

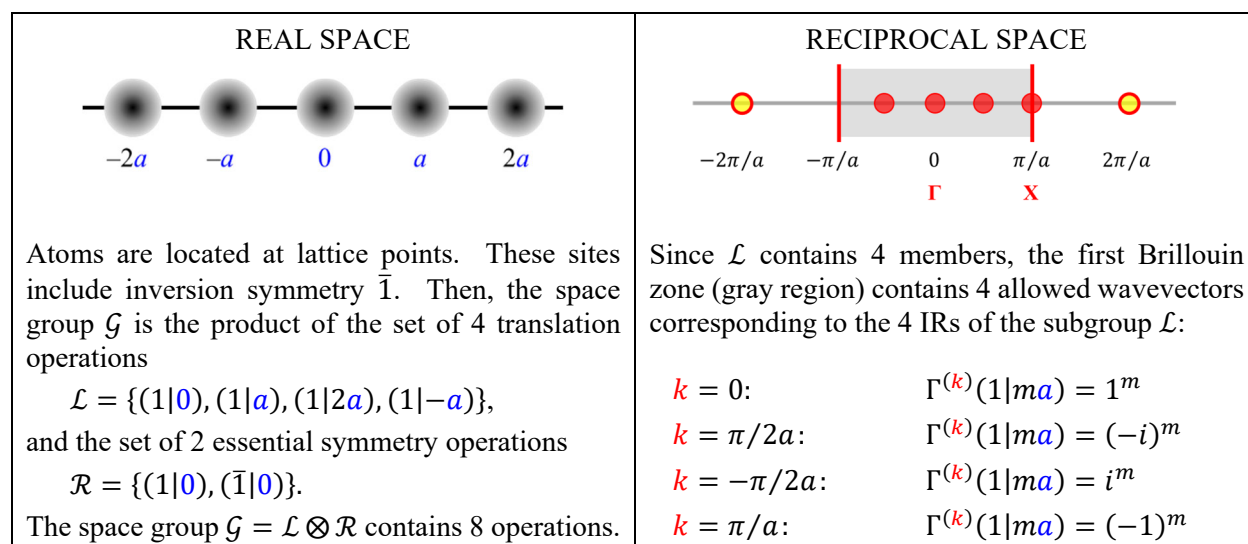
IRREDUCIBLE REPRESENTATIONS OF SPACE GROUPS

Determining the IRs for the space group \mathcal{G} of a crystalline structure can be useful when analyzing electronic structure or vibrational modes because the eigenfunctions of the Hamiltonian $H(\mathbf{r})$ are basis functions of the IRs (see slide (38)). Bloch functions are basis functions for the 1-d IRs of the group of lattice translations \mathcal{L} , which is an invariant subgroup of \mathcal{G} . However, due to the inclusion of rotations in the space group, these IRs are no longer necessarily 1-d. Evaluating the similarity transformation of the lattice translation operation $(1|\mathbf{T})$ with respect to $(R|\boldsymbol{\tau}_R)$ yields:

$$(R|\boldsymbol{\tau}_R)^{-1}(1|\mathbf{T})(R|\boldsymbol{\tau}_R) = (R^{-1}|-R^{-1}\boldsymbol{\tau}_R)(1|\mathbf{T})(R|\boldsymbol{\tau}_R) = (1|R^{-1}\mathbf{T}).$$

Since the two lattice operations $(1|\mathbf{T})$ and $(1|R^{-1}\mathbf{T})$ belong to the same class, the space group has degenerate IRs. Although each lattice translation is no longer a distinct class, Bloch functions can still be used to construct the basis functions for IRs of a space group. When periodic boundary conditions are applied, space groups are finite groups and orthogonality relationships between IRs apply to construct the character table and elucidate basis functions for the IRs.

THE 1-d CHAIN of ATOMS: To demonstrate how translational and rotational symmetry combine to give the IRs of a space group, we determine the character table and IRs for the space group associated with a 1-d chain of atoms using the simplified periodic boundary condition $(1|4a) \equiv (1|0)$:



To build the character table of \mathcal{G} , the different classes must be enumerated. There are two general types of operations in this group, $(1|ma)$ and $(\bar{1}|ma)$, which lead to 4 expressions of similarity transformations:

$$\begin{aligned} (1|na)^{-1}(1|ma)(1|na) &= (1|-na)(1|ma)(1|na) = (1|ma) \\ (\bar{1}|na)^{-1}(1|ma)(\bar{1}|na) &= (\bar{1}|na)(1|ma)(\bar{1}|na) = (1|-ma) \\ (1|na)^{-1}(\bar{1}|ma)(1|na) &= (1|-na)(\bar{1}|ma)(1|na) = (\bar{1}|(m-2n)a) \\ (\bar{1}|na)^{-1}(\bar{1}|ma)(\bar{1}|na) &= (\bar{1}|na)(\bar{1}|ma)(\bar{1}|na) = (\bar{1}|(-m+2n)a). \end{aligned}$$

According to these expressions, the 4 translation operations form the 3 classes: $\{(1|0)\}$, $\{(1|a), (1|-a)\}$, and $\{(1|2a)\}$; and the 4 inversion operations form 2 classes: $\{(\bar{1}|0), (\bar{1}|2a)\}$ and $\{(\bar{1}|a), (\bar{1}|-a)\}$. Therefore, this small model of a space group consists of 5 IRs, which are summarized in the following character table:

	(1 0)	(1 a) (1 -a)	(1 2a)	($\bar{1}$ 0) ($\bar{1}$ 2a)	($\bar{1}$ a) ($\bar{1}$ -a)	Basis Functions $\psi_{nk}(x) = A(x)e^{ikx}$
Γ_g	1	1	1	1	1	$k = 0, A(-x) = A(x)$
Γ_u	1	1	1	-1	-1	$k = 0, A(-x) = -A(x)$
X_g	1	-1	1	1	-1	$k = \pi/a, A(-x) = A(x)$
X_u	1	-1	1	-1	1	$k = \pi/a, A(-x) = -A(x)$
Δ	2	0	-2	0	0	$k = \pi/2a$ and $-\pi/2a$

- Two 1-d IRs correspond to the wavevector $k = 0$ (lattice point Γ in reciprocal space). These IRs have +1 characters for all translation operations, and their basis functions have the full periodicity of the 1-d lattice, but they differ in their response to inversion: for $(\bar{1}|ma)\psi_{n\Gamma}(x) = +\psi_{n\Gamma}(x)$, the IR is *even* (*gerade* = g); for $(\bar{1}|ma)\psi_{n\Gamma}(x) = -\psi_{n\Gamma}(x)$, the IR is *odd* (*ungerade* = u). Therefore, the labels of these IRs are Γ_g and Γ_u .
- Two 1-d IRs correspond to the wavevector $k = \pi/a$ (boundary point X of the first Brillouin zone). These IRs have +1 characters for even translations and -1 characters for odd translations. Their basis functions also differ in their response to inversion. As a result, the IR labels are X_g and X_u .
- One 2-d IR corresponds to wavevectors $k = \pi/2a$ and $-\pi/2a$ (interior points Δ of the first Brillouin zone). Using these Bloch functions as a basis, the matrix representatives for the translation operations $(1|ma)$ are diagonal matrices:

$$(1|0) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; (1|a) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}; (1|2a) = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}; (1|-a) = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}.$$

The two wavevectors and their Bloch functions are related to each other by inversion, so the matrix representatives for the inversion operations $(\bar{1}|ma)$ are matrices with 0-valued diagonal elements:

$$(\bar{1}|0) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; (\bar{1}|a) = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}; (\bar{1}|2a) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}; (\bar{1}|-a) = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}.$$

Therefore, inversion takes $\psi_{nk}(x)$ into $\psi_{n(-k)}(x)$, and vice versa. As a result, this IR is not specifically labeled for inversion (Δ).

To summarize the results of the analysis of this simplified 1-d space group:

- (1) The rotations, 1 and $\bar{1}$, give distinct sets of classes. The set $\mathcal{L} = \{(1|ma)\}$ forms 3 classes due to inversion, but $(\bar{1}|0)$ of \mathcal{R} belongs to the class that includes $(\bar{1}|2a)$. As a result, \mathcal{L} is an invariant subgroup of \mathcal{G} , but \mathcal{R} is not. Nevertheless, \mathcal{R} is a group, so this space group is symmorphic.
- (2) Plane-wave Bloch functions can serve as basis functions for the IRs of a space group. The amplitude function adopts rotational symmetry characteristics that depend on the wavevector k .
- (3) The wavevectors Γ (a reciprocal lattice point) and X (a first Brillouin zone boundary point) have inversion symmetry in reciprocal space. As a result, the IRs associated with these two wavevectors can each be designated as *gerade* (even) and *ungerade* (odd).
- (4) The IR Δ is doubly degenerate, corresponding to wavevectors k and $-k$, which are related to each other by inversion. However, the rotational symmetry for each separate wavevector is just the identity operation. Nevertheless, the eigenfunctions of the Hamiltonian for these two wavevectors are degenerate: $E_n(\pi/2a) = E_n(-\pi/2a)$.

This example of the 1-d chain illustrates how the rotations of a space group create equivalent translations resulting in degenerate IRs. It also points out the enhanced symmetry of reciprocal lattice points and boundary points of the first Brillouin zone vis-à-vis general interior points. The

procedure can be applied to build the character table of any space group, but determining the classes of these large-order groups can be tedious. Therefore, we desire a different approach that takes advantage of features of the space group (see slide (29)):

- Every space group \mathcal{G} is the product of a Bravais lattice group $\mathcal{L} = \{(1|\mathbf{T})\}$ and a finite set of essential symmetry operations $\mathcal{R} = \{(R|\boldsymbol{\tau}_R)\}$, which leads to the sum of cosets:

$$\begin{aligned}\mathcal{G} &= \mathcal{L} \otimes \mathcal{R} = \{(1|\mathbf{T})\} \otimes \{(1|\mathbf{0}), (R_2|\boldsymbol{\tau}_2), \dots, (R_h|\boldsymbol{\tau}_h)\} \\ &= \{(1|\mathbf{T})\} + \{(R_2|\boldsymbol{\tau}_2 + \mathbf{T})\} + \dots + \{(R_h|\boldsymbol{\tau}_h + \mathbf{T})\}.\end{aligned}$$

- The set $\mathcal{G}_0 = \{1, R_2, \dots, R_h\}$ of proper and improper rotations in the operations $(R|\boldsymbol{\tau}_R)$ of \mathcal{R} is a group, called the point group of the space group, and identifies the crystal class.
- The displacements $\boldsymbol{\tau}_R$ are either $\mathbf{0}$ or rational fractions of lattice vectors.
- For symmorphic space groups, $\boldsymbol{\tau}_R = \mathbf{0}$ for all operations $(R|\boldsymbol{\tau}_R)$ and \mathcal{R} is a group isomorphous with \mathcal{G}_0 .
- For nonsymmorphic space groups, $\boldsymbol{\tau}_R \neq \mathbf{0}$ for some operations $(R|\boldsymbol{\tau}_R)$ and \mathcal{R} is not a group.
- \mathcal{L} is an invariant subgroup of \mathcal{G} , and the factor group \mathcal{G}/\mathcal{L} is also isomorphous with \mathcal{G}_0 .
- Each coset $\{(R_i|\boldsymbol{\tau}_i + \mathbf{T})\}$ in \mathcal{G}/\mathcal{L} corresponds to R_i in \mathcal{G}_0 , and \mathcal{L} serves as the identity member.

Therefore, to determine the IRs of \mathcal{G} , it is advantageous to start with the IRs of \mathcal{L} .

