Projection operator approach to unfolding supercell band structures

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While the methodology of band structure unfolding has been established in several publications, the original derivations of spectral weights are cumbersome partly because they involve a reference Hamiltonian or Bloch function. The recent introduction of a unified projection operator allows a more straightforward approach and an easier derivation of unfolding formulas. By using this method, simplified descriptions of unfolded spectral weights are developed in this work for both plane waves and localized orbitals. Several pedagogical examples are also presented to illustrate the procedures and various aspects of band structure unfolding.

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I. INTRODUCTION

The band structure property of electron or phonon spectra of a solid is a consequence of the description of the periodic system in terms of a primitive unit cell. For some systems it is more convenient to use a supercell (SC), consisting of several primitive unit cells, to describe the system and calculate its electronic structure. This results in folded bands in a smaller Brillouin zone (BZ), which makes it harder to interpret the band structure. A challenging question is how to recover, from the supercell calculation alone, the original band structure in the larger primitive Brillouin zone (PBZ). An unfolding procedure must reproduce the original bands if the system is perfectly periodic, or give an effective band structure (EBS) if it contains imperfections and is only approximately periodic. The EBS has great interpretative value as it is easy to compare it with the band structure of the perfect system and to discover perturbations caused by disorder. Furthermore, it is the EBS rather than the folded bands that is in correspondence with angle-resolved photoemission spectroscopy (ARPES) measurements.

In the past few years, several studies have developed unfolding methods based on the symmetry properties of SC eigenfunctions. These are based on comparing the eigenfunction with a reference Bloch function belonging to the underlying lattice. Although, these projecting functions are required by the formalism, the final results are independent of them. A key idea that facilitates the conceptual description is to express the band structure in terms of the spectral function. This naturally leads to unfolded spectral weights, which can be conveniently used to unfold the band structure. The unfolding formulas depend on basis functions used in the electronic structure calculation and have been derived for plane-waves, the tight-binding method based on Wannier functions, and linear combination of atomic orbitals (LCAO). However, while the spectral weight expressions are simple to understand, some of the derivations are tedious. A few studies have circumvented lengthy derivations and simply defined the spectral weight formulas based on heuristic reasoning.

Some recent papers have discussed the group theoretical aspects of the unfolding method. A second key idea that has emerged from these studies and which can be used to develop an unfolding procedure is a \( k \) projection operator. The virtue of this approach is that it does not require an artificial reference system, as it generates its own. However, it is equivalent to the previous approach based on the analysis of the spectral function.

There are a great number of publications that use unfolding to interpret first-principles electronic structure calculations of alloys, surfaces and disordered solids. Applications have also appeared that generalize unfolding to other operators.

The purpose of this paper is to present simplified derivations of unfolding formulas, which is made possible by using the projection operator. A detailed description is given in Sec. II. A number of pedagogical examples are also presented in detail, in Sec. III, to illustrate the unfolding procedure and various aspects of effective band structures.

II. THEORY

A. The projection operator

The notational convention to be followed in this paper is to use upper and lower case letters for supercell (SC) and primitive cell (PC) variables. A supercell contains a number \( N \) of primitive unit cells at positions \( r_j \). A set of \( N \) reciprocal lattice vectors of the SC system, \( G_i \), unfold a wavevector \( K \) in the supercell Brillouin zone (SBZ) onto wavevectors \( k = K + G_i \) in the primitive Brillouin zone (PBZ). Using the translation operator, defined by \( \mathcal{T}(r)\psi(x) = \psi(x + r) \), it was shown in Ref. [9] that the operator

\[
\mathcal{P}_{K+G_i} = \frac{1}{N} \sum_{j=1}^{N} \mathcal{T}(r_j)e^{-i(K+G_i) \cdot r_j},
\]

projects out of a supercell eigenfunction with wavevector \( K \) a Bloch function with wavevector \( k \). Equation (1) can...
also be justified on the basis of the general projection operator of group theory,
\[ P_k = \frac{1}{N} \sum_{j=1}^{N} \Gamma^{(k)} \{ \mathcal{G}(r_j) \} \mathcal{G}(r_j), \]  
(2)

where \( \Gamma \) is an irreducible representation of the group, which is \( e^{i \mathbf{k} \cdot \mathbf{r}} \) for the translation group. An elementary proof that Eq. (1) has the desired projective property is given below.

**Spectral weight**

The projected components of an eigenstate \( | \mathbf{K}, \mathbf{J} \rangle \) are not normalized. Their norms, generally in the \([0,1] \) interval, can be used as spectral weights of the unfolding procedure,
\[ W_{\mathbf{K}, \mathbf{J}}(G_i) = \langle P_k \psi_{\mathbf{K}, \mathbf{J}} | P_k \psi_{\mathbf{K}, \mathbf{J}} \rangle = \langle \mathbf{K}, \mathbf{J} | P_k | \mathbf{K}, \mathbf{J} \rangle, \]
(3)

where the idempotent and Hermitian properties of projection operator are used in the last step.

