Group theory, representations and their applications in solid state

TMS 2018

Outline of the course

1. Introduction: Symmetries, degeneracies and representations.

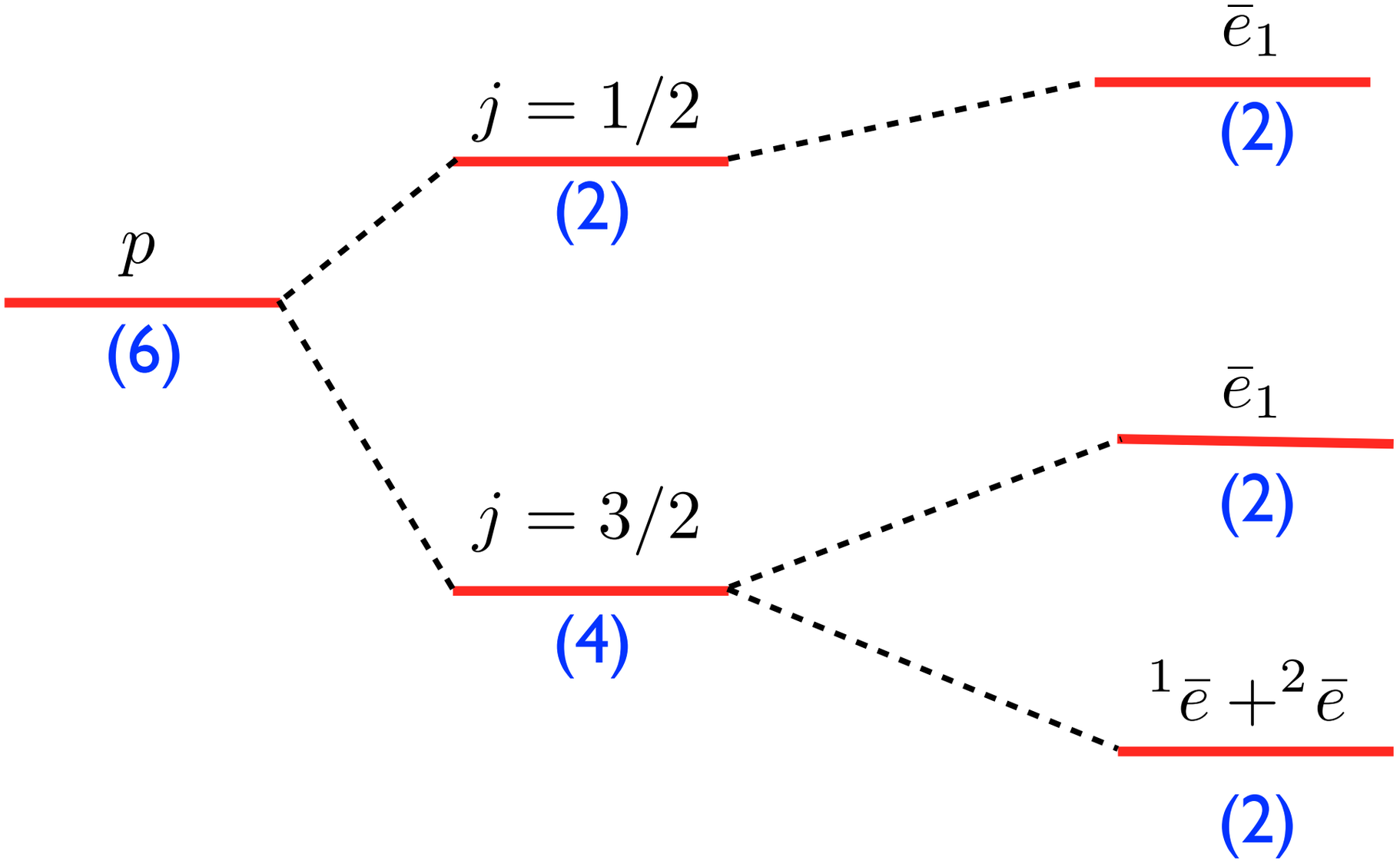
2. Irreducible representations as building blocks. Application to molecular vibrations.

