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Band structure, density waves and symmetries of aperiodic crystals

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There are three types of invariants in crystals. The first two, corresponding to electronic degeneracies, are well known, but the third is novel, realized in incommensurate crystals of non-minimal rank. Since the first two invariants have consequences in band structure, it is natural to look there for the third type as well. Rather than developing an atomic or tiling model with the third type of symmetry, we introduce a tight-binding approach based on a density-wave pattern, which is easy to generate from the Rokhsar–Wright–Mermin phase functions.

Symmetries have consequences. In solids, the space group has long served as a launching point for the study of electronic band structure. Two developments in aperiodic crystallography have refocused attention on the connection between space-group symmetry and its electronic consequences. The first is the Rokhsar–Wright–Mermin Fourier-space approach [1, 2]. Beside yielding the first correct enumeration of the icosahedral space groups [3, 4] and a simplification in presentation, this approach also provides a compact notation for one elementary consequence of symmetry, the necessary extinctions in diffraction that occur for all but two of the 157 non-symmorphic periodic space groups in three dimensions [5–7]. In this approach, the Fourier component $\rho(\mathbf{K})$ of the electronic density at a reciprocal-lattice vector $\mathbf{K}$ is related to that at $g\mathbf{K}$, where g is any operation in the point group G, by

$$\rho(g\mathbf{K}) = \exp(2\pi i \Phi_g(\mathbf{K}))\rho(\mathbf{K}). \tag{1}$$

All the information customarily found in the space group is encoded in the phase function, Φ. It follows that if

$$\Phi_g(\mathbf{K}) \neq 0 (\mathrm{mod}\ 1) \quad \text{and} \quad g\mathbf{K} = \mathbf{K}, \tag{2}$$

then $\rho(\mathbf{K}) = 0$, an extinction. Values of Φ_g are determined only up to integers. There is an additional degree of gauge freedom, corresponding to arbitrary translations of the origin and (for aperiodic crystals) uniform phason strain: one can add to $\Phi_g(\mathbf{K})$

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any lattice-linear function of the form $\chi(g\mathbf{K}-\mathbf{K})$ without changing any translationally invariant physical properties [6]. If $g\mathbf{K}=\mathbf{K}$, the phase value $\Phi_g(\mathbf{K})$ is gauge-invariant, so choice of gauge cannot remove an extinction. When a Bragg peak $\mathbf{K}$ is absent in diffraction, the corresponding Fourier component of the potential is also absent, so bands meeting at the Bragg plane bisecting $\mathbf{K}$ cross (see figure 1, centre column) instead of repelling (left column). The value given by equation (2) is called a type-I invariant.

Two space groups, $I2_13$ and $I2_12_12_1$, require no extinctions but instead exhibit a peculiar kind of "band-sticking" (see figure 1, right column). It has long been known that in some space groups, at particular points $\mathbf{q}$, all electronic levels are at least doubly degenerate [8, 9]. König and Mermin re-examine this phenomenon [6, 10–12]. In these space groups, there exist no gauge-invariant quantities of the form given by equation (2); however, there is a gauge-invariant linear combination of phase-function values,