**B. Plane-wave representation**

To prove that Eq. (1) is the required projection operator, two conditions must be satisfied. First, the operator must project out of an SC wave function a PC Bloch function and, second, it must be idempotent. An elementary proof can be given by using a plane-wave representation, while unfolded spectral weights are found as a corollary.

An SC eigenfunction can be represented as an expansion in plane waves,
\[ \psi_{\mathbf{K}}(\mathbf{x}) = \sum_{\mathbf{G}} C_{\mathbf{K} - \mathbf{G}} e^{i(\mathbf{K} - \mathbf{G}) \cdot \mathbf{x}}, \]
(4)

where the sum is over the set of all reciprocal lattice vectors of the SC system. It is easy to verify a useful Fourier relation,
\[ \frac{1}{N} \sum_{j=1}^{N} e^{-i(\mathbf{G} + \mathbf{G}_i) \cdot \mathbf{r}_j} = \sum_{\mathbf{g}} \delta_{\mathbf{G} + \mathbf{G}_i, \mathbf{g}}, \]  
(5)

where \( \{ \mathbf{g} \} \subset \{ \mathbf{G} \} \) are the PC reciprocal lattice vectors. Applying the operator \( \mathcal{P} \) to wave function \( \psi_{\mathbf{K}} \) and using the Fourier relation \( \mathcal{P} \) gives
\[ \mathcal{P}_{\mathbf{K} + \mathbf{G}_i} \psi_{\mathbf{K}}(\mathbf{x}) = \sum_{\mathbf{g}} C_{\mathbf{K} + \mathbf{G}_i - \mathbf{g}} e^{i(\mathbf{K} + \mathbf{G}_i - \mathbf{g}) \cdot \mathbf{r}}, \]  
(6)

which is a PC Bloch function with wavevector \( \mathbf{K} + \mathbf{G}_i \). This proves the first condition. Applying \( \mathcal{P} \) a second time, and observing that \( e^{-i \mathbf{g} \cdot \mathbf{r}} = 1 \), the second condition, \( \mathcal{P}^2 = \mathcal{P} \), is also proved. This completes the proof.

**C. Atomic orbital representation**

In this section unfolding formulas for localized basis functions are derived. This covers both the linear combination of atomic orbitals (LCAO), which uses non-orthogonal basis functions, and tight-binding models with orthogonal basis functions which includes Wannier functions. Since the tight-binding method is a special
The spectral weight formula, Eq. (3), can be applied to find the projection of an eigenstate, Eq. (15), the general expansion in Bloch functions, where $J$ is a band index and the Bloch functions are given by

$$|K_j\rangle = \sum_N C_N^{K_j}|KN\rangle,$$

(10)

where $J$ is a band index and the Bloch functions are given by

$$|KN\rangle = \frac{1}{\sqrt{L}} \sum_{\mathbf{R}} e^{i \mathbf{K} \cdot \mathbf{R}}|\mathbf{R}N\rangle.$$  

(11)

The eigenvectors $C^K$ are solutions of a generalized eigenvalue problem

$$H^K = E^K S(K) C^K$$

(12)

where the overlap matrix $S(K)$ is a Fourier sum of $\langle 0M|\mathbf{R}N\rangle = S_{0M,\mathbf{R}N}$ matrix elements reflecting the non-orthogonality of atomic orbitals.

Projection of an eigenstate [10] depends on the projection of a Bloch function [11], which in turn depends on the projection of an SC orbital $|\mathbf{R}N\rangle$,

$$\mathcal{P}_k|\mathbf{R}M\rangle = \frac{1}{N} \sum_{j=1}^{N} e^{-i \mathbf{k} \cdot \mathbf{r}_j} \mathcal{T}(\mathbf{r}_j)|\mathbf{r}(M), m(M)\rangle.$$  

(13)

Noting that the action of translation operator on a ket is $\mathcal{T}(\mathbf{r}_j)|\mathbf{r}, m\rangle = |\mathbf{r}-\mathbf{r}_j, m\rangle$, and making a change of variable $\mathbf{r}(M) - \mathbf{r}_j \rightarrow \mathbf{r}_j$,

$$\mathcal{P}_k|\mathbf{R}M\rangle = \frac{1}{N} \sum_{j=1}^{N} e^{-i \mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}(M))} |\mathbf{r}_j, m(M)\rangle.$$  

(14)