3. Operations with representations: Physical properties and spectra.

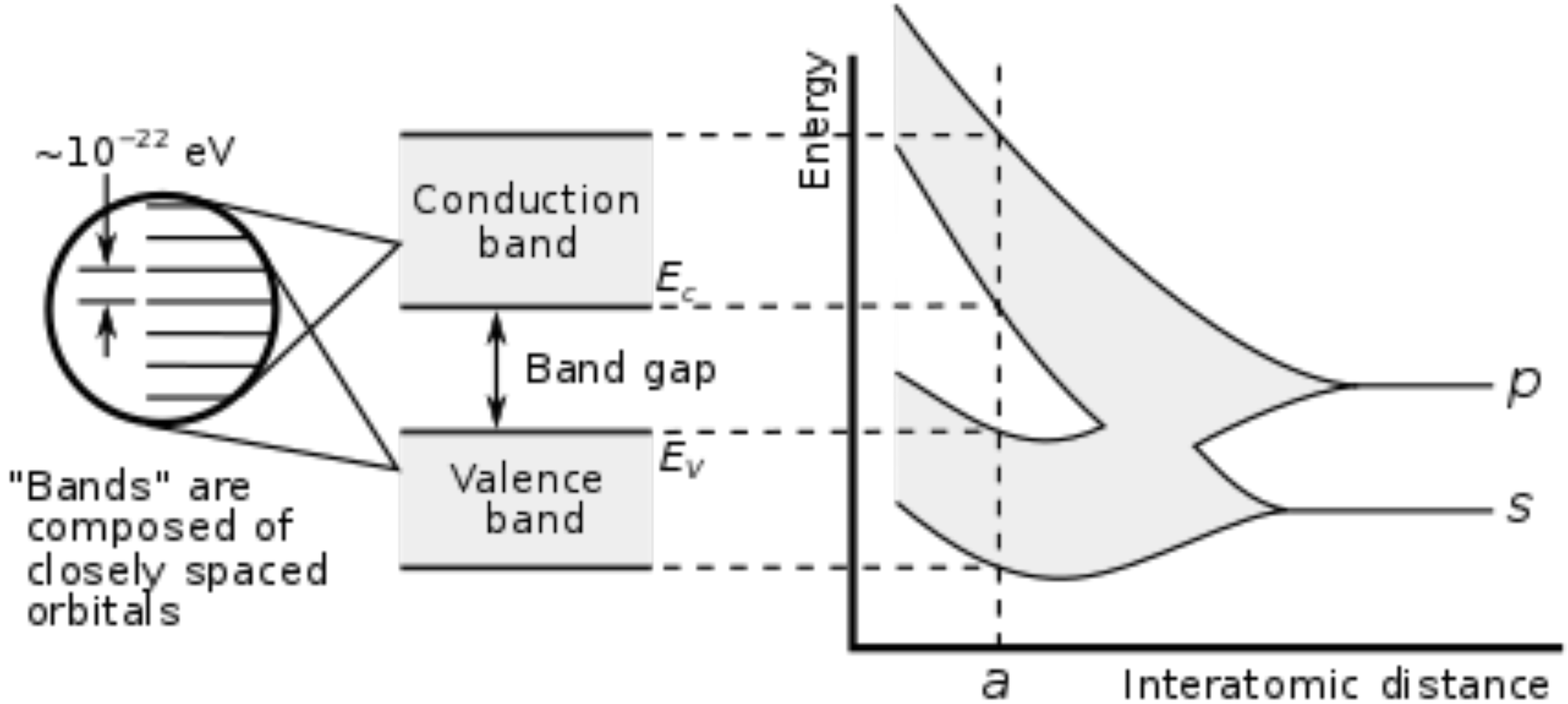
4. Spin and double valued representations. Splitting of atomic orbitals in crystals.