Rotational Symmetry of Bloch Functions: Any Bloch function $\psi_{n\mathbf{k}}(\mathbf{r})$ is a basis function for the 1-d IR $\Gamma^{(\mathbf{k})}$ of the Bravais lattice group \mathcal{L} . The representative of $\Gamma^{(\mathbf{k})}(1|\mathbf{T})$ is $e^{-i\mathbf{k}\cdot\mathbf{T}}$ and

$$(1|\mathbf{T})\psi_{n\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(\mathbf{r}).$$

Now, how does the operation $(R|\boldsymbol{\tau}_R)$ of \mathcal{R} affect a Bloch function $\psi_{n\mathbf{k}}(\mathbf{r})$? To answer this question, examine the effect of $(1|\mathbf{T})$ on $(R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}(\mathbf{r})$:

$$\begin{aligned}(1|\mathbf{T})\{(R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}(\mathbf{r})\} &= (R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}((1|\mathbf{T})^{-1}\mathbf{r}) = (R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}(\mathbf{r} - \mathbf{T}) \\ &= \psi_{n\mathbf{k}}((R|\boldsymbol{\tau}_R)^{-1}(\mathbf{r} - \mathbf{T})) = \psi_{n\mathbf{k}}(R^{-1}(\mathbf{r} - \boldsymbol{\tau}_R) - R^{-1}\mathbf{T}) \\ &= (1|R^{-1}\mathbf{T})\psi_{n\mathbf{k}}(R^{-1}(\mathbf{r} - \boldsymbol{\tau}_R)) = e^{-i\mathbf{k}\cdot R^{-1}\mathbf{T}}\psi_{n\mathbf{k}}(R^{-1}(\mathbf{r} - \boldsymbol{\tau}_R)).\end{aligned}$$

At this point, apply a useful identity for the dot product of vectors \mathbf{k} and \mathbf{T} when one of them is transformed by an orthogonal matrix R : $\mathbf{k} \cdot R^{-1}\mathbf{T} = R\mathbf{k} \cdot \mathbf{T}$, so that

$$(1|\mathbf{T})\{(R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}(\mathbf{r})\} = e^{-R\mathbf{k}\cdot\mathbf{T}}\psi_{n\mathbf{k}}(R^{-1}(\mathbf{r} - \boldsymbol{\tau}_R)).$$

Therefore, $(R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}(\mathbf{r})$ behaves like a Bloch function with wavevector $R\mathbf{k}$. Also, the coordinate \mathbf{r} is transformed to $R^{-1}(\mathbf{r} - \boldsymbol{\tau}_R)$, so that

$$(R|\boldsymbol{\tau}_R)\psi_{n\mathbf{k}}(\mathbf{r}) = \psi_{n\mathbf{k}}(R^{-1}(\mathbf{r} - \boldsymbol{\tau}_R)) \equiv \psi_{n(R\mathbf{k})}(\mathbf{r} - \boldsymbol{\tau}_R).$$

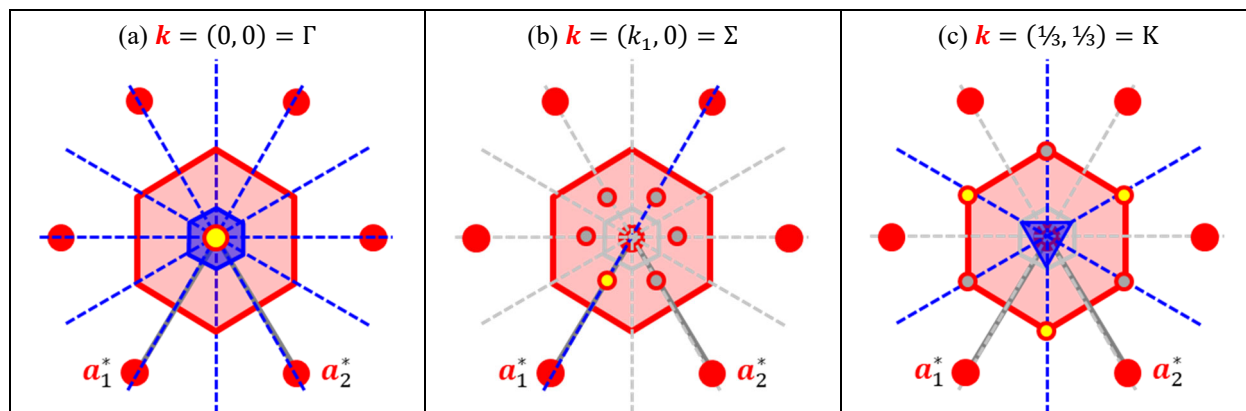
As a result, the members $(R|\boldsymbol{\tau}_R)$ of the set of essential symmetry operations \mathcal{R} transform every wavevector \mathbf{k} among various wavevectors $R\mathbf{k}$ and may introduce a change of origin, i.e., phase change, to the corresponding Bloch functions.

All allowed wavevectors \mathbf{k} for the IRs of \mathcal{L} belong to the first Brillouin zone of the reciprocal lattice, a region which is the Wigner-Seitz cell for any reciprocal lattice point. Every boundary point of the first Brillouin zone is equivalent to at least one other boundary point because two boundary points are separated by a reciprocal lattice vector \mathbf{K} . Now, the effect of any rotation operation R of \mathcal{G}_0 on a wavevector \mathbf{k} has one of three possible outcomes:

- (1) $R\mathbf{k} = \mathbf{k}$: R generates the *same wavevector*. Therefore, \mathbf{k} must lie along the symmetry element of R , i.e., \mathbf{k} is parallel to the rotation axis or falls in the reflection plane (line).
- (2) $R\mathbf{k} = \mathbf{k} + \mathbf{K}$ ($\mathbf{K} \neq \mathbf{0}$, a reciprocal lattice vector): R generates an *equivalent wavevector*. This outcome only occurs for wavevectors on the first Brillouin zone boundary.

- (3) $R\mathbf{k} = \mathbf{k}' \neq \mathbf{k}$ or $\mathbf{k} + \mathbf{K}$: R generates a *different wavevector*. These wavevectors are inside the first Brillouin zone and do not lie along symmetry elements of R .

For a given wavevector \mathbf{k} in the first Brillouin zone, the h rotations of \mathcal{G}_0 generate a set of wavevectors $\mathcal{S}(\mathbf{k}) = \{\mathbf{k}, R_2\mathbf{k}, \dots, R_h\mathbf{k}\}$, not all necessarily distinct, called the *star of \mathbf{k}* . The subset of q rotations ($q \leq h$) that take \mathbf{k} to the same wavevector \mathbf{k} or an equivalent wavevector $\mathbf{k} + \mathbf{K}$ form a group $\mathcal{G}_0(\mathbf{k}) = \{E, R_2, \dots, R_q\}$, called the *point group of the wavevector \mathbf{k}* . These features are illustrated below for three different wavevectors $\mathbf{k} = k_1\mathbf{a}_1^* + k_2\mathbf{a}_2^* \equiv (k_1, k_2)$, shown as yellow dots, of the hexagonal system with $\mathcal{G}_0 = 6mm$. The members of $\mathcal{G}_0(\mathbf{k})$ are highlighted in blue:



- (a) $\Gamma = (0, 0)$ is a reciprocal lattice point. The 6-fold rotation and all six mirror planes keep Γ invariant. Therefore, $\mathcal{G}_0(\Gamma) = \mathcal{G}_0 = 6mm$ with order 12, and $\mathcal{S}(\Gamma)$ contains just one wavevector $\mathbf{k} = (0, 0)$.
- (b) $\Sigma = (k_1, 0)$ designates any wavevector $k_1\mathbf{a}_1^*$ for $0 < k_1 < \pi/a$. Only one mirror plane keeps Σ invariant. $\mathcal{G}_0(\Sigma) = m$ with order 2, and $\mathcal{S}(\Sigma)$ contains six wavevectors in the first Brillouin zone: $\mathbf{k} = (k_1, 0)$; $6\mathbf{k} = (0, k_1)$; $6^2\mathbf{k} = (-k_1, k_1)$; $6^3\mathbf{k} = (-k_1, 0)$; $6^4\mathbf{k} = (0, -k_1)$; $6^5\mathbf{k} = (k_1, -k_1)$.
- (c) $K = (\frac{1}{3}, \frac{1}{3})$ is located at a corner of the first Brillouin zone. The 3-fold (6^2 -fold) rotation and three mirror planes keep K invariant or send it to an equivalent point at either $(-\frac{2}{3}, \frac{1}{3})$ or $(\frac{1}{3}, -\frac{2}{3})$. $\mathcal{G}_0(K) = 3m$ with order 6, and $\mathcal{S}(K)$ contains two wavevectors on the boundary of the first Brillouin zone: $\mathbf{k} = (\frac{1}{3}, \frac{1}{3})$; $6\mathbf{k} = (-\frac{1}{3}, \frac{2}{3})$.

As this example illustrates, for each wavevector \mathbf{k} of the first Brillouin zone,

$$\text{Order of } \mathcal{G}_0 = \text{Order of } \mathcal{G}_0(\mathbf{k}) \times \text{Number of distinct wavevectors in } \mathcal{S}(\mathbf{k}).$$

Both sets $\mathcal{G}_0(\mathbf{k})$ and $\mathcal{S}(\mathbf{k})$ are important to determine the IRs of \mathcal{G} . Each distinct wavevector in $\mathcal{S}(\mathbf{k})$ has the same abstract point group, but $\mathcal{G}_0(\mathbf{k})$ is formed by different operations of \mathcal{G}_0 .

Group of the Wavevector \mathbf{k} : Each operation of the point group of the space group \mathcal{G}_0 is associated with one member of the set of essential symmetry operations \mathcal{R} . Likewise, each operation of $\mathcal{G}_0(\mathbf{k})$ is associated with one member of the subset $\mathcal{R}(\mathbf{k}) = \{(1|\mathbf{0}), \dots, (R_q|\boldsymbol{\tau}_q)\}$, in which every rotation R takes \mathbf{k} to \mathbf{k} or $\mathbf{k} + \mathbf{K}$. The product $\mathcal{L} \otimes \mathcal{R}(\mathbf{k}) = \mathcal{G}(\mathbf{k})$ is the *group of the wavevector \mathbf{k}* , also called the *little group*, which leads to the sum of cosets:

$$\begin{aligned} \mathcal{G}(\mathbf{k}) = \mathcal{L} \otimes \mathcal{R}(\mathbf{k}) &= \{(1|\mathbf{T})\} \otimes \{(1|\mathbf{0}), (R_2|\boldsymbol{\tau}_2), \dots, (R_q|\boldsymbol{\tau}_q)\} \\ &= \{(1|\mathbf{T})\} + \{(R_2|\boldsymbol{\tau}_2 + \mathbf{T})\} + \dots + \{(R_q|\boldsymbol{\tau}_q + \mathbf{T})\}. \end{aligned}$$

$\mathcal{G}(\mathbf{k})$ is a subgroup of the space group \mathcal{G} and the corresponding factor group $\mathcal{G}(\mathbf{k})/\mathcal{L}$ is isomorphous with $\mathcal{G}_0(\mathbf{k})$, which is a subgroup of \mathcal{G}_0 . \mathcal{L} is the identity member of this factor group, but now each representative for $(1|\mathbf{T})$ is $e^{-i\mathbf{k}\cdot\mathbf{T}}E$, where E is the identity matrix.

