Bloch wave vector **q**. This condition is applied to all cubic and icosahedral centrosymmetric nonsymmorphic space groups, and to the two nonsymmorphic space groups of periodic crystals that have no systematic extinctions. [S0163-1829(97)00146-X]

One of the more subtle applications of the theory of group representations in solid-state physics is the demonstration that in nonsymmorphic crystals the orbital electronic energy levels at certain wave vectors are necessarily degenerate. We have reformulated that analysis in a manner that makes no use of translational symmetry, applying equally well to periodic or aperiodic crystals. Our reformulation is based on the Fourier-space approach to crystal symmetry discovered by Bienenstock and Ewald,[1] and extended to aperiodic crystals by Rokhsar, Wright, and Mermin.[2] The link between nonsymmorphic crystal symmetry and level degeneracy emerges so directly when that symmetry is characterized in terms of the ''phase-functions'' of Fourier-space crystallography, that our analysis may also be of use to those interested only in periodic crystals.

Consider the orbital levels of an electron in a potential $V(\mathbf{r})$ produced by a periodic or quasiperiodic array of ions with charge density $\rho(\mathbf{r})$:

$$V(\mathbf{r})=\int d^3\mathbf{r}'\,v(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}'), \tag{1}$$

or in Fourier space,

$$V(\mathbf{k})=v(\mathbf{k})\rho(\mathbf{k}). \tag{2}$$

If $v(\mathbf{r})$ is taken to be the bare Coloumb interaction then $v(\mathbf{k})$ will depend only on the magnitude of $\mathbf{k}$, but if a screened interaction is used it might have lower symmetry. In what follows we shall assume that $v(\mathbf{k})$ is at least invariant under every operation g in the point group of the ionic density ρ. This ensures that the Fourier coefficients of the one-electron potential $V(\mathbf{k})$ have all the symmetry-related properties possessed by the ionic Fourier coefficients $\rho(\mathbf{k})$. We review these properties in the next paragraph. (A more extensive review can be found in Sec. II of Ref. 3.)

The $V(\mathbf{k})$ are zero except on a set L of three-dimensional wave vectors consisting of all integral linear combinations of D integrally independent wave vectors, for some $D\geqslant 3$, known as the *rank* of L. When $D=3$ the potential is periodic and the set of wave vectors L is the familiar reciprocal lattice. When D exceeds 3, the potential is quasiperiodic. The point group G of the potential V is that subgroup of the point group G_L of L under which the $V(\mathbf{k})$ are invariant except for an appropriate change of phase:

$$V(g\mathbf{k})=e^{2\pi i\Phi_g(\mathbf{k})}V(\mathbf{k}). \tag{3}$$

The $V(\mathbf{k})$ acquire this property from the analogous property for the Fourier coefficients $\rho(\mathbf{k})$ and the invariance of the interaction $v(\mathbf{k})$ under the operations in G. The *phase functions* Φ_g are linear (modulo unity) on L and satisfy the *group compatibility condition*

$$\Phi_{gh}(\mathbf{k})\equiv\Phi_g(h\mathbf{k})+\Phi_h(\mathbf{k}) \tag{4}$$

(where ''$\equiv$'' denotes equality modulo unity.) These restrictions on the phase functions are necessary and sufficient for the potential (or the ionic density) to have its positionally averaged autocorrelation functions of all orders invariant under all operations of G. Two sets of phase functions Φ and Φ' characterize the same symmetry type and are said to be *gauge equivalent* if there is a *gauge function* χ, linear (modulo unity) on L, such that

$$\Phi'_g(\mathbf{k})\equiv\Phi_g(\mathbf{k})+\chi(g\mathbf{k}-\mathbf{k}). \tag{5}$$

The existence of such a gauge function is necessary and sufficient for the two sets of phase functions to characterize potentials with identical autocorrelation functions of all orders. In the periodic case $\Phi_g(\mathbf{k})$ must be of the form $\mathbf{a}_g\cdot\mathbf{k}$ where $\mathbf{a}_g$ is a translation that combines with g to leave the potential identical to what it was before g was applied, and a change of gauge is simply the change in $\mathbf{a}_g$ brought about by a change in the origin about which g acts. In the aperiodic case point-group symmetry is defined entirely in terms of positionally averaged autocorrelation functions so no origin is relevant. No translation of the rotated quasiperiodic potential is identical to its unrotated form, and the more general formulation in terms of phase and gauge functions is necessary. Space-group types are specified in terms of gauge-equivalence classes of phase functions, and have been tabulated for a variety of cases in Refs. 3 and 4.