5. Representation theory and electronic bands.

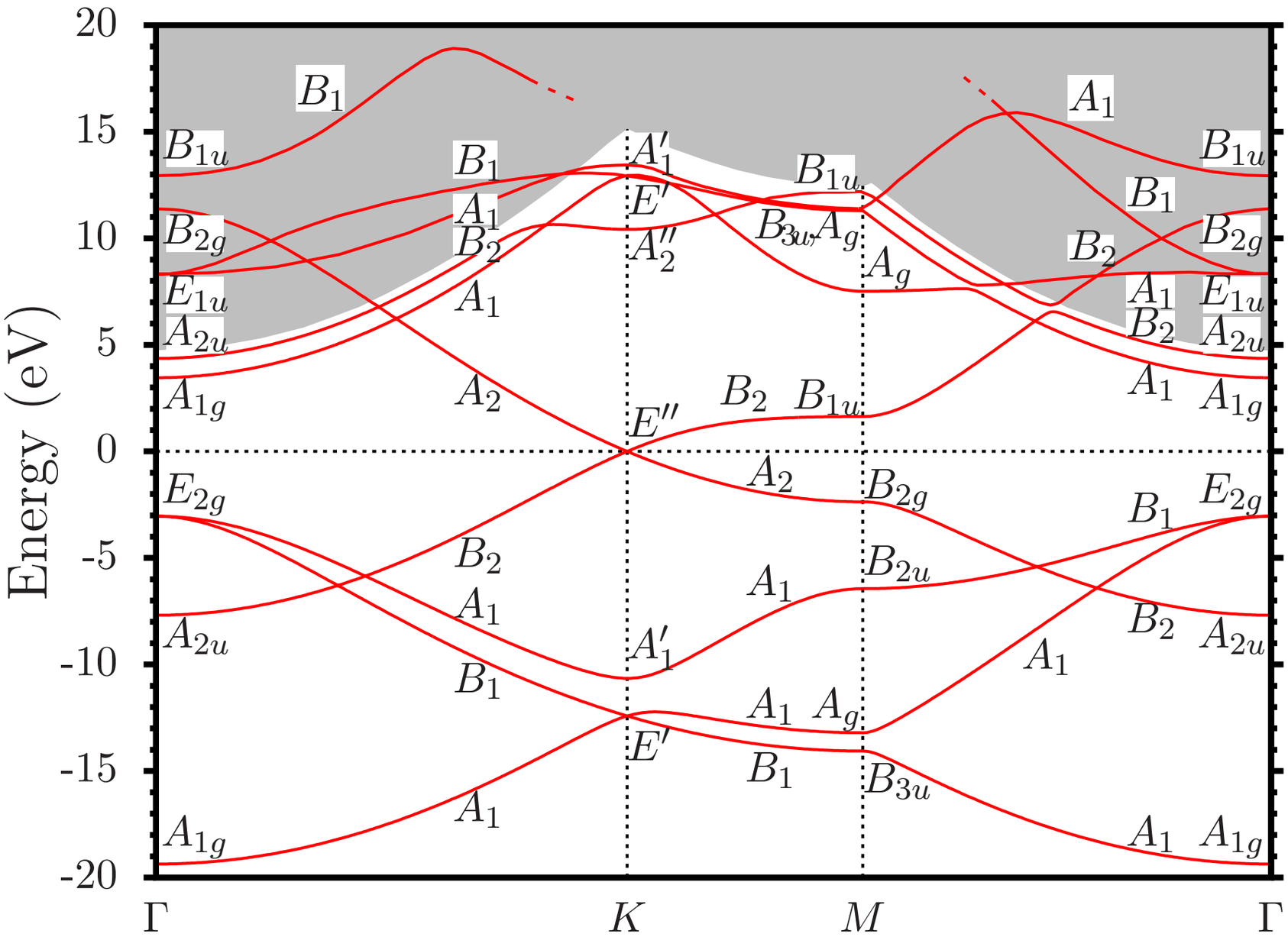
Splitting of p-orbitals in a crystal field *(strong spin-orbit)*