Let $D^{(\mathbf{k}\mu)}$ be an IR of $\mathcal{G}(\mathbf{k})$. Then,

$$\begin{aligned} D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i + \mathbf{T}) &= \Gamma^{(\mathbf{k})}(1|\mathbf{T}) D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) = e^{-i\mathbf{k}\cdot\mathbf{T}} D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) \text{ and} \\ D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) D^{(\mathbf{k}\mu)}(R_j|\boldsymbol{\tau}_j) &= D^{(\mathbf{k}\mu)}(R_i R_j|\boldsymbol{\tau}_i + R_i \boldsymbol{\tau}_j). \end{aligned}$$

Now, define the corresponding *loaded representation* $\widehat{D}^{(\mathbf{k}\mu)}$ of $\mathcal{G}(\mathbf{k})$ as follows:

$$\widehat{D}^{(\mathbf{k}\mu)}(R_i) \equiv e^{i\mathbf{k}\cdot\boldsymbol{\tau}_i} D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i), \text{ so that } D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) = e^{-i\mathbf{k}\cdot\boldsymbol{\tau}_i} \widehat{D}^{(\mathbf{k}\mu)}(R_i).$$

According to this definition, the single matrix $\widehat{D}^{(\mathbf{k}\mu)}(R_i)$ represents every member of the coset $\{(R_i|\boldsymbol{\tau}_i + \mathbf{T})\}$ in the coset expansion of $\mathcal{G}(\mathbf{k})$. Since each coset is a distinct member of the factor group $\mathcal{G}(\mathbf{k})/\mathcal{L}$, examine the product of two loaded representatives:

$$\begin{aligned} \widehat{D}^{(\mathbf{k}\mu)}(R_i) \widehat{D}^{(\mathbf{k}\mu)}(R_j) &= e^{i\mathbf{k}\cdot\boldsymbol{\tau}_i} e^{i\mathbf{k}\cdot\boldsymbol{\tau}_j} D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) D^{(\mathbf{k}\mu)}(R_j|\boldsymbol{\tau}_j) = e^{i\mathbf{k}\cdot\boldsymbol{\tau}_i} e^{i\mathbf{k}\cdot\boldsymbol{\tau}_j} D^{(\mathbf{k}\mu)}(R_i R_j|\boldsymbol{\tau}_i + R_i \boldsymbol{\tau}_j) \\ &= e^{i\mathbf{k}\cdot\boldsymbol{\tau}_i} e^{i\mathbf{k}\cdot\boldsymbol{\tau}_j} e^{-i\mathbf{k}\cdot(\boldsymbol{\tau}_i + R_i \boldsymbol{\tau}_j)} \widehat{D}^{(\mathbf{k}\mu)}(R_i R_j) = e^{i\mathbf{k}\cdot\boldsymbol{\tau}_j} e^{-i\mathbf{k}\cdot R_i \boldsymbol{\tau}_j} \widehat{D}^{(\mathbf{k}\mu)}(R_i R_j) \\ &= e^{i\mathbf{k}\cdot\boldsymbol{\tau}_j} e^{-iR_i^{-1} \mathbf{k}\cdot\boldsymbol{\tau}_j} \widehat{D}^{(\mathbf{k}\mu)}(R_i R_j). \end{aligned}$$

Since R_i belongs to $\mathcal{G}_0(\mathbf{k})$, so does the inverse R_i^{-1} . If $R_i^{-1} \mathbf{k} \equiv \mathbf{k} + \mathbf{K}_i$, then the product becomes

$$\widehat{D}^{(\mathbf{k}\mu)}(R_i) \widehat{D}^{(\mathbf{k}\mu)}(R_j) = e^{-i\mathbf{K}_i \cdot \boldsymbol{\tau}_j} \widehat{D}^{(\mathbf{k}\mu)}(R_i R_j).$$

Therefore, the loaded representation $\widehat{D}^{(\mathbf{k}\mu)}$ of $\mathcal{G}(\mathbf{k})$ is an example of a *projective representation* in which the numerical factor $e^{-i\mathbf{K}_i \cdot \boldsymbol{\tau}_j}$ depends on the two operations in the product and the order of their multiplication. If $e^{-i\mathbf{K}_i \cdot \boldsymbol{\tau}_j}$ always equals 1, then all products follow the normal definition of a group, and the loaded representation $\widehat{D}^{(\mathbf{k}\mu)}$ is an IR $D_0^{(\mathbf{k}\mu)}$ of the point group $\mathcal{G}_0(\mathbf{k})$. If $e^{-i\mathbf{K}_i \cdot \boldsymbol{\tau}_j}$ does not equal 1 for some products, then additional analysis is required to establish the IRs of $\mathcal{G}(\mathbf{k})$.

The factor $e^{-i\mathbf{K}_i \cdot \boldsymbol{\tau}_j} = 1$ when $\mathbf{K}_i \cdot \boldsymbol{\tau}_j = 0$, which occurs for $\boldsymbol{\tau}_j = \mathbf{0}$, $\mathbf{K}_i = \mathbf{0}$, and $\mathbf{K}_i \perp \boldsymbol{\tau}_j$. To apply these restrictions, it is advantageous to consider symmorphic and nonsymmorphic space groups separately:

SYMMORPHIC SPACE GROUPS: $\boldsymbol{\tau}_j = \mathbf{0}$ for all $(R_j|\boldsymbol{\tau}_j)$ and $\mathcal{R}(\mathbf{k}) = \mathcal{G}_0(\mathbf{k})$. As a result, $\mathcal{G}(\mathbf{k})$ can always be factored into the product of two groups, \mathcal{L} and $\mathcal{R}(\mathbf{k})$, and the IRs for $\mathcal{G}(\mathbf{k})$ are the products of the IRs for \mathcal{L} and $\mathcal{G}_0(\mathbf{k})$:

$$D^{(\mathbf{k}\mu)}(R_i|\mathbf{T}) = \Gamma^{(\mathbf{k})}(1|\mathbf{T}) D^{(\mathbf{k}\mu)}(R_i|\mathbf{0}) = e^{-i\mathbf{k}\cdot\mathbf{T}} \widehat{D}^{(\mathbf{k}\mu)}(R_i) = e^{-i\mathbf{k}\cdot\mathbf{T}} D_0^{(\mathbf{k}\mu)}(R_i).$$

This outcome will be illustrated for the π -bands of graphene in slides (56–61).

NONSYMMORPHIC SPACE GROUPS: $\boldsymbol{\tau}_j \neq \mathbf{0}$ for some $(R_j|\boldsymbol{\tau}_j)$. For all wavevectors \mathbf{k} inside the first Brillouin zone, $\mathbf{K}_i = \mathbf{0}$ for every R_i in $\mathcal{G}_0(\mathbf{k})$ and the IRs for $\mathcal{G}(\mathbf{k})$ are the products of the IRs for $\mathcal{G}_0(\mathbf{k})$ and \mathcal{L} , just as for symmorphic space groups, but with an additional phase factor arising from the nonzero displacements $\boldsymbol{\tau}_j$:

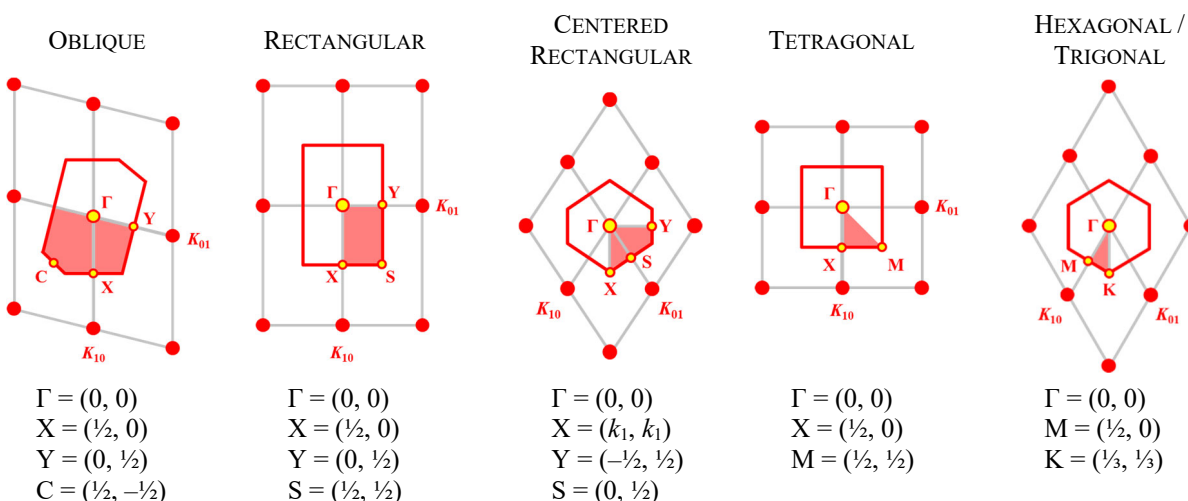
$$D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i + \mathbf{T}) = \Gamma^{(\mathbf{k})}(1|\mathbf{T}) D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) = e^{-i\mathbf{k}\cdot\mathbf{T}} e^{-i\mathbf{k}\cdot\boldsymbol{\tau}_i} D_0^{(\mathbf{k}\mu)}(R_i).$$

For certain wavevectors on the first Brillouin zone boundary, $\mathbf{K}_i \neq \mathbf{0}$ or \mathbf{K}_i is not perpendicular to $\boldsymbol{\tau}_j$, which means $e^{-i\mathbf{K}_i \cdot \boldsymbol{\tau}_j} \neq 1$ and some products $\widehat{D}^{(\mathbf{k}\mu)}(R_i) \widehat{D}^{(\mathbf{k}\mu)}(R_j) \neq \widehat{D}^{(\mathbf{k}\mu)}(R_i R_j)$. This outcome leads to only degenerate IRs for $\mathcal{G}_0(\mathbf{k})$ and $\mathcal{G}(\mathbf{k})$. To determine the characters of these IRs, further analysis is required:

$$D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i + \mathbf{T}) = \Gamma^{(\mathbf{k})}(1|\mathbf{T}) D^{(\mathbf{k}\mu)}(R_i|\boldsymbol{\tau}_i) = e^{-i\mathbf{k}\cdot\mathbf{T}} e^{-i\mathbf{k}\cdot\boldsymbol{\tau}_i} \widehat{D}^{(\mathbf{k}\mu)}(R_i).$$

Determining the IRs of $\mathcal{G}(\mathbf{k})$ for various wavevectors normally concludes this analysis, because these IRs are important for classifying states in electronic band structures and phonon dispersion curves. However, to evaluate the IRs of the entire space group \mathcal{G} , one final step remains that makes use of the star of \mathbf{k} .

Star of \mathbf{k} : The groups $\mathcal{G}(\mathbf{k})$ for each member of $\mathcal{S}(\mathbf{k})$ are isomorphous with each other, which means they have identical IRs although the respective basis functions may be different. Consequently, there is a region within the first Brillouin zone, called the *irreducible wedge*, from which all wavevectors of the first Brillouin zone can be generated by the rotations of the point group of the space group \mathcal{G}_0 . For example, the irreducible wedges for the five 2-d Bravais lattice systems are illustrated below:



As a result of the rotational symmetry of reciprocal space, the eigenvalues of the electronic or vibrational Hamiltonian $H(\mathbf{k})$ for some wavevector \mathbf{k} of the irreducible wedge will be the same for every wavevector in $\mathcal{S}(\mathbf{k})$. Therefore, computations focus on wavevectors belonging just to the irreducible wedge, and the number of members in $\mathcal{S}(\mathbf{k})$ leads to degeneracies of the IRs.

By using the members of $\mathcal{S}(\mathbf{k})$ as a basis, each member of \mathcal{G}_0 is a permutation matrix, which has “0” or “1” as matrix elements. The dimension of these matrices equals the number of distinct members of $\mathcal{S}(\mathbf{k})$. If $R_j \mathbf{k}_i = \mathbf{k}_j$ or $\mathbf{k}_j + \mathbf{K}$, then the matrix element of the i^{th} row and j^{th} column is “1”; all other matrix elements in the same row and column are “0”. The complete IRs for the space group \mathcal{G} are then constructed by placing the IRs $D^{(\mathbf{k})}$ of $\mathcal{G}(\mathbf{k})$ in these permutation matrices where matrix elements equal “1”. In this way, every IR for the space group can be worked out. However, the complete matrices are seldom used and knowing their characters is often sufficient.