Substituting this into Eq. (11) gives

$$\mathcal{P}_k|KN\rangle = \frac{1}{N\sqrt{L}} \sum_{\mathbf{r}} e^{-i \mathbf{k} \cdot (\mathbf{r} - \mathbf{r}(M))} |\mathbf{r}, m(M)\rangle,$$

(15)

where the sum runs over the whole set of $\mathbf{r}$ vectors. Having the projection of an eigenstate, Eq. (15), the general spectral weight formula, Eq. (3), can be applied to find

$$W_{KJ} = \frac{1}{N} \sum_{NM} C_N^{KJ} C_M^{KJ} e^{-i \mathbf{k} \cdot (\mathbf{r}(M) - \mathbf{r}(M))} S_{0N,\mathbf{r}m(M)}.$$  

(16)

In the last step, the periodicity of SC was used to replace $\sum_{\mathbf{R}} \rightarrow L \delta_{\mathbf{R},0}$. For orthogonal tight-binding, the overlap integral becomes[12]

$$S_{0N,\mathbf{r}m(M)} = S_{\mathbf{r}(N)\mathbf{r}(M)} = \delta_{\mathbf{r}(N),\mathbf{r}(M)} \delta_{n(N),m(M)},$$

(17)

so that the spectral weights, Eq. (16), simplify to

$$W_{KJ} = \frac{1}{N} \sum_{NM} C_N^{KJ} C_M^{KJ} \times e^{-i \mathbf{k} \cdot (\mathbf{r}(N) - \mathbf{r}(M))} \delta_{n(N),m(M)}.$$  

(18)

For the LCAO and tight-binding models, in addition to Eq. (9), there is another sum rule given by

$$\sum_{J} W_{KJ} = \frac{M}{N},$$

(19)

where $M$ is the number of orbitals in a supercell, so the right-hand side is just the average number of orbitals in a primitive cell. The proof can be understood by noting that a complete basis per PC must consist of $M/N$ orbitals.

### III. NUMERICAL EXAMPLES

A number of toy models are worked out to illustrate the unfolding formulas of Sec. [11]. The examples are chosen for the purpose of understanding the unfolding procedure but they are also relevant to real materials.
A. One-dimensional plane-wave model

This example shows that the unfolding formula, Eq. (7), can be used to obtain the band structure of a one-dimensional chain in the extended zone scheme. For this purpose, the primitive cell, a line of length $a$, will be taken as the supercell, while unfolding is carried out by considering a fictitious primitive cell which is a fraction of $a$.

The electrons move in a periodic one-dimensional potential of period $a$. The reciprocal lattice parameter is then $b = \frac{2\pi}{a}$. The electronic structure is obtained by solving the Schrödinger equation in momentum space, leading to the spectral weights (18). Writing the eigenvector coefficients $C^K_N$ simply as $C_N$ the spectral weight of a band is given for this example by

$$W = \frac{1}{2} (C_1^* + C_2^* e^{ika})(C_1 + C_2 e^{-ika}).$$

The corresponding unfolded bands are shown in Fig. 2(b).

B. One-dimensional tight-binding model

In this example, the one-dimensional chain is assumed to have undergone a Peierls distortion. This doubles the period to $2a$. The nearest-neighbor tight-binding model consists of two alternating hoppings $t$ and $t'$, and the transfer integral matrix is given by

$$H^K = \begin{pmatrix} 0 & t' + t e^{-2ika} \\ t' + t e^{2ika} & 0 \end{pmatrix}.$$  

The two energy bands are shown in Fig. 2(a).

These bands can be unfolded to the BZ of the underlying cell of period $a$ via the spectral weights (15). Writing the eigenvector coefficients $C^K_N$ simply as $C_N$ we obtain the band structure of a one-dimensional chain with the spectral weights (16). These bands can be unfolded to the BZ of the underlying cell of period $a$ via the spectral weights (15).

The two energy bands are shown in Fig. 2(a).

C. One-dimensional LCAO model

The LCAO model is similar to the tight-binding model but in addition to the hoppings $t$ and $t'$ there are overlap integrals $s$ and $s'$. This creates an asymmetry in the band structure. The overlap integral matrix to be used in the generalized eigenvalue equation is

$$S(K) = \begin{pmatrix} 1 & s' + s e^{-2iKa} \\ s + s e^{2iKa} & 1 \end{pmatrix}.$$  

The resulting bands are shown in Fig. 2(c).

The unfolded spectral weights, Eq. (16), can be written as

$$W = \frac{1}{2} (C_1^* A + C_2^* e^{ika} A^*)(C_1 + C_2 e^{-ika}),$$

where $A = 1 + s e^{-ika} + s' e^{ika}$. The unfolded bands are shown in Fig. 2(d).