From atoms to crystals

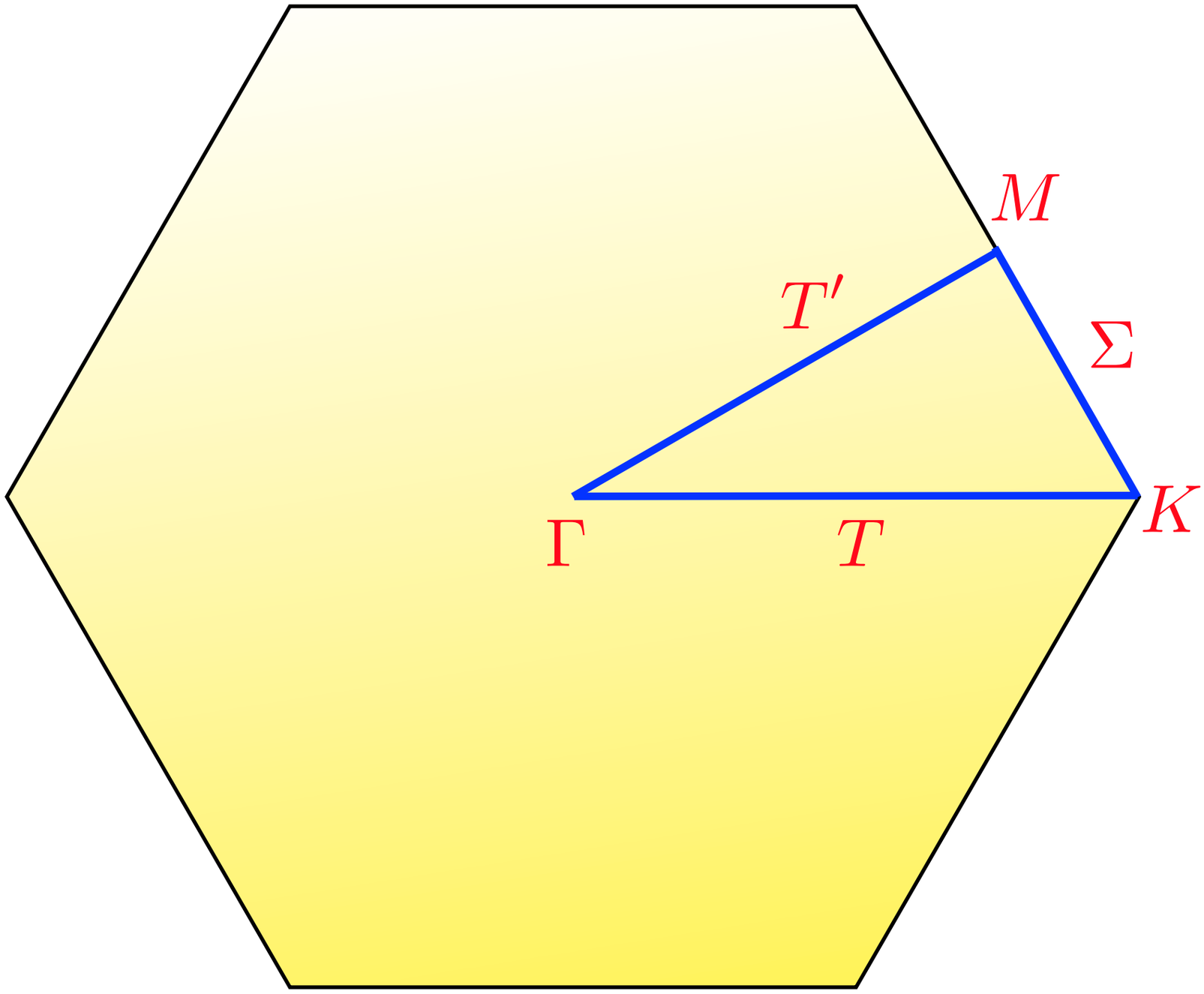


Electron bands in graphene



E. Kogan, V.U. Nazarov, V.M. Silkin, M. Kaveh, Phys. Rev. B 89, 165430 (2014)

First Brillouin zone for graphene



From atoms to crystals

A crystal may be obtained by placing replicas of a "molecule" at all the points in a *Bravais lattice*

$$\boxed{\vec{t} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3 \in \mathcal{T}}$$