As in the periodic case, the one-electron Schrödinger equation in Fourier space only couples wave vectors differing by a vector of L, so solutions are of the form

$$\psi_{\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{k}\ \text{in}\ L} \psi_{\mathbf{q}}(\mathbf{k}) e^{i(\mathbf{q}+\mathbf{k})\cdot\mathbf{r}}. \tag{6}$$

The general eigenvalue problem separates into independent problems for each generalized Bloch wave vector $\mathbf{q}$, with an effective Hamiltonian $h_{\mathbf{q}}$ given in the momentum representation by

$$\langle \mathbf{k}|h_{\mathbf{q}}|\mathbf{k}'\rangle = t(\mathbf{k}+\mathbf{q})\,\delta_{\mathbf{k},\mathbf{k}'} + V(\mathbf{k}-\mathbf{k}'). \tag{7}$$

The Hamiltonian h_q acts on the space $\mathcal{H}_L$ spanned by plane waves with wave vectors from L. For fixed $\mathbf{q}$ we investigate whether this eigenvalue problem has any degeneracies stemming from the behavior (3) of the potential V under rotations, and from the rotational invariance of the kinetic energy t:

$$t(g\mathbf{k}) = t(\mathbf{k}). \tag{8}$$

If we define unitary operators $W(g)$ on $\mathcal{H}_L$ that permute the vectors $\mathbf{k}$ of L by rotations g in the point group G,

$$W(g)|\mathbf{k}\rangle = |g\mathbf{k}\rangle, \tag{9}$$

then we have

$$\begin{aligned}\langle \mathbf{k}|W(g)^{\dagger} h_{\mathbf{q}} W(g)|\mathbf{k}'\rangle &= \langle g\mathbf{k}|h_{\mathbf{q}}|g\mathbf{k}'\rangle \\ &= t(g\mathbf{k}+\mathbf{q})\,\delta_{\mathbf{k}\mathbf{k}'} + e^{2\pi i \Phi_g(\mathbf{k}-\mathbf{k}')} V(\mathbf{k}-\mathbf{k}').\end{aligned} \tag{10}$$

Because of the phase acquired by the potential energy and the shift in wave vector acquired by the kinetic energy, $W(g)$ fails to be a symmetry of $h_{\mathbf{q}}$. One can, however, remove the phase factor from the potential energy without altering the kinetic energy by an additional unitary transformation, diagonal in the basis $|\mathbf{k}\rangle$. And if the wave vector $\mathbf{q}$ has the special property that

$$\mathbf{k}_g = \mathbf{q} - g\mathbf{q} \tag{11}$$

is in L, then one can remove the shift in wave vector from the kinetic energy without altering the potential energy by a further unitary transformation that shifts L by $-\mathbf{k}_g$. Thus the unitary operator $U(g)$ defined by

$$U(g)|\mathbf{k}\rangle = e^{2\pi i \Phi_g(\mathbf{k})}|g\mathbf{k}-\mathbf{k}_g\rangle, \tag{12}$$

can be directly verified to satisfy

$$U(g)^{\dagger} h_{\mathbf{q}} U(g) = h_{\mathbf{q}}. \tag{13}$$

The set of all operations from G for which the momentum space translation (11) is a vector of L (which could be 0) is the *little group* $G_{\mathbf{q}}$ of $\mathbf{q}$. The little group is a subgroup of G: if $\mathbf{k}_g$ and $\mathbf{k}_h$ are in L then so is $\mathbf{k}_{gh}$, since L is closed under addition and under operations g of G, and

$$\mathbf{k}_{gh} = \mathbf{k}_g + g\mathbf{k}_h. \tag{14}$$

The complete expression of the point-group symmetry of the potential at the level of the effective Hamiltonian $h_{\mathbf{q}}$ is that $h_{\mathbf{q}}$ commutes with the unitary operators $U(g)$ for all g in the subgroup $G_{\mathbf{q}}$.