$$\Phi_g(\mathbf{q}-h\mathbf{q})-\Phi_h(\mathbf{q}-g\mathbf{q}), \tag{3}$$

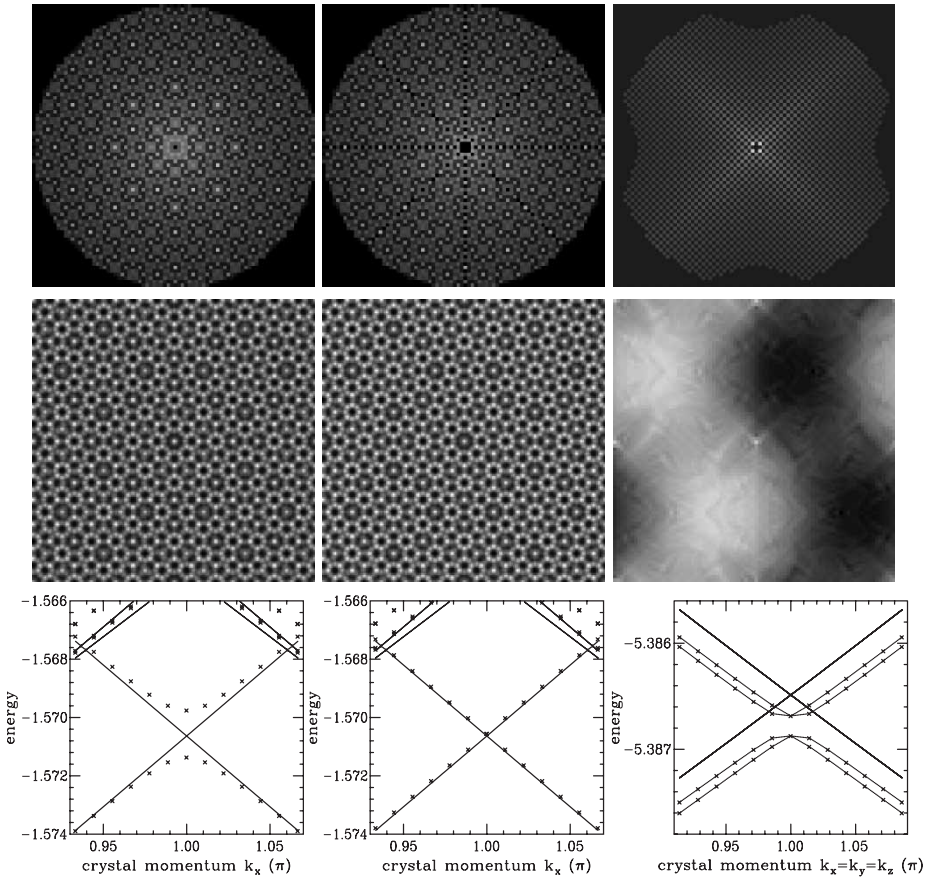

Figure 1. Three density-wave patterns and associated band structures: from left to right, *p*8*mm* (band repulsion), *p*8*gm* (level crossing), and $I2_12_12_1$ (band sticking). Top to bottom, log diffraction intensity, part of a density-wave pattern, band structure. Solid lines are free-electron bands.

where $\mathbf{q}$ is not in the lattice but $\mathbf{q} - g\mathbf{q}$ and $\mathbf{q} - h\mathbf{q}$ are, and where g and h commute. The non-vanishing of this gauge invariant (called type-II) implies degeneracy at $\mathbf{q}$ in all bands.

The second development connecting symmetry and band structure is the application of ideas and methods from algebraic topology to the Fourier-space approach [13–17]. Viewed this way, gauge invariants given by equations (2)–(3) are distinct classes in homology. Beside having the advantage of a certain conciseness, the homological approach has overcome the requirement, common to both "superspace" [18, 19] and Fourier-space [20–22] approaches, of proceeding one lattice at a time. Homology was also key to proving the existence of a third type of irreducible gauge invariant, of the form $\frac{2}{N}\sigma \cap c$, where $\sigma \in H^1(H, L)$, $c \in Z_2(H, \mathbb{Z})$, and $H \subseteq G$ (notation as in Fisher and Rabson [17]). The simplest example of a space group that will exhibit this invariant has the (crystallographic) point group 422 (D_4), generated by a fourfold rotation r and perpendicular dihedral rotation d along the $\hat{x}$ axis. The reciprocal lattice generated by vectors b, db, rb, and rdb in the $z = 0$ plane and by the out-of-plane vector $b_5 = \hat{z} + ((1 + r)/2)(b - db)$ is periodic in the $\hat{z}$ direction and (provided the tangent of the angle between b and the $\hat{x}$-axis is irrational) has two incommensurate modulations in the plane. For this example, Fisher and Rabson have calculated [23] that the phase function given by $\Phi_g(\mathbf{K}) = 0$ if $\mathbf{K}$ lies in the xy plane and $\Phi_g(\mathbf{K}) = j/2$ if $\mathbf{K} = b_5$ and $g = r^j$ or $g = dr^j$ exhibits the type-III invariant. The non-zero gauge-invariant quantity comparable to equations (2)–(3) is $\Phi_r(b_5) - \Phi_d(b_1) = 1/2$. We note that tetragonal structures with two incommensurate modulations have been reported [24, 25], helping to motivate the present work.