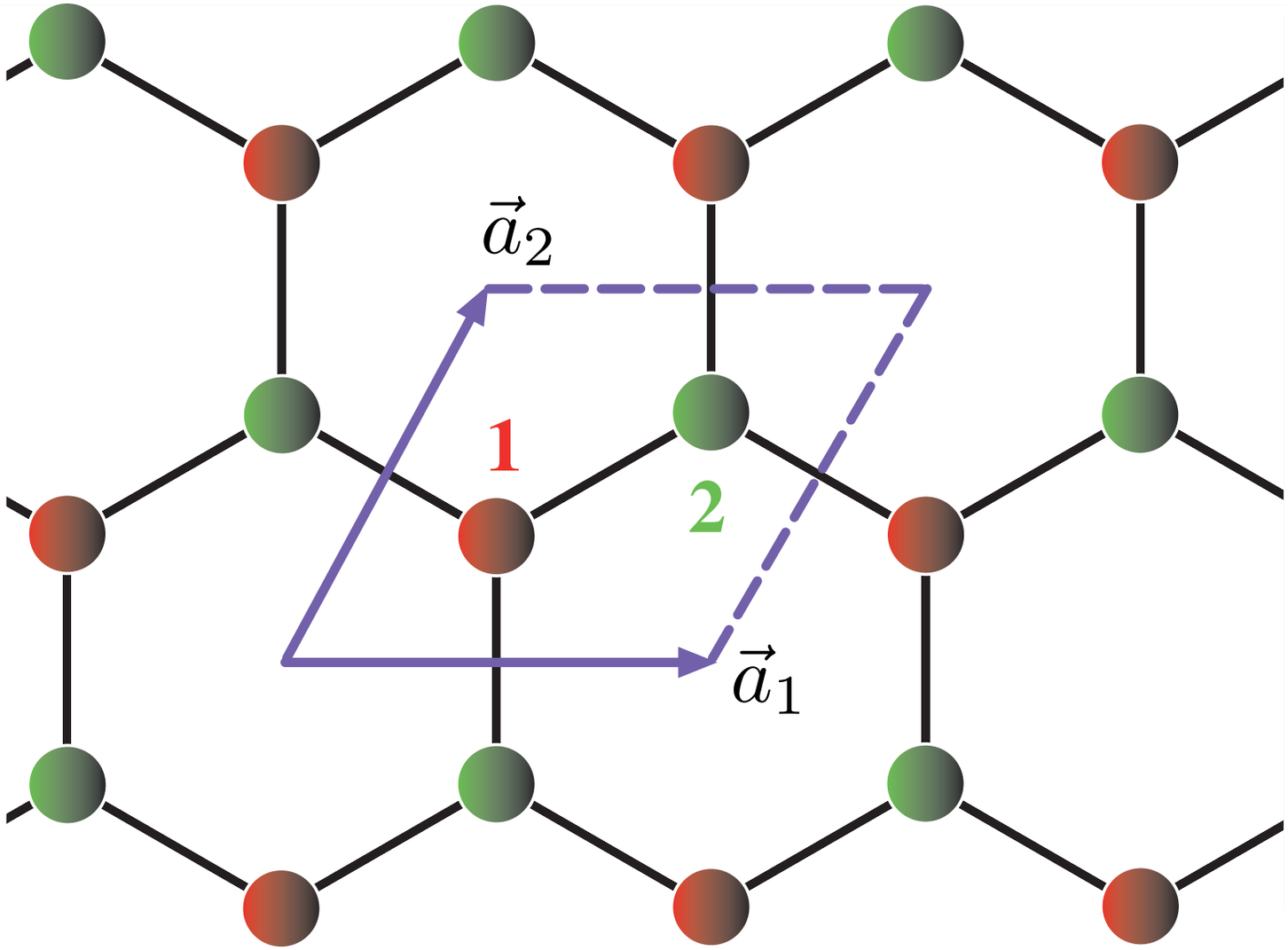
where $\{\vec{a}_i\}$ are linearly independent vectors.

By construction, the crystal is invariant under translations

$$\vec{t} : \vec{r} \to \vec{r} + \vec{t}, \quad \forall \vec{t} \in \mathcal{T}$$

and the Bravais lattice can be identified with the *translation group* $\mathcal{T}$ of the crystal.

Honeycomb lattice: two atoms per unit cell



The translation group

Representations of the translation group

The translation group is *abelian*.

As a consequence, all the IRs are *one-dimensional*.

One-dimensional unitary matrices are just *unimodular complex* numbers $z \in \mathbb{C},\ |z| = 1$. Each IR can specified by a $\vec{k}$-vector according to

$$\tau_{\vec{k}}(\vec{t}\,) = e^{i\vec{k}\cdot\vec{t}}$$

Note that this respects the translation group structure

$$\tau(\vec{t}_1)\tau(\vec{t}_2) = \tau(\vec{t}_1 + \vec{t}_2)$$

The translation group

Reciprocal space

Define the *reciprocal basis* $\{\vec{b}_i\}$ by

$$\boxed{\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}}$$

Then a vector in *reciprocal space (RS)* can be written

$$\vec{k} = k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3$$

Note that

$$\boxed{\tau_{\vec{k}}(\vec{t}) = e^{i\vec{k}\cdot\vec{t}} = e^{2\pi i(n_1k_1+n_2k_2+n_3k_3)}}$$