To summarize how IRs for a space group \mathcal{G} are determined:

- Select a wavevector \mathbf{k} belonging to the irreducible wedge of the first Brillouin zone. This wavevector determines the Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$.
- Determine the group of the wavevector \mathbf{k} , $\mathcal{G}(\mathbf{k})$, and its corresponding point group, $\mathcal{G}_0(\mathbf{k})$, from the set of essential symmetry operations \mathcal{R} .
- If the space group is symmorphic, then every operation $(R_i|T)$ takes the form $(1|T)(R_i|\mathbf{0})$, and the IRs for $\mathcal{G}(\mathbf{k})$ are $e^{-i\mathbf{k}\cdot T}$ times the IRs of R_i for $\mathcal{G}_0(\mathbf{k})$.

- If the space group is nonsymmorphic, then operations take the form $(R_i|\tau_i + \mathbf{T})$ and the IRs for $\mathcal{G}(\mathbf{k})$ are $e^{-i\mathbf{k}\cdot\mathbf{T}}e^{-i\mathbf{k}\cdot\tau_i}$ times the IRs of R_i determined from the loaded representations of $\mathcal{G}_0(\mathbf{k})$. For all wavevectors \mathbf{k} in the interior region of the first Brillouin zone, the loaded representations for $\mathcal{G}_0(\mathbf{k})$ correspond to the IRs for $\mathcal{G}_0(\mathbf{k})$. For wavevectors on the boundary of the first Brillouin zone, then the products $\widehat{D}^{(\mathbf{k})}(R_i)\widehat{D}^{(\mathbf{k})}(R_j)$ must be evaluated. If $\widehat{D}^{(\mathbf{k})}(R_i)\widehat{D}^{(\mathbf{k})}(R_j) = \widehat{D}^{(\mathbf{k})}(R_iR_j)$ for all members of $\mathcal{G}_0(\mathbf{k})$, then the loaded representations for $\mathcal{G}_0(\mathbf{k})$ correspond to the IRs for $\mathcal{G}_0(\mathbf{k})$. If $\widehat{D}^{(\mathbf{k})}(R_i)\widehat{D}^{(\mathbf{k})}(R_j) \neq \widehat{D}^{(\mathbf{k})}(R_iR_j)$ for some members of $\mathcal{G}_0(\mathbf{k})$, then the loaded representations for $\mathcal{G}_0(\mathbf{k})$ are exclusively degenerate.
- To complete the IRs for \mathcal{G} , construct the permutation matrices for each member of $\mathcal{S}(\mathbf{k})$ and insert the relevant IRs of $\mathcal{G}(\mathbf{k})$ into these matrices where “1” is located.

To examine the difference between symmorphic and nonsymmorphic space groups, we compare the irreducible representations of the monoclinic space groups $P2$ and $P2_1$ along the \mathbf{b}^* direction of the first Brillouin zone. The space groups are expressed as the product of their lattice subgroups and the set of essential symmetry operations; this latter set contains 2 members. From the choices of wavevectors, $\mathbf{k} = u\mathbf{a}^* + v\mathbf{b}^* + w\mathbf{c}^* = v\mathbf{b}^*$, and $\mathbf{k}\cdot\mathbf{T}_{mnp} = 2\pi nv$ ($0 \leq v \leq 1/2$).

$$P2 = \{(1|\mathbf{T}_{mnp})\} \times \{(1|\mathbf{0}), (2_{010}|\mathbf{0})\}$$

$$\mathbf{k} = \mathbf{0} (\Gamma): \mathbf{k}\cdot\mathbf{T}_{mnp} = 0$$

$$\mathcal{G}(\Gamma) = \{(1|\mathbf{T}_{mnp}), (2_{010}|\mathbf{T}_{mnp})\}$$

	$(1 \mathbf{T}_{mnp})$	$(2_{010} \mathbf{T}_{mnp})$
$\Gamma^{(1)} \equiv a$	1	1
$\Gamma^{(2)} \equiv b$	1	-1

The IRs are either symmetric or antisymmetric with respect to the 2-fold rotation. For Γ , there are no phase changes for any lattice translation. The star of Γ , $\mathcal{S}(\Gamma)$, contains just a single wavevector.

$$\mathbf{k} = v\mathbf{b}^* (\Delta): \mathbf{k}\cdot\mathbf{T}_{mnp} = 2\pi nv$$

$$\mathcal{G}(\Delta) = \{(1|\mathbf{T}_{mnp}), (2_{010}|\mathbf{T}_{mnp})\}$$

	$(1 \mathbf{T}_{mnp})$	$(2_{010} \mathbf{T}_{mnp})$
$\Delta^{(1)}$	$e^{-2\pi inv}$	$e^{-2\pi inv}$
$\Delta^{(2)}$	$e^{-2\pi inv}$	$-e^{-2\pi inv}$

The two complex IRs are symmetric and antisymmetric with respect to the 2-fold rotation. $\mathcal{S}(\Delta)$ contains two wavevectors, $\pm v\mathbf{b}^*$.

$$\mathbf{k} = 1/2\mathbf{b}^* (\mathbf{Z}): \mathbf{k}\cdot\mathbf{T}_{mnp} = \pi n$$

$$\mathcal{G}(\mathbf{Z}) = \{(1|\mathbf{T}_{mnp}), (2_{010}|\mathbf{T}_{mnp})\}$$

	$(1 \mathbf{T}_{mnp})$	$(2_{010} \mathbf{T}_{mnp})$
$\mathbf{Z}^{(1)}$	$(-1)^n$	$(-1)^n$
$\mathbf{Z}^{(2)}$	$(-1)^n$	$-(-1)^n$

The two real IRs are nondegenerate. $\mathcal{S}(\mathbf{Z})$ contains just one wavevector.

$$P2_1 = \{(1|\mathbf{T}_{mnp})\} \times \{(1|\mathbf{0}), (2_{010}|\mathbf{b}/2)\}$$

$$\mathbf{k} = \mathbf{0} (\Gamma): \mathbf{k}\cdot\mathbf{T}_{mnp} = 0$$

$$\mathcal{G}(\Gamma) = \{(1|\mathbf{T}_{mnp}), (2_{010}|\mathbf{b}/2 + \mathbf{T}_{mnp})\}$$

	$(1 \mathbf{T}_{mnp})$	$(2_{010} \mathbf{b}/2 + \mathbf{T}_{mnp})$
$\Gamma^{(1)} \equiv a$	1	1
$\Gamma^{(2)} \equiv b$	1	-1

The IRs are either symmetric or antisymmetric with respect to the 2-fold rotation. For Γ , there are no phase changes for any lattice translation. The star of Γ , $\mathcal{S}(\Gamma)$, contains just a single wavevector.

$$\mathbf{k} = v\mathbf{b}^* (\Delta): \mathbf{k}\cdot\mathbf{T}_{mnp} = 2\pi nv$$

$$\mathcal{G}(\Delta) = \{(1|\mathbf{T}_{mnp}), (2_{010}|\mathbf{b}/2 + \mathbf{T}_{mnp})\}$$

	$(1 \mathbf{T}_{mnp})$	$(2_{010} \mathbf{b}/2 + \mathbf{T}_{mnp})$
$\Delta^{(1)}$	$e^{-2\pi inv}$	$e^{-2\pi inv}e^{-\pi iv}$
$\Delta^{(2)}$	$e^{-2\pi inv}$	$-e^{-2\pi inv}e^{-\pi iv}$

The two complex IRs are symmetric and antisymmetric with respect to the 2-fold rotation. $\mathcal{S}(\Delta)$ contains two wavevectors, $\pm v\mathbf{b}^*$.

$$\mathbf{k} = 1/2\mathbf{b}^* (\mathbf{Z}): \mathbf{k}\cdot\mathbf{T}_{mnp} = \pi n$$

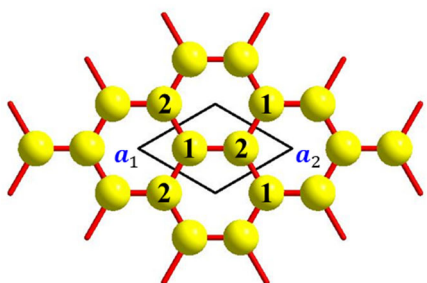
$$\mathcal{G}(\mathbf{Z}) = \{(1|\mathbf{T}_{mnp}), (2_{010}|\mathbf{b}/2 + \mathbf{T}_{mnp})\}$$

	$(1 \mathbf{T}_{mnp})$	$(2_{010} \mathbf{b}/2 + \mathbf{T}_{mnp})$
$\mathbf{Z}^{(1)}$	$(-1)^n$	$-i(-1)^n$
$\mathbf{Z}^{(2)}$	$(-1)^n$	$i(-1)^n$

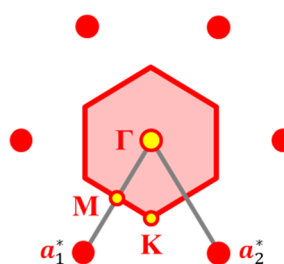
The two IRs are complex conjugates of each other and, therefore, degenerate. $\mathcal{S}(\mathbf{Z})$ has just one wavevector.

To see the significance of determining the irreducible representations of space groups for electronic band structures and phonon dispersion curves, we examine and analyze the symmetry characteristics of the electronic π -bands of graphene.

(53) Graphene π -Bands: Graphene is a planar, honeycomb network of carbon atoms adopting the 2-d space group $p6mm$. The hexagonal unit cell contains two carbon atoms and the lattice points (unit cell corners) are the centers of every hexagon. Also, carbon atoms “1” are bonded solely to three carbon atoms “2” and vice versa.



Real space structure of graphene with carbon atoms in one hexagonal unit cell and their nearest neighbors labelled. The lattice points occur at the centers of every hexagon.



Reciprocal lattice for hexagonal symmetry. The first Brillouin zone is the shaded hexagonal region around reciprocal lattice point Γ . M and K are important wavevectors for plotting the π -band structure.