FIG. 3. Band structure of honeycomb lattice with Kekulé distortion. The hoppings are $t = -1.1$ and $t' = -0.8$ producing a band gap of 0.6 about zero energy. The special points $\Gamma$, $K$, and $M$ refer to center, corner, and side of the hexagonal BZ, respectively. $P$ and $Q$ are special points of SBZ and correspond to $K$ and $M$ respectively. (a) Reduced zone bands. Both $K$ points of the primitive cell Brillouin zone are folded onto the $\Gamma$ point of supercell Brillouin zone. (b) Unfolded bands showing the gap opening at the $K$ point. There are more gaps at the zone boundaries of supercell Brillouin zone.
FIG. 4. Energy spectrum of tight-binding electrons on a finite chain. (a) Chain of 11 atoms. Hoppings at both ends are enhanced by a factor of 2. Black points at \( K = 0 \) are the eigenvalues. The lowest and the highest values each consist of two nearly degenerate eigenvalues. The black curve is the exact dispersion of infinite chain, \( E = -2t \cos(ka) \). The grey points smeared in \( k \) have come from unfolding. The lowest and highest unfolded energies span the whole Brillouin zone which indicates localization. They are edge states. (b) Chain of 21 atoms. Same description.

D. Honeycomb lattice with Kekulé distortion

In two dimensions the honeycomb lattice can support an alternating bond texture, known as Kekulé distortion\(^{19} \) It can be described by a commensurate lattice whose basic translations are related to those of the honeycomb lattice by a nonsingular transformation matrix with integer elements,

\[
\begin{pmatrix}
A_1 \\
A_2
\end{pmatrix}
=\begin{pmatrix}
2 & 1 \\
1 & 2
\end{pmatrix}
\begin{pmatrix}
\hat{a}_1 \\
\hat{a}_2
\end{pmatrix}.
\]

The new unit cell is a \( \sqrt{3} \times \sqrt{3}R30^\circ \) supercell with 3 times the area of the primitive unit cell. (See Ref. \(^{20} \) for more details.) There are two sites, or basis orbitals, per primitive unit cell and six sites per supercell.

The effect of Kekulé distortion is to open a gap in the spectrum of honeycomb lattice. The band gap is related to the two hoppings of the tight-binding model by \( E_g = 2|t - t'| \). The transfer integral matrix is given by

\[
H^K = \begin{pmatrix}
0 & t & 0 & t' e^{-iK \cdot A_1} & 0 & 0 \\
t & 0 & t & 0 & t' e^{-iK \cdot A_1} & 0 \\
0 & t & 0 & 0 & t & 0 \\
t' e^{iK \cdot A_1} & 0 & 0 & t & 0 & t \\
0 & t' e^{-iK \cdot A_1} & 0 & 0 & t & 0 \\
\end{pmatrix}.
\]

The band structure, in reduced zone and unfolded extended zone schemes, respectively, are shown in Fig. 3. This result is particularly graphic in showing the usefulness of unfolding. While the SC folded bands have little resemblance to the bands of the perfect system, the unfolded effective band structure is quite comparable to the unperturbed one different only in band gaps at the \( K \) point and the zone boundaries.

E. Finite one-dimensional chain of atoms

It is common to study the surface states of a crystal by using a slab of several layers of atoms and forming a supercell by the addition of a vacuum layer. As the vacuum is thick enough to prevent interaction between the slabs only the \( K = 0 \) point is needed for the vertical component. Unfolding can be applied to this kind of calculation to uncover the electronic structure of the surface states.

The slab approach is illustrated here with a finite one-dimensional chain of atoms. The Hamiltonian matrix of a nearest-neighbor tight-binding model of electrons in a finite one-dimensional chain is given by

\[
H = \begin{pmatrix}
0 & t' & 0 & \ldots & 0 & 0 \\
t' & 0 & t & \ldots & 0 & 0 \\
0 & t & 0 & \ldots & 0 & 0 \\
\vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & \ldots & t & 0 \\
0 & 0 & \ldots & t & 0 & t' \\
0 & 0 & \ldots & 0 & t' & 0
\end{pmatrix}.
\]
IV. CONCLUSIONS

Supercell electronic structures can be unfolded by analyzing the symmetries of the eigenfunctions. Two key concepts that have emerged in the methodology are the spectral function and the projection operator. The two approaches based on these ideas lead to the same unfolding formulas which can be used to obtain effective band structures. Starting from the projection operator, obviates a reference system and considerably simplifies the conceptual description, as well as the analysis. Toy models in one and two dimensions were used to illustrate the procedure and the utility of band structure unfolding. In general, band structure unfolding is a simple yet extremely useful method for simplifying complicated supercell calculations.

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