The translation group

Reciprocal lattice and first Brillouin zone

The set of vectors

$$\vec{k}_R = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3, \quad m_i \in \mathbb{Z}$$

constitute the *reciprocal lattice (RL)*. Then

$$e^{i\vec{k}_R\cdot\vec{t}} = e^{2\pi i(n_1m_1+n_2m_2+n_3m_3)} = 1$$

implies

$$\boxed{e^{i(\vec{k}+\vec{k}_R)\cdot\vec{t}} = e^{i\vec{k}\cdot\vec{t}} = 1}$$

This is usually written as $\vec{k} + \vec{k}_R \equiv \vec{k}$.

Thus we may think of the *first Brillouin zone* as *the set of non-equivalent IRs of the translation group of the crystal*.

Bloch waves

For 1-electron systems, the *symmetry-adapted basis* for an IR of the translation group is a wavefunction such that

$$\tau_{\vec{k}}\left(\vec{t}\right)\psi(\vec{r}) = \psi(\vec{r}+\vec{t}) = e^{i\vec{k}\cdot\vec{t}}\,\psi(\vec{r})$$

This is solved by

$$\boxed{\psi(\vec{r}) = u(\vec{r})e^{i\vec{k}\cdot\vec{r}}}$$

where *u* is invariant under the translation group

$$\boxed{u(\vec{r}) = u(\vec{r}+\vec{t})\ ,\ \ \forall\vec{t}\in\mathcal{T}}$$

If the multiplicity of $\tau_{\vec{k}}$ is $m_{\vec{k}}$, the energy eigenstates are obtained by diagonalizing a $m_{\vec{k}} \times m_{\vec{k}}$ hermitian matrix. The eigenstates are *Bloch wavefunctions*.

From atomic orbitals to Bloch waves

Given an atomic orbital $\phi^a(\vec{r})$ we can construct Bloch waves by forming the linear combinations

$$\psi^a_{\vec{k}}(\vec{r}) = \sum_{\vec{t}\in\mathcal{T}} \phi^a(\vec{r} - \vec{r}_a - \vec{t})\, e^{i\vec{k}\cdot\vec{t}}$$

These combinations satisfy

$$\psi^a_{\vec{k}}(\vec{r} + \vec{t}) = e^{i\vec{k}\cdot\vec{t}}\, \psi^a_{\vec{k}}(\vec{r})$$

and belong to the $\tau_{\vec{k}}$ IR of the translation group.

Bloch waves with different values of $\vec{k}$ belong to different IRs of the translation group and can not be coupled by the hamiltonian.

There is one Bloch wave for each orbital in the primitive cell. Taking $\{\psi^a_{\vec{k}}\}$ as a basis, the hamiltonian must be diagonal in $\vec{k}$

$$\boxed{\langle \psi^a_{\vec{k}} | \mathcal{H} | \psi^b_{\vec{k}'} \rangle = \mathcal{H}^{ab}(\vec{k}) \delta_{\vec{k},\vec{k}'}}$$

Thus if we consider a set $\{\phi^a\}$ of N_o orbitals per primitive cell, we will have to diagonalize a $\vec{k}$-dependent $N_o \times N_o$ matrix. This will yield N_o bands