The first Brillouin zone for the hexagonal system contains all allowed wavevectors that assign the translational symmetry characteristics of the electronic wavefunctions. Using these allowed wavevectors, a tight-binding (L.C.A.O.-type) electronic structure calculation follows these steps:

- *FORM Bloch functions for each AO in the basis set of one unit cell:*

Each carbon atom utilizes one $2p_z$ AO to form the π -electronic bands. Designate $\varphi_1(\mathbf{r})$ and $\varphi_2(\mathbf{r})$ for these AOs. Then, the two general Bloch functions are

$$\psi_{1\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_1 N_2}} \sum_m \sum_n e^{i\mathbf{k} \cdot \mathbf{T}_{mn}} \varphi_1(\mathbf{r} - \mathbf{T}_{mn});$$

$$\psi_{2\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_1 N_2}} \sum_m \sum_n e^{i\mathbf{k} \cdot \mathbf{T}_{mn}} \varphi_2(\mathbf{r} - \mathbf{T}_{mn}).$$

Now, choose the periodic boundary conditions to be $N_1 = N_2 = N$, and replace the vector notation in the phase factors by coordinates. In real space, $\mathbf{T}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2$; in reciprocal space, $\mathbf{k} = k_1\mathbf{a}_1^* + k_2\mathbf{a}_2^*$. Then $\mathbf{k} \cdot \mathbf{T}_{mn} = 2\pi(mk_1 + nk_2)$. Lastly, substitute $\varphi_1(m, n)$ and $\varphi_2(m, n)$, respectively, for $\varphi_1(\mathbf{r} - \mathbf{T}_{mn})$ and $\varphi_2(\mathbf{r} - \mathbf{T}_{mn})$. Then

$$\psi_{1\mathbf{k}}(\mathbf{r}) = \frac{1}{N} \sum_m \sum_n e^{2\pi i m k_1} e^{2\pi i n k_2} \varphi_1(m, n);$$

$$\psi_{2\mathbf{k}}(\mathbf{r}) = \frac{1}{N} \sum_m \sum_n e^{2\pi i m k_1} e^{2\pi i n k_2} \varphi_2(m, n).$$

- *CONSTRUCT the Hamiltonian matrix $H(\mathbf{k})$ for a wavevector \mathbf{k} using these Bloch functions:*

For simplicity, use the Hückel approximation, which considers just nearest neighbor orbital overlap. With two basis functions per unit cell, $H(\mathbf{k})$ is a 2×2 matrix. By taking the connectivities of carbon atoms into account, the (on-site) coulomb integrals are

$$\alpha_p = \langle \varphi_1(m, n) | H | \varphi_1(m, n) \rangle = \langle \varphi_2(m, n) | H | \varphi_2(m, n) \rangle \sim \text{energy of C } 2p_z \text{ AO,}$$

and the (inter-site) resonance integrals between nearest neighbor atoms are

$$\begin{aligned}\beta_{zz} &= \langle \varphi_1(m, n) | H | \varphi_2(m, n) \rangle = \langle \varphi_1(m, n) | H | \varphi_2(m+1, n) \rangle = \langle \varphi_1(m, n) | H | \varphi_2(m, n-1) \rangle \\ &= \langle \varphi_2(m, n) | H | \varphi_1(m, n) \rangle = \langle \varphi_2(m, n) | H | \varphi_1(m-1, n) \rangle = \langle \varphi_2(m, n) | H | \varphi_1(m, n+1) \rangle.\end{aligned}$$

All other inter-site integrals, i.e., integrals for atom pairs that exceed nearest neighbor contacts, are 0. The numerical values of α_p and β_{zz} are negative-valued. Then, the Hamiltonian matrix elements are:

$$\begin{aligned}\langle \psi_{1\mathbf{k}} | H | \psi_{1\mathbf{k}} \rangle &= \frac{1}{N^2} \sum_{m, m'} \sum_{n, n'} e^{2\pi i(m-m')k_1} e^{2\pi i(n-n')k_2} \langle \varphi_1(m', n') | H | \varphi_1(m, n) \rangle \\ &= \frac{1}{N} \sum_m \sum_n \langle \varphi_1(m, n) | H | \varphi_1(m, n) \rangle = \alpha_p. \\ \langle \psi_{2\mathbf{k}} | H | \psi_{2\mathbf{k}} \rangle &= \frac{1}{N} \sum_m \sum_n \langle \varphi_2(m, n) | H | \varphi_2(m, n) \rangle = \alpha_p. \\ \langle \psi_{1\mathbf{k}} | H | \psi_{2\mathbf{k}} \rangle &= \frac{1}{N^2} \sum_{m, m'} \sum_{n, n'} e^{2\pi i(m-m')k_1} e^{2\pi i(n-n')k_2} \langle \varphi_1(m', n') | H | \varphi_2(mn) \rangle \\ &= \frac{1}{N} \sum_m \sum_n \langle \varphi_1(m, n) | H | \varphi_2(m, n) \rangle + e^{2\pi i k_1} \langle \varphi_1(m, n) | H | \varphi_2(m+1, n) \rangle + \\ &\quad e^{-2\pi i k_2} \langle \varphi_1(m, n) | H | \varphi_2(m, n-1) \rangle \\ &= \beta_{zz} + \beta_{zz} e^{2\pi i k_1} + \beta_{zz} e^{-2\pi i k_2}. \\ \langle \psi_{2\mathbf{k}} | H | \psi_{1\mathbf{k}} \rangle &= \beta_{zz} + \beta_{zz} e^{-2\pi i k_1} + \beta_{zz} e^{2\pi i k_2} = \langle \psi_{1\mathbf{k}} | H | \psi_{2\mathbf{k}} \rangle^*.\end{aligned}$$

The Hamiltonian matrix is:

$$H(\mathbf{k}) = \begin{pmatrix} \alpha_p & \beta_{zz}(1 + e^{2\pi i k_1} + e^{-2\pi i k_2}) \\ \beta_{zz}(1 + e^{-2\pi i k_1} + e^{2\pi i k_2}) & \alpha_p \end{pmatrix}.$$

- *DIAGONALIZE* $H(\mathbf{k})$ to obtain Energies $E_n(\mathbf{k})$ and Wavefunctions $\Psi_{n\mathbf{k}}(\mathbf{r})$:

The two eigenfunctions are linear combinations of the two Bloch functions:

$$\begin{aligned}\Psi_{1\mathbf{k}}(\mathbf{r}) &= c_{11}(\mathbf{k})\psi_{1\mathbf{k}}(\mathbf{r}) + c_{12}(\mathbf{k})\psi_{2\mathbf{k}}(\mathbf{r}), \text{ and} \\ \Psi_{2\mathbf{k}}(\mathbf{r}) &= c_{21}(\mathbf{k})\psi_{1\mathbf{k}}(\mathbf{r}) + c_{22}(\mathbf{k})\psi_{2\mathbf{k}}(\mathbf{r}).\end{aligned}$$

The resulting Schrödinger equation becomes

$$\begin{aligned}H(\mathbf{k})\Psi_{n\mathbf{k}}(\mathbf{r}) &= \begin{pmatrix} \alpha_p & \beta_{zz} + \beta_{zz}e^{2\pi i k_1} + \beta_{zz}e^{-2\pi i k_2} \\ \beta_{zz} + \beta_{zz}e^{-2\pi i k_1} + \beta_{zz}e^{2\pi i k_2} & \alpha_p \end{pmatrix} \begin{pmatrix} c_{n1}(\mathbf{k}) \\ c_{n2}(\mathbf{k}) \end{pmatrix} \\ &= E_n(\mathbf{k}) \begin{pmatrix} c_{n1}(\mathbf{k}) \\ c_{n2}(\mathbf{k}) \end{pmatrix} = E_n(\mathbf{k})\Psi_{n\mathbf{k}}(\mathbf{r}),\end{aligned}$$

which is solved by setting the secular determinant to 0:

$$\det \begin{pmatrix} \alpha_p - E_n(\mathbf{k}) & \beta_{zz}(1 + e^{2\pi i k_1} + e^{-2\pi i k_2}) \\ \beta_{zz}(1 + e^{-2\pi i k_1} + e^{2\pi i k_2}) & \alpha_p - E_n(\mathbf{k}) \end{pmatrix} = 0.$$

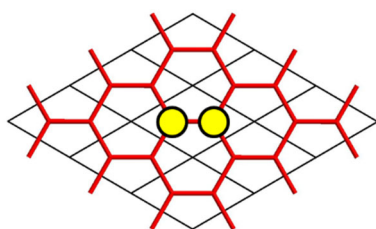
The eigenvalues (π -band energies) are:

$$\begin{aligned}E_1(\mathbf{k}) &= E_1(k_1, k_2) = \alpha_p + \beta_{zz} \sqrt{3 + 2 \cos 2\pi k_1 + 2 \cos 2\pi k_2 + 2 \cos 2\pi(k_1 + k_2)} \\ E_2(\mathbf{k}) &= E_2(k_1, k_2) = \alpha_p - \beta_{zz} \sqrt{3 + 2 \cos 2\pi k_1 + 2 \cos 2\pi k_2 + 2 \cos 2\pi(k_1 + k_2)}.\end{aligned}$$

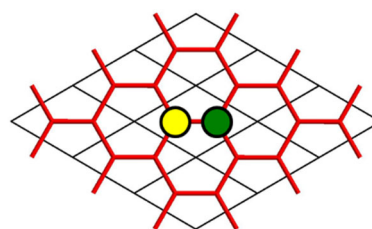
Since $\beta_{zz} < 0$, $E_1(\mathbf{k}) \leq \alpha_p$ and $E_2(\mathbf{k}) \geq \alpha_p$. The coefficients of the Bloch functions for each eigenfunction are $c_{11}(\mathbf{k}) = c_{12}(\mathbf{k}) = 1/\sqrt{2}$ and $c_{21}(\mathbf{k}) = -c_{22}(\mathbf{k}) = 1/\sqrt{2}$:

$$\begin{aligned}\Psi_{1\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{2}}\psi_{1\mathbf{k}}(\mathbf{r}) + \frac{1}{\sqrt{2}}\psi_{2\mathbf{k}}(\mathbf{r}) = \frac{1}{N}\sum_m\sum_n e^{2\pi imk_1}e^{2\pi ink_2} \frac{1}{\sqrt{2}}(\varphi_1(m,n) + \varphi_2(m,n)) \\ &= \frac{1}{N}\sum_m\sum_n e^{2\pi imk_1}e^{2\pi ink_2} \pi_1(m,n) \equiv \Pi_{\mathbf{k}}(\mathbf{r}) \\ \Psi_{2\mathbf{k}}(\mathbf{r}) &= \frac{1}{\sqrt{2}}\psi_{1\mathbf{k}}(\mathbf{r}) - \frac{1}{\sqrt{2}}\psi_{2\mathbf{k}}(\mathbf{r}) = \frac{1}{N}\sum_m\sum_n e^{2\pi imk_1}e^{2\pi ink_2} \frac{1}{\sqrt{2}}(\varphi_1(m,n) - \varphi_2(m,n)) \\ &= \frac{1}{N}\sum_m\sum_n e^{2\pi imk_1}e^{2\pi ink_2} \pi_2(m,n) \equiv \Pi_{\mathbf{k}}^*(\mathbf{r})\end{aligned}$$

Both eigenfunctions of the Hamiltonian $H(\mathbf{k})$ are also Bloch functions, but they are formed by two molecular orbitals in a single unit cell: $\pi_1(\mathbf{r})$ is the in-phase, π -bonding combination of p_z AOs; and $\pi_2(\mathbf{r})$ is the out-of-phase, π -antibonding combination of p_z AOs:¹⁵



$$\pi_1(0,0) = \frac{1}{\sqrt{2}}(\varphi_1(0,0) + \varphi_2(0,0))$$

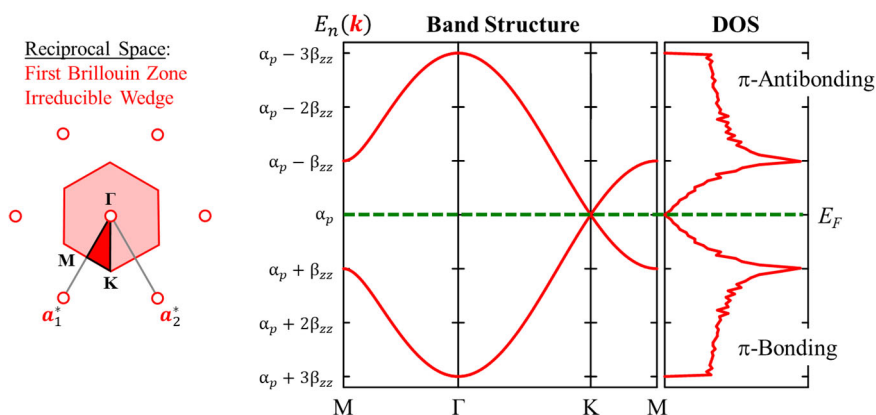


$$\pi_2(0,0) = \frac{1}{\sqrt{2}}(\varphi_1(0,0) - \varphi_2(0,0))$$

As a result, we “rename” $\Psi_{1\mathbf{k}}(\mathbf{r})$ and $\Psi_{2\mathbf{k}}(\mathbf{r})$ by $\Pi_{\mathbf{k}}(\mathbf{r})$ and $\Pi_{\mathbf{k}}^*(\mathbf{r})$, respectively, to emphasize that they are derived from the π -bonding and π -antibonding combinations of p_z AOs.