This brings us to electronic structure. Although we have described completely the space-group symmetry of the third invariant [17], the consequences of this symmetry are not immediately obvious. Extrapolating from the first two types of homological invariant, it seems sensible to examine band structure. However, it is not always simple to come up with an atomistic or tiling model for a given symmetry. We have therefore developed a program for calculating a tight-binding band structure based on a density-wave pattern. It is simple to generate a density-wave pattern with a space-group symmetry prescribed in Fourier space: for example, Rokhsar *et al.* [2] constructed density-wave patterns for the space groups *p8mm* and *p8gm*. By contrast, establishing a tiling for the latter required a long calculation [26].

Without an atomistic model, we sample an external potential on a discrete simple-cubic lattice of side u, applying the tight-binding Hamiltonian [27],

$$\mathcal{H} = \text{const.} - t \sum_{\langle i,j \rangle} \left(c_i^\dagger c_j + c_j^\dagger c_i \right) + \sum_i V(x_i) c_i^\dagger c_i, \tag{4}$$

where the first sum runs over nearest-neighbour sample points and c_i is the annihilation operator for a spinless electron at site x_i. The pseudopotential V is chosen to have the desired space-group symmetry.

We have not seen precisely this method applied previously, although others have investigated dynamical systems on a quasiperiodic density-wave pattern [28] or done tight-binding calculations in which in quasiperiodicity is provided by the geometry of nearest-neighbour connections or by spatial modulation of t [29–36]. Equation (4) is related to the treatment of Ueda and Tsunetsugu [37], although there the potential takes on only discrete values and separability makes an analytical transfer-matrix approach feasible. We emphasise that V is chosen only to have the desired symmetry;