$$\mathcal{E}_\alpha(\vec{k}),\ \alpha = 1, \ldots, N_o$$

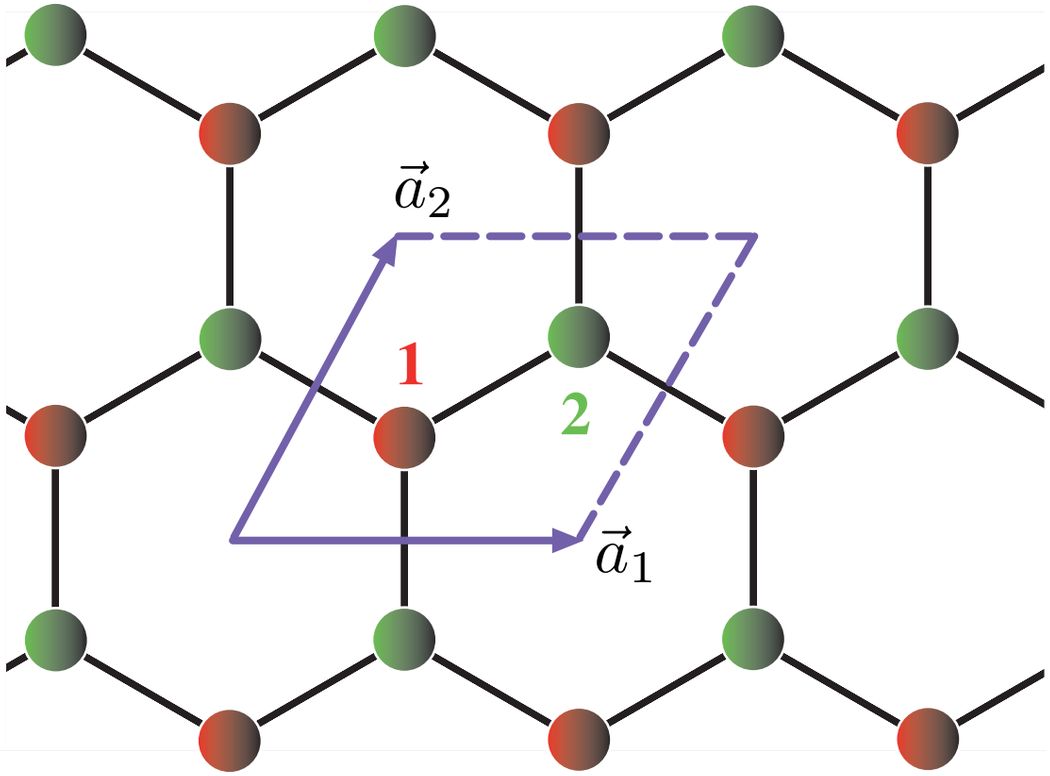
So far we have just rephrased Bloch's theorem in group theory language.

Orbitals in graphene

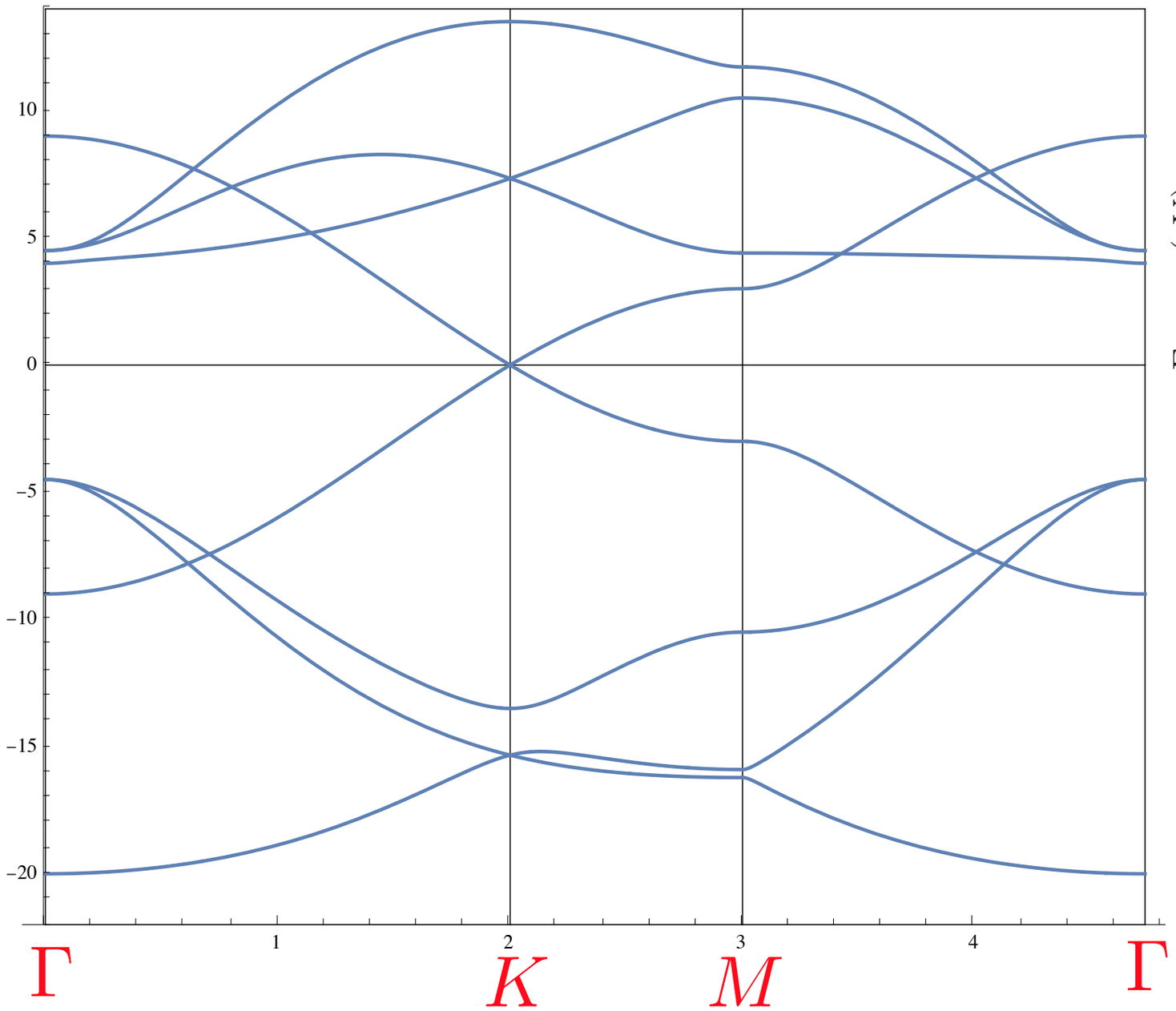
Graphene is made of carbon atoms.
The ground configuration for carbon is $1s^2 2s^2 2p^2$.