(54) In this problem, $E_n(\mathbf{k})$ are analytical expressions of wavevector. Generally, determining the eigenvalues and eigenvectors involves diagonalizing $H(\mathbf{k})$ for selected wavevectors in the irreducible wedge of the first Brillouin zone. After this is accomplished, the next step is to

- *PLOT the Band Structure and Electronic Density of States (DOS) Curves:*



Wavevectors for the hexagonal system are $\mathbf{k} = k_1\mathbf{a}_1^* + k_2\mathbf{a}_2^* \equiv (k_1, k_2)$, and the irreducible wedge is the triangular region identified by a reciprocal lattice point $\Gamma = (0,0)$, a corner $K = (\frac{1}{3}, \frac{1}{3})$, and an edge center $M = (\frac{1}{2}, 0)$. The electronic band structure shows the eigenvalues as a function of wavevector along the borders of the irreducible wedge: $M-\Gamma-K-M$. The density of states (DOS) curve is determined by evaluating the eigenvalues for a dense set of

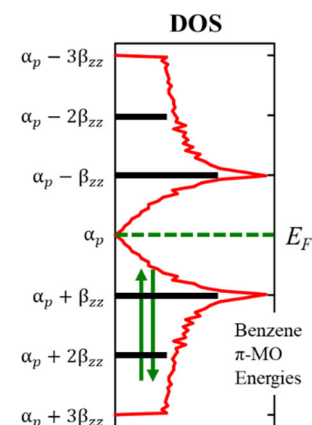
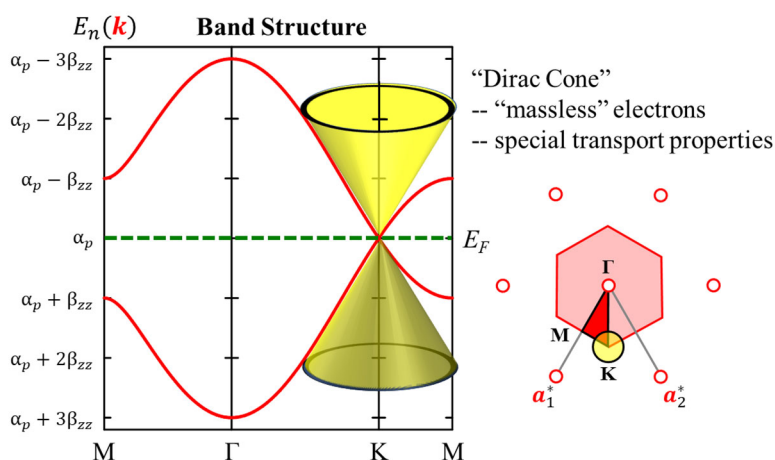
¹⁵ In the crystal orbital figures for the graphene π -bands, only p -AO lobes on one side of the plane are illustrated.

wavevectors uniformly distributed throughout the irreducible wedge. The dashed line indicates the Fermi level E_F , which is the highest energy of the occupied states in the DOS. Since each C $2p_z$ AO is assigned one electron, then this two-band system contains two electrons and $E_F = \alpha_p$. According to the band structure, the Fermi wavevector is K. As will be revealed from analysis of the eigenfunctions, states below E_F are π -bonding and states above E_F are π -antibonding.

The band structure also reveals that the two π -bands cross at the wavevector K. From the rotational symmetry of $E_n(\mathbf{k})$ in the vicinity of K, the energy bands form two cones with their tips meeting at $E_n(\mathbf{K})$. This feature of the band structure is called *Dirac cones*, which lead to unusual electronic transport properties of graphene and other topological insulators.¹⁶ Dirac cones occur for certain 2-d

materials and exhibit *linear dispersion* of electronic energy with wavevector near the contact points in reciprocal space. For these cases, electronic conduction is explained by massless charge carriers, which are revealed by applying relativistic effects to the Hamiltonian operator.

The accompanying density of states curve shows symmetrical distributions of π -electronic states around the Fermi level α_p . Because the density of states at α_p goes to zero, graphene is called a *zero-gap semiconductor*. A small analogue to graphene is the hexagonal molecule benzene C_6H_6 . The result of a Hückel-type calculation of the π MOs of benzene yields a pattern of 6 MOs with energies: $\alpha_p + 2\beta_{zz}$ (totally bonding; $1\times$); $\alpha_p + \beta_{zz}$ (net bonding; $2\times$); $\alpha_p - \beta_{zz}$ (net antibonding; $2\times$); and $\alpha_p - 2\beta_{zz}$ (totally antibonding; $1\times$). The density of states curve for the π -bands of graphene shows strong similarities to the MO energy pattern of benzene. For example, the doubly degenerate MOs of benzene line up exactly with the two largest peaks in the density of states curve of graphene. Six π -electrons fill all three bonding π MOs and leave all three antibonding π MOs empty.



The exercise to calculate the π -band structure of graphene illustrates the significance of Bloch functions as useful starting sets of wavefunctions to calculate the electronic structure of a crystalline solid. Since Bloch functions are eigenfunctions of translational symmetry operations, the logical question arises, *how does rotational symmetry influence the outcome?* The answer is embedded in the diagonalization of the Hamiltonian $H(\mathbf{k})$, a procedure which yields the complete

¹⁶ I.N. Yakovkin, *Crystals*, **2016**, 6, 143; S. Das Sarma, S. Adam, E.H. Hwang, E. Rossi, *Rev. Mod. Phys.* **2011**, 83, 407-470.

wavefunctions and must be eigenfunctions of all symmetry operations of the group of the wavevector $\mathcal{G}(\mathbf{k})$. These characteristics of the wavefunctions produce the degeneracy in the π -band structure at wavevector \mathbf{K} . In the following, we incorporate rotational symmetry of graphene to identify the IRs for the π -bands in the band structure.

(55) Graphene π -Bands - Symmetry Analysis: The atomic structure of graphene adopts the 2-d space group $p6mm$, which is the product of the following sets:

$$\mathcal{R} = \left\{ \begin{array}{l} (6|0), (6^2|0), (6^3|0), (6^4|0), (6^5|0), (1|0), \\ (m_{10}|0), (m_{01}|0), (m_{11}|0), (m_{21}|0), (m_{12}|0), (m_{\bar{1}\bar{1}}|0) \end{array} \right\} = \text{point group } 6mm; \text{ and}$$

$$\mathcal{L} = \{(1|\mathbf{T}_{mn}) : \mathbf{T}_{mn} = m\mathbf{a}_1 + n\mathbf{a}_2; m, n = \text{integer}; \alpha_1 = \alpha_2, \alpha_3 = 120^\circ\} = \text{Bravais lattice group.}$$

Each eigenfunction of $H(\mathbf{k})$ transforms according to one of the IRs of $\mathcal{G}(\mathbf{k})$, which is a subgroup of $p6mm$. Because $p6mm$ is symmorphic, these IRs are products of the IRs of \mathcal{L} and $\mathcal{G}_0(\mathbf{k})$:

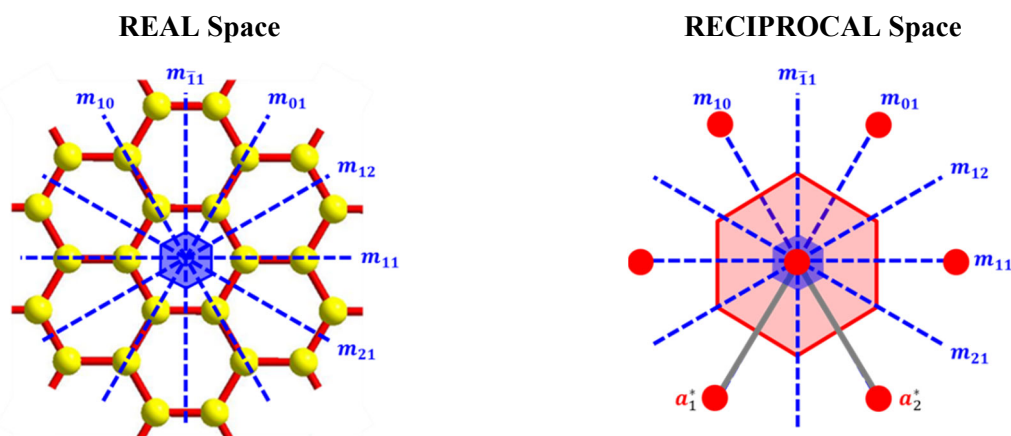
$$D^{(k\mu)}(R_i|\mathbf{T}_{mn}) = e^{-\mathbf{k}\cdot\mathbf{T}_{mn}} D_0^{(k\mu)}(R_i).$$

We will demonstrate this outcome for selected wavevectors in the band structure diagram. To accomplish this, we use the form of Bloch's theorem that relates the wavefunction for any unit cell positioned at \mathbf{T}_{mn} with respect to the Bloch function at the origin cell \mathbf{T}_{00} :

$$\pi\text{-bonding:} \quad \Pi_{\mathbf{k}}(\mathbf{r} + \mathbf{T}_{mn}) = e^{i\mathbf{k}\cdot\mathbf{T}_{mn}} \Pi_{\mathbf{k}}(\mathbf{r}) = e^{2\pi i m k_1} e^{2\pi i n k_2} \Pi_{\mathbf{k}}(\mathbf{r}),$$

$$\pi\text{-antibonding:} \quad \Pi_{\mathbf{k}}^*(\mathbf{r} + \mathbf{T}_{mn}) = e^{i\mathbf{k}\cdot\mathbf{T}_{mn}} \Pi_{\mathbf{k}}^*(\mathbf{r}) = e^{2\pi i m k_1} e^{2\pi i n k_2} \Pi_{\mathbf{k}}^*(\mathbf{r}).$$

For each wavevector, we must identify $\mathcal{G}_0(\mathbf{k})$ to determine the appropriate IR for each wavefunction. The nodal characteristics of each crystal orbital will rationalize its energy relative to α_p . This analysis starts by recognizing how the rotational symmetry operations of $6mm$ are oriented in the real space structure and the corresponding reciprocal lattice:

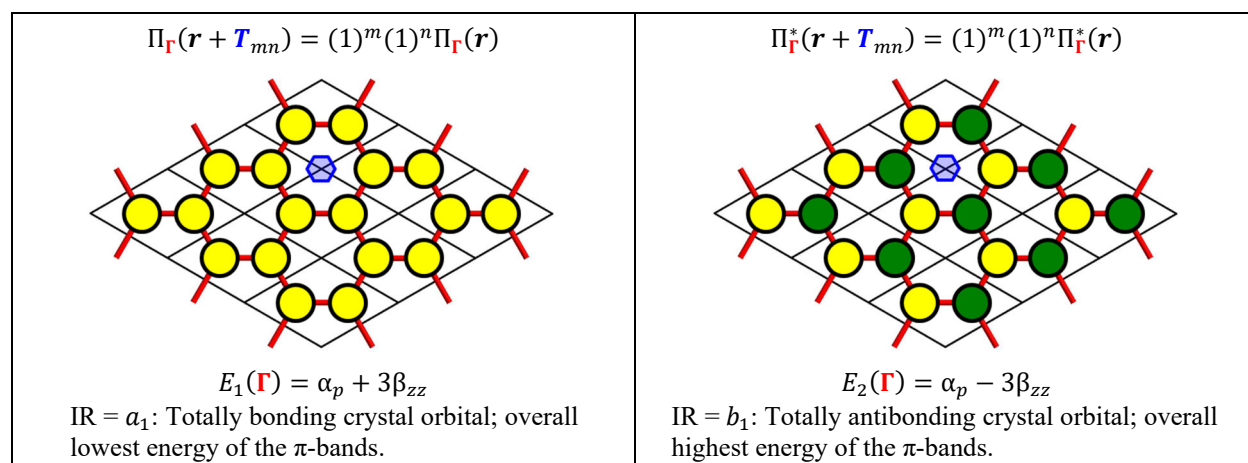


(56) Γ -point (0,0): All operations of \mathcal{G}_0 keep (0,0) invariant, so $\mathcal{G}_0(\Gamma)$ is $6mm$. The character table indicates 6 classes divided into the proper rotations and two sets of reflections. For order 12, there are four 1-d and two 2-d IRs. The phase factors for Bloch-type wavefunctions are unity along both \mathbf{a}_1 and \mathbf{a}_2 :

$$e^{2\pi i(0m+0n)} = (1)^m(1)^n.$$

$6mm$	1	6 6^5	3 3^2	2	m_{10} m_{01} m_{11}	m_{11} m_{21} m_{12}	Basis Functions*
\mathbf{a}_1	1	1	1	1	1	1	$\cos 6\theta$
\mathbf{a}_2	1	1	1	1	-1	-1	$\sin 12\theta$
\mathbf{b}_1	1	-1	1	-1	1	-1	$\sin 3\theta$
\mathbf{b}_2	1	-1	1	-1	-1	1	$\cos 3\theta$
\mathbf{e}_1	2	1	-1	-2	0	0	$\cos \theta, \sin \theta$
\mathbf{e}_2	2	-1	-1	2	0	0	$\cos 2\theta, \sin 2\theta$

* θ = angle from lattice vector \mathbf{a}_1

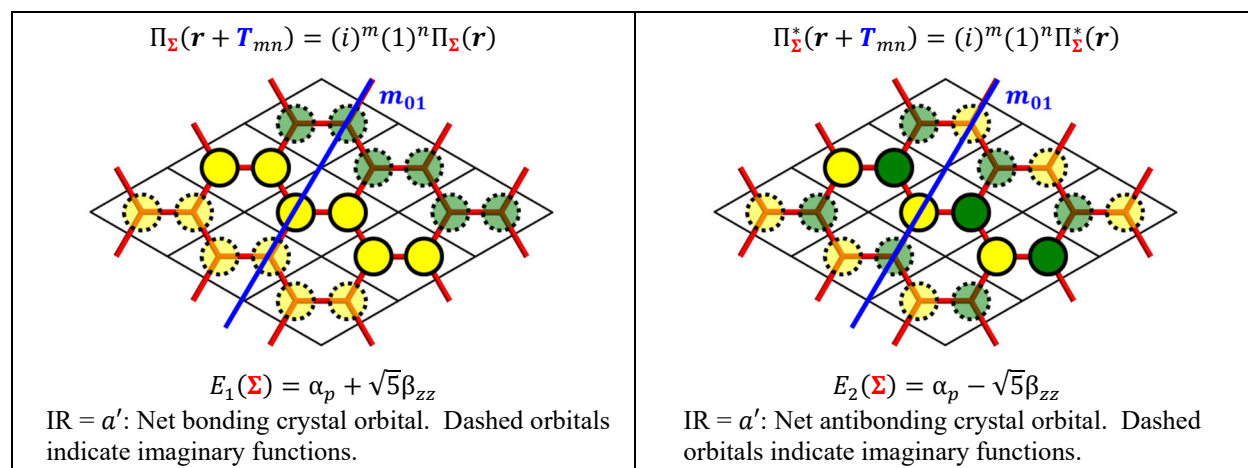


The star of Γ contains one wavevector, so these crystal orbitals are each nondegenerate.

(57) Σ -point ($k_1, 0$): Only m_{01} keeps ($k_1, 0$) invariant, so $\mathcal{G}_0(\Sigma)$ is $m = \{1, m_{01}\}$. There are two 1-d IRs, which are either symmetric or antisymmetric with respect to m_{01} . The phase factors for Bloch-type wavefunctions vary along \mathbf{a}_1 and are unity along \mathbf{a}_2 . At ($1/4, 0$), wavefunctions alternate between real and imaginary values along \mathbf{a}_1 :

$$e^{2\pi i(\frac{1}{4}m+0n)} = (e^{i\pi/2})^m(1)^n = (i)^m(1)^n.$$

m	1	m_{01}	Basis Functions
\mathbf{a}'	1	1	$\cos \theta$
\mathbf{a}''	1	-1	$\sin \theta$

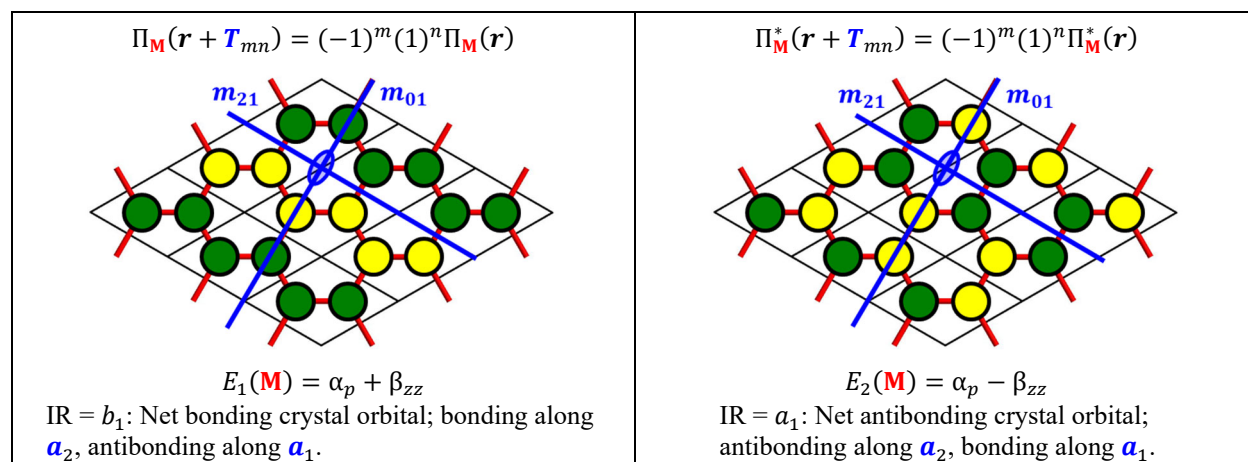


The star of Σ contains six wavevectors, so these crystal orbitals are each 6-fold degenerate.

(58) M-point ($\frac{1}{2}, 0$): This boundary point has one equivalent point at $(-\frac{1}{2}, 0)$. The operations taking $(\frac{1}{2}, 0)$ into either $(\frac{1}{2}, 0)$ or $(-\frac{1}{2}, 0)$ are m_{01} , 2, and m_{21} . Therefore, $\mathcal{G}_0(\mathbf{M})$ is $2mm = \{1, 2, m_{01}, m_{21}\}$. The phase factors for Bloch-type wavefunctions alternate signs along \mathbf{a}_1 and are unity along \mathbf{a}_2 :

$$e^{2\pi i(\frac{1}{2}m+0n)} = (e^{i\pi})^m (1)^n = (-1)^m (1)^n.$$

$2mm$	1	2	m_{01}	m_{21}	Basis Functions
a_1	1	1	1	1	$\cos 2\theta$
a_2	1	1	-1	-1	$\sin 2\theta$
b_1	1	-1	1	-1	$\cos \theta$
b_2	1	-1	-1	1	$\sin \theta$

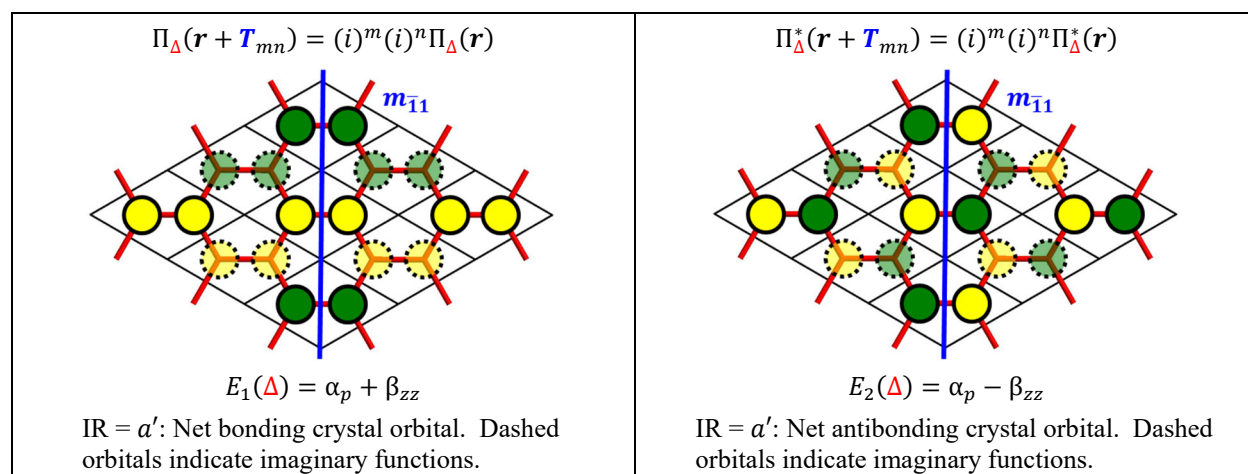


The star of \mathbf{M} contains three wavevectors, so these crystal orbitals are each 3-fold degenerate.

(59) Δ -point (k_1, k_1): Only $m_{\bar{1}1}$ keeps (k_1, k_1) invariant, so $\mathcal{G}_0(\Delta)$ is $m = \{1, m_{\bar{1}1}\}$. There are two 1-d IRs, which are either symmetric or antisymmetric with respect to $m_{\bar{1}1}$. The phase factors for Bloch-type wavefunctions vary along \mathbf{a}_1 and \mathbf{a}_2 . At $(\frac{1}{4}, \frac{1}{4})$, wavefunctions alternate between real and imaginary values along \mathbf{a}_1 and \mathbf{a}_2 :

$$e^{2\pi i(m/4+n/4)} = (e^{i\pi/2})^m (e^{i\pi/2})^n = (i)^m (i)^n.$$

m	1	$m_{\bar{1}1}$	Basis Functions
a'	1	1	$\cos(\theta - \frac{\pi}{6})$
a''	1	-1	$\sin(\theta - \frac{\pi}{6})$

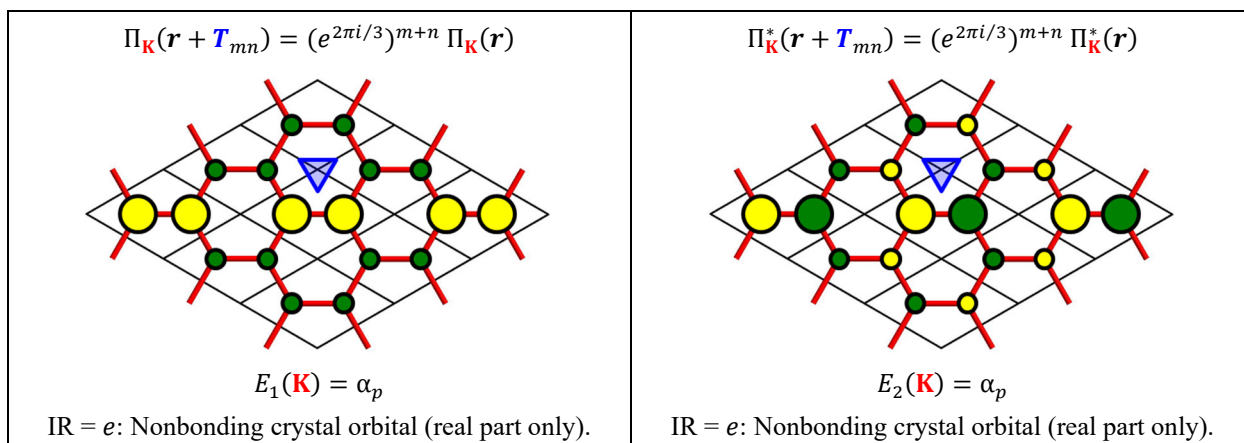


The star of Δ contains six wavevectors, so these crystal orbitals are each 6-fold degenerate.