It follows from the definition (12) and the group compatibility condition (4) that

$$U(g)U(h) = e^{-2\pi i \Phi_g(\mathbf{k}_h)} U(gh). \tag{15}$$

The $U(g)$ are said to constitute a unitary *ray representation* of the little group $G_{\mathbf{q}}$ with *factor system*

$$\lambda(g,h) = e^{-2\pi i \Phi_g(\mathbf{k}_h)}. \tag{16}$$

Since each $U(g)$ commutes with $h_{\mathbf{q}}$, a nondegenerate electronic level constitutes a one-dimensional invariant subspace of this ray representation; conversely the energy levels of $h_{\mathbf{q}}$ will be necessarily degenerate if and only if this ray representation of the little group has no one-dimensional invariant subspace.

At this point the analysis makes contact with the conventional theory of ray representations.[5–11] The novelty of the aperiodic case consists of the relevance of ray representations (15) for ''noncrystallographic'' point groups and/or the possibility of novel ray representations for point groups of periodic crystals when the rank D exceeds 3. We do not pursue this further here, focusing instead on a simple and important necessary condition for the existence of nondegenerate levels.

Let g and h be two elements of the little group $G_{\mathbf{q}}$ that *commute*. It follows from Eq. (15) that

$$U(g)U(h) = e^{-2\pi i[\Phi_g(\mathbf{k}_h) - \Phi_h(\mathbf{k}_g)]} U(h)U(g). \tag{17}$$

But since the combined action of $U(g)$ and $U(h)$ on any *one*-dimensional invariant subspace must be independent of the order in which they are applied, if such a subspace exists then

$$\Phi_g(\mathbf{k}_h) - \Phi_h(\mathbf{k}_g) \equiv 0. \tag{18}$$

Consequently, if

$$\Phi_g(\mathbf{k}_h) - \Phi_h(\mathbf{k}_g) \not\equiv 0 \tag{19}$$

for two commuting elements of the little group, then all levels of $h_{\mathbf{q}}$ must be degenerate. We call such a degeneracy a *necessary* degeneracy. Note that under a change of gauge (5)

$$\Phi'_g(\mathbf{k}_h) - \Phi'_h(\mathbf{k}_g) = \Phi_g(\mathbf{k}_h) - \Phi_h(\mathbf{k}_g) + \chi(hg\mathbf{q} - gh\mathbf{q}), \tag{20}$$

so if g and h commute then the combination of phase functions appearing in the critical condition (19) is invariant over gauge equivalence classes.

In Fourier space crystallography up to now the only such invariant phases of direct physical interest have been the values of a phase function Φ_g at vectors of L in the invariant space of g. Nonzero values require the extinction of the Bragg peaks associated with such wave vectors.[12] For commuting g and h in the little group of a wave vector $\mathbf{q}$ not in L, the combination

$$\Phi_g(\mathbf{q} - h\mathbf{q}) - \Phi_h(\mathbf{q} - g\mathbf{q}) \tag{21}$$

emerges here as another distinct example of a physically relevant invariant phase, whose nonvanishing (modulo unity) requires the degeneracy of all electronic levels with wavevector $\mathbf{q}$ modulo L. Note that (21) necessarily vanishes if $\mathbf{q}$ itself is in L, as a consequence of the group compatibility

condition (4) applied to $gh=hg$. Necessary degeneracies do not occur at wave vectors in L. We conclude with two examples, one periodic and one more general, of such necessary degeneracies.

Non-symmorphic space groups without extinctions. The space group $I2_12_12_1$ and the space group $I2_13$ to which it expands when the orthorhombic symmetry degenerates to cubic are unique among the 230 symmetry types of three-dimensional periodic crystals in being nonsymmorphic space groups that give rise to no Bragg-peak extinctions. In the language of Fourier-space crystallography there is no phase function Φ_g with any nonzero values for $\mathbf{k}$ in the invariant subspace of g, and there are therefore no extinctions. Yet there is no gauge in which all phase functions are zero, so the space-group symmetry is nonsymmorphic. (In the special language of periodic crystals, every point-group operation leaves the density invariant without the need for an additional translation when applied about some appropriate origin, but there is no single origin about which every point-group operation leaves the density invariant.)