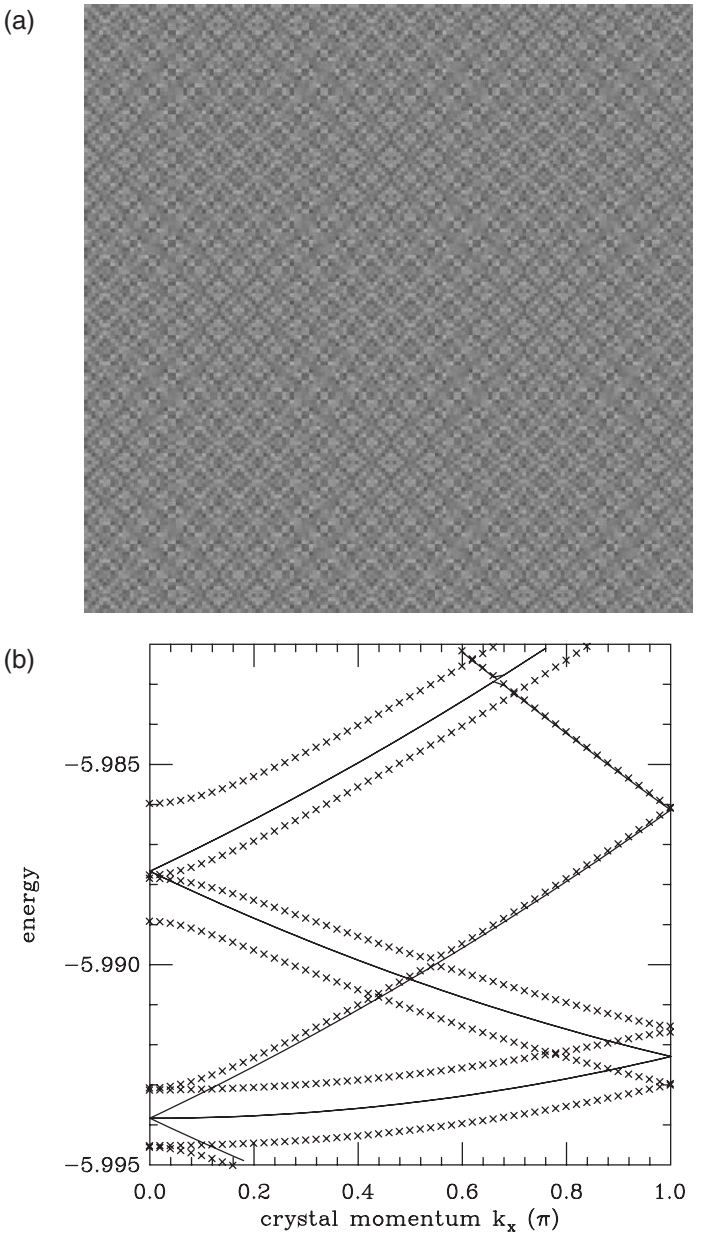

Figure 2. (a) Portion of a density-wave pattern that should exhibit the type-III invariant. (b) A variety of band splittings from the type-III density compared to free-electron dispersion (solid).

we are not starting with a known material, nor do we account for the symmetry requirements of an incommensurate phase transition [38]. In general, V will not be suitable for a total-energy calculation.

We start with a set of Fourier amplitudes $\rho(\mathbf{K})$ satisfying equation (1) as well as the condition of reality in direct space, $\rho(-\mathbf{K}) = \rho(\mathbf{K})^*$. For a type-I

non-symmorphic Φ, this means that the complex number $\rho(\mathbf{K})$ will vanish at certain points, while for types II and III it will satisfy additional phase relationships. The magnitudes of $\rho(\mathbf{K})$ fall off with distance from the origin and with the sum of the absolute values of the coefficients of the lattice generators. The support for possible $\mathbf{K}$ points is itself discrete, so approximants are necessary. For example, the generating vectors for the eightfold lattice in two dimensions may be chosen as $\{(17, 0), (12, 12), (0, 17) (-12, 12)\}$ (in units of $2\pi/u$). The pseudopotential V is then the Fourier transform of ρ.

For a periodic space group, the resulting density-wave pattern constitutes a unit cell. For any $\mathbf{q}$ in reciprocal space, Bloch's theorem applied to a stacking of unit cells on a torus reduces equation (4) to a finite matrix, which is diagonalized with the Lanczos algorithm using the HLZPACK package (O.A. Marques, 2000). Quasiperiodic patterns are treated the same way; as the approximant cells become larger, the electronic features due to periodicity should become less important.

Figure 1 gives three examples of the method, each compared to free-electron dispersion (solid). The left column of the figure shows generic band repulsion in the quasiperiodic symmorphic space group *p*8*mm*. The top shows a diffraction pattern, the middle, four resulting square unit cells, centred on a point of approximate eightfold symmetry, and the bottom an example of band repulsion. The centre column of the figure shows the related non-symmorphic space group, *p*8*gm*; where bands repelled in *p*8*mm*, they cross in *p*8*gm* due to the extinction of a Bragg peak. The right column of the figure shows part of a density-wave pattern with space group $I2_12_12_1$ and an example of band sticking at the R point of the conventional orthorhombic cell. (The same point for the symmorphic space group *I*222 [not shown] has bands repelling instead of sticking.)

Using homology to construct the Rokhsar–Wright–Mermin phase function, we place constraints on the Fourier and therefore real-space density, the latter of which serves as an external potential for a tight-binding electronic calculation on a discretised space. We have demonstrated that the calculation identifies expected features for the type-I and type-II invariants (figure 1). This sets the stage for applying the same procedure to a type-III density (figure 2).

Acknowledgments

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