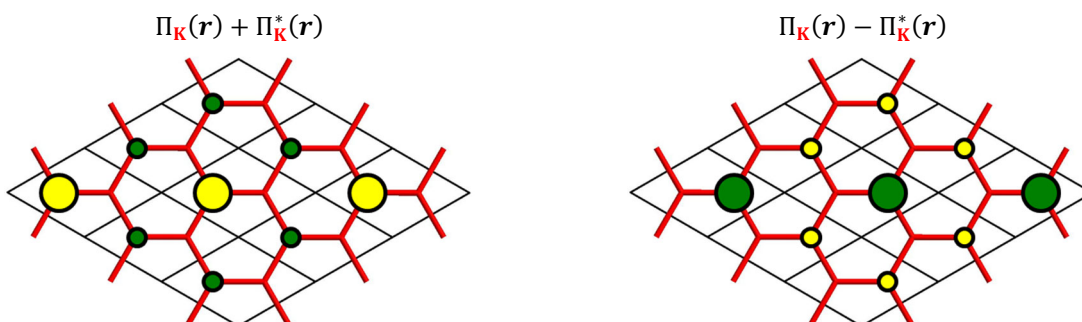
(60) K-point ($1/3, 1/3$): This boundary point has two equivalent points at $(-2/3, 1/3)$ and $(1/3, -2/3)$. The operations of \mathcal{G}_0 that take $(1/3, 1/3)$ into itself or one of its equivalent points are members of the point group $\mathcal{G}_0(\mathbf{K}) = 3m = \{1, 3, 3^2, m_{\bar{1}1}, m_{21}, m_{12}\}$, which has three classes. There are two 1-d and one 2-d IRs. The phase factors for Bloch-type wavefunctions vary along both \mathbf{a}_1 and \mathbf{a}_2 :

$$e^{2\pi i(m/3+n/3)} = (e^{2\pi i/3})^m (e^{2\pi i/3})^n = (e^{2\pi i/3})^{m+n}.$$

$3m$	1	3 3^2	$m_{\bar{1}1}$ m_{21} m_{12}	Basis Functions
\mathbf{a}_1	1	1	1	$\sin 3\theta$
\mathbf{a}_2	1	1	-1	$\cos 3\theta$
e	2	-1	0	$\cos \theta, \sin \theta$

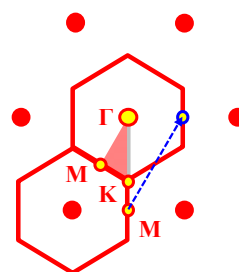


From this visualization of the real parts of these Bloch functions, it may not be apparent that they are nonbonding. Because any linear combination of degenerate wavefunctions creates new degenerate wavefunctions, construct the new pair $\Pi_{\mathbf{K}}(\mathbf{r}) \pm \Pi_{\mathbf{K}}^*(\mathbf{r})$, which yields functions showing zero nearest neighbor orbital interactions:



The star of \mathbf{K} contains two wavevectors, so these crystal orbitals are 4-fold degenerate.

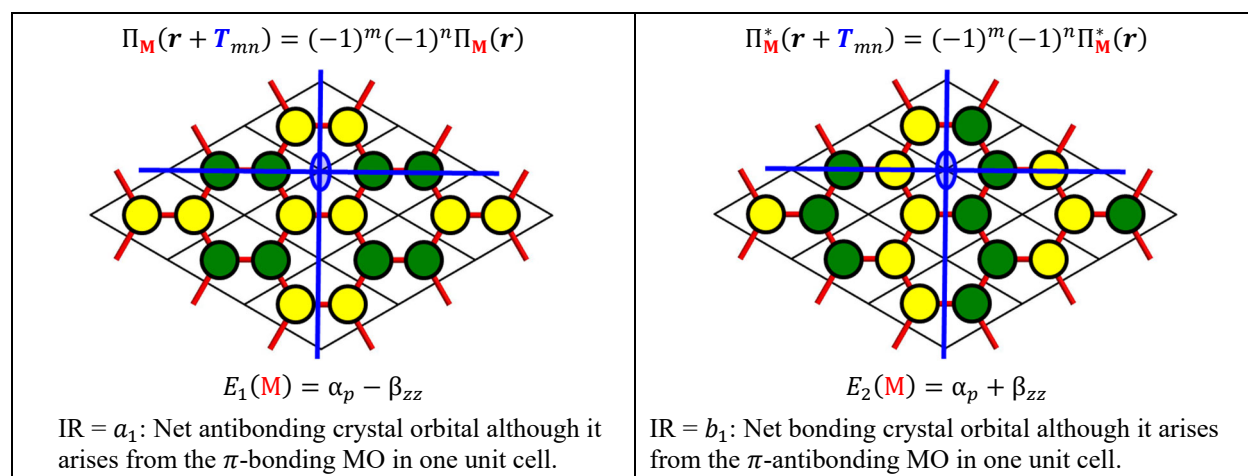
(61) M-point ($1/2, 1/2$): The final piece of the band structure plots energies along the K–M direction. Rather than proceed from $(1/3, 1/3)$ to $(1/2, 0)$, the calculation continues along the Δ -line beyond K to $(1/2, 1/2)$, which is equivalent to $(-1/2, 1/2)$ as pointed out to the right by the dashed blue line:



The point $(-\frac{1}{2}, \frac{1}{2})$ is a member of the star of M , and $\mathcal{G}_0(\mathbf{M}) = 2mm = \{1, 2, m_{11}, m_{\bar{1}1}\}$, which has 4 classes and 4 1-d IRs. The phase factors for Bloch-type wavefunctions alternate signs along both \mathbf{a}_1 and \mathbf{a}_2 :

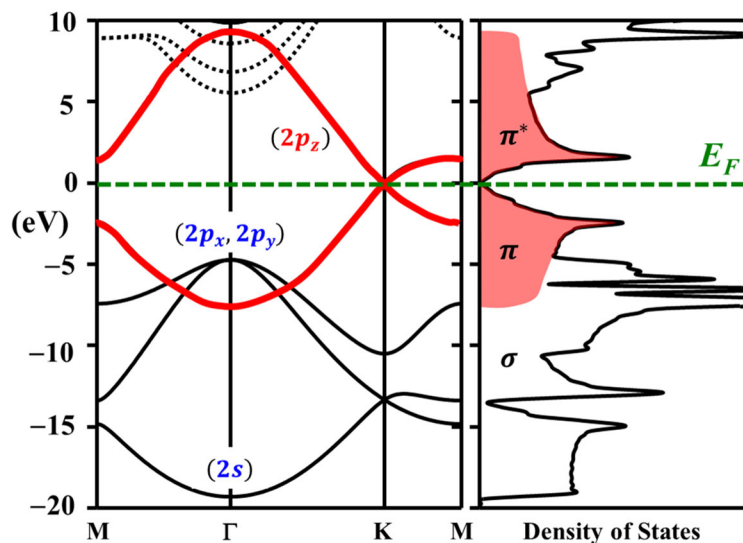
$$e^{2\pi i(m/2+n/2)} = (-1)^m(-1)^n:$$

$2mm$	1	2	m_{11}	$m_{\bar{1}1}$	Basis Functions
a_1	1	1	1	1	$\cos 2(\theta - \frac{\pi}{6})$
a_2	1	1	-1	-1	$\sin 2(\theta - \frac{\pi}{6})$
b_1	1	-1	1	-1	$\sin(\theta - \frac{\pi}{6})$
b_2	1	-1	-1	1	$\cos(\theta - \frac{\pi}{6})$



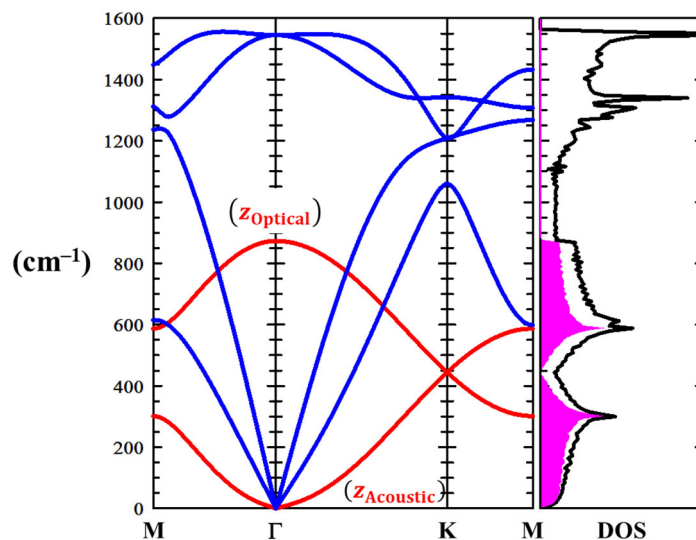
NOTE: The $\Pi_{\mathbf{k}}(\mathbf{r})$ and $\Pi_{\mathbf{k}}^*(\mathbf{r})$ crystal orbitals remain orthogonal along the entire Γ -K-M direction in reciprocal space. As a result, these two bands may cross each other, which they do at K as determined by the hexagonal symmetry of the graphene structure. Therefore, the unusual transport characteristics of graphene arise from its structural symmetry.

(62) Graphene Band Structure and Density of States: Carbon atom valence orbitals are $2s$, $2p_x$, $2p_y$ and $2p_z$ AOs, the first three of which build σ -bands and provide the strongest interatomic attractions. The graphene electronic band structure calculated by density functional theory indicates that the π -bands cross the σ -bands near the Γ point. In fact, the totally π -bonding crystal orbital at Γ drops below the 2-fold degenerate σ -bonding crystal orbital formed by the $2p_x$ and $2p_y$ AOs. Along both Γ -M and Γ -K directions, the 2-fold degeneracy breaks. Although symmetry allows the σ -bands and π -bands to cross in reciprocal space, the Fermi level occurs at the energy of the π -bands at K. Both the band structure and the density of states curve illustrate that the electronic states within ± 5 eV of the Fermi level arise from the π -bands exclusively. Also, the density of states goes to zero at E_F .



(63) Graphene Phonon Dispersion:

Normal mode analysis using the harmonic approximation yields the phonon dispersion and density of states curves shown here.¹⁷ There are 6 modes per unit cell because there are 2 C atoms per unit cell and 3 independent modes per atom. At the Γ point, 3 acoustic modes at $\omega = 0 \text{ cm}^{-1}$ and 3 optical modes at $\omega > 0 \text{ cm}^{-1}$ occur. Like the electronic band structure, phonon modes perpendicular to the graphene plane (z -direction) cross the in-plane modes (x, y -directions) because these functions are orthogonal. Also note that the out-of-plane phonon dispersions, shown in red, mimic the π -band structure.



¹⁷ Based on the results of Falkovsky, L.A., *Phys. Lett. A* **2008**, 372, 5189-5192.