The nonsymmorphic character of $I2_12_12_1$ is concisely established in Ref. 3 by the display of a gauge-independent linear combination of phase functions which is nonzero, even though any one of those phase functions vanishes in some gauge. There is no obvious *geometrical* interpretation to such a combination of phase functions associated with more than a single point-group operation, but, as noted below, it does have a direct *physical* interpretation in terms of condition (19) for a necessary degeneracy.

The basis of the face-centered-orthorhombic reciprocal lattice L consists of the three vectors $\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3$ that can be expressed in terms of three mutually orthogonal vectors $\mathbf{a},\mathbf{b},\mathbf{c}$ of different lengths as

$$\mathbf{b}_1=\mathbf{b}+\mathbf{c},\quad \mathbf{b}_2=\mathbf{c}+\mathbf{a},\quad \mathbf{b}_3=\mathbf{a}+\mathbf{b}. \tag{22}$$

The generators of the point group $G=222$ can be taken to be the two twofold rotations r_a and r_b about the axes $\mathbf{a}$ and $\mathbf{b}$. These commute and the rotation about $\mathbf{c}$ is their product, $r_c=r_ar_b$. The wave vector

$$\mathbf{q}=\tfrac{1}{4}(\mathbf{b}_1,\mathbf{b}_2,\mathbf{b}_3)=\tfrac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c}), \tag{23}$$

(called the ''R point'') has the entire point group

$$G=222=\{e,r_a,r_b,r_c\} \tag{24}$$

as its little group $G_{\mathbf{q}}$. The reciprocal-lattice vectors $\mathbf{k}_g=\mathbf{q}-g\mathbf{q}$ are easily verified to be

$$\mathbf{k}_{r_a}=\mathbf{b}_1,\quad \mathbf{k}_{r_b}=\mathbf{b}_2,\quad \mathbf{k}_{r_c}=\mathbf{b}_3. \tag{25}$$

The phase functions for the twofold rotations can be taken in an appropriate gauge to be (see Table XVII of Ref. 3)

$$\begin{aligned}
&\Phi_{r_a}(\mathbf{b}_1)=\tfrac{1}{2},\quad \Phi_{r_a}(\mathbf{b}_2)=\tfrac{1}{2},\quad \Phi_{r_a}(\mathbf{b}_3)=0,\\
&\Phi_{r_b}(\mathbf{b}_1)=0,\quad \Phi_{r_b}(\mathbf{b}_2)=\tfrac{1}{2},\quad \Phi_{r_b}(\mathbf{b}_3)=\tfrac{1}{2},\\
&\Phi_{r_c}(\mathbf{b}_1)=\tfrac{1}{2},\quad \Phi_{r_c}(\mathbf{b}_2)=0,\quad \Phi_{r_c}(\mathbf{b}_3)=\tfrac{1}{2}.
\end{aligned} \tag{26}$$

[This can easily be confirmed by checking that (26) satisfies the group compatibility condition (4) for all possible choices of g and h from (24).]

With these phase functions we have, for example,

$$\Phi_{r_a}(\mathbf{k}_{r_b})-\Phi_{r_b}(\mathbf{k}_{r_a})\not\equiv 0. \tag{27}$$

Since r_a and r_b commute, it follows from the general analysis above that the levels of $h_{\mathbf{q}}$ are necessarily degenerate. This nonzero linear combination of phases appearing in Eq. (27) is precisely the gauge-independent linear combination pulled, as it were, out of a hat, on p. 33 of Ref. 3 to demonstrate that $I2_12_12_1$ was nonsymmorphic in spite of the absence of any gauge-independent nonzero values of individual phase functions. The nonsymmorphicity of $I2_12_12_1$ (and, by a similar argument, $I2_13$) manifests itself not in extinctions, but in the existence of necessary degeneracies.

Centro-symmetric space groups with mirror planes. Since the inversion i commutes with any other point-group element, opportunities to satisfy condition (19) for necessary degeneracies are easy to find in space groups with centrosymmetric point groups G. Note that because

$$i\mathbf{k}=-\mathbf{k}, \tag{28}$$

if $\Phi_i\not\equiv 0$ for some wave vectors $\mathbf{k}$, then with a change of gauge (5) that takes as the gauge function $\chi=\frac{1}{2}\Phi_i$, one can take

$$\Phi_i(\mathbf{k})\equiv 0 \tag{29}$$

for all $\mathbf{k}$ in L. Within this gauge all other phase functions are restricted to have the values 0 or $\frac{1}{2}$. This follows from expanding both sides of the identity $\Phi_{gi}\equiv\Phi_{ig}$ using the group compatibility condition (4).

Consider as an example the case where G also contains a mirror m, and consider a wave vector $\mathbf{q}$ that has both i and m in its little group $G_{\mathbf{q}}$. If i is in $G_{\mathbf{q}}$ then $\mathbf{k}_i=\mathbf{q}-i\mathbf{q}=2\mathbf{q}$ must be in L, so we are restricted to wave vectors $\mathbf{q}$ of the form

$$\mathbf{q}=\tfrac{1}{2}\mathbf{k} \tag{30}$$

for any $\mathbf{k}$ in L. If the mirror m is also to be in $G_{\mathbf{q}}$ then $\mathbf{k}_m=\mathbf{q}-m\mathbf{q}$ must also be in L. The vector $\mathbf{k}_m$, however, is just the component $\mathbf{k}_\perp$ of $2\mathbf{q}=\mathbf{k}$ normal to the plane of m. But if $\mathbf{k}$ and its component $\mathbf{k}_\perp$ normal to the plane of m are both in L then so is its component $\mathbf{k}_\parallel$ in the invariant plane of m.

The wave vectors $\mathbf{q}$ that have i and m in their little group are therefore just those of the form

$$\mathbf{q}=\tfrac{1}{2}(\mathbf{k}_\perp+\mathbf{k}_\parallel), \tag{31}$$

where $\mathbf{k}_\perp$ and $\mathbf{k}_\parallel$ are any vectors of L (including 0), respectively, perpendicular to and contained in the invariant plane of m.

In the gauge in which Φ_i vanishes, condition (19) for a necessary degeneracy at such a $\mathbf{q}$ reduces simply to

$$\Phi_m(\mathbf{k}_i)\equiv\Phi_m(2\mathbf{q})\equiv\Phi_m(\mathbf{k}_\perp)+\Phi_m(\mathbf{k}_\parallel)\not\equiv 0. \tag{32}$$

For both of the centrosymmetric nonsymmorphic rank-6 icosahedral space groups $P\overline{5}\,\overline{3}(2/q)$ and $I^*\overline{5}\,\overline{3}(2/q)$, as well as for all the centrosymmetric nonsymmorphic rank-3 cubic space groups it can be shown that the mirror phases at vectors $\mathbf{k}_\perp$ of L perpendicular to the mirror vanish in the gauge in which $\Phi_i\equiv 0$. For example, in the case of

$P\bar{5}3(2/q)$ Table VIII in Ref. 3 gives the following phases on a basis of vectors along the six fivefold axes, $\mathbf{v}_1,..,\mathbf{v}_6$:

$$\Phi_m = \tfrac{1}{2}\tfrac{1}{2}0000. \tag{33}$$

The vectors of L perpendicular to the plane of m in this basis are all the integral linear combinations of

$$\mathbf{v}_3+\mathbf{v}_6 \quad \text{and} \quad \mathbf{v}_4+\mathbf{v}_5, \tag{34}$$

to both of which Eq. (33) assigns a vanishing mirror phase. Tables II–VIII in Ref. 3 lead to the same conclusion for the other centrosymmetric rank-3 cubic and rank-6 icosahedral space groups. So for these cubic and icosahedral space groups we have $\Phi_m(\mathbf{k}_\perp)=0$, and the rule for degeneracies reduces to the condition $\Phi_m(\mathbf{k}_\parallel)\neq 0$. This is just the extinction condition for the component of $2\mathbf{q}$ in the plane of m. So a vector $\mathbf{q}$ will have necessarily degenerate energy levels if it is half of a vector $\mathbf{k}$ of L whose projection into the plane of m is an extinguished vector of L.

The more general condition (32) is relevant in some of the nonsymmorphic space groups of periodic orthorhombic crystals, where the Φ_m need not vanish on reciprocal-lattice vectors normal to the plane of m. Considerations along the above lines offer a straightforward way to understand level degeneracies in crystals with nonsymmorphic symmetry, while developing that subject in a way that applies uniformly to periodic and aperiodic crystals.

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