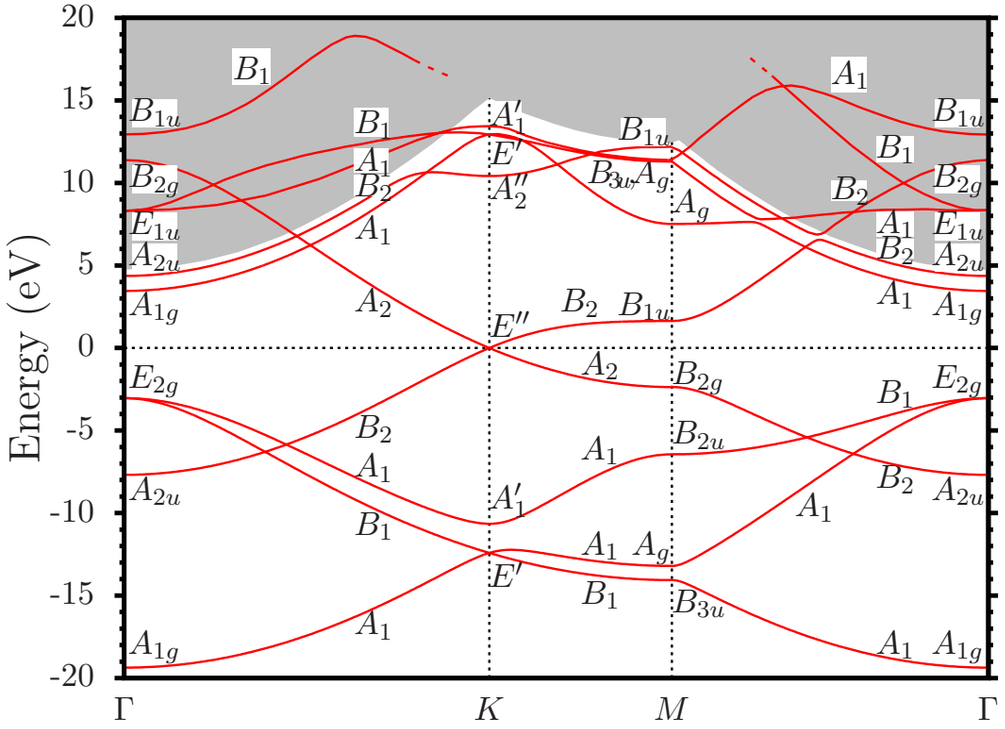
Valence electrons live in *2s* and *2p* orbitals. Thus we may take the following basis of *8* atomic orbitals

$$\{\phi_s^1, \phi_{p_x}^1, \phi_{p_y}^1, \phi_{p_z}^1, \phi_s^2, \phi_{p_x}^2, \phi_{p_y}^2, \phi_{p_z}^2\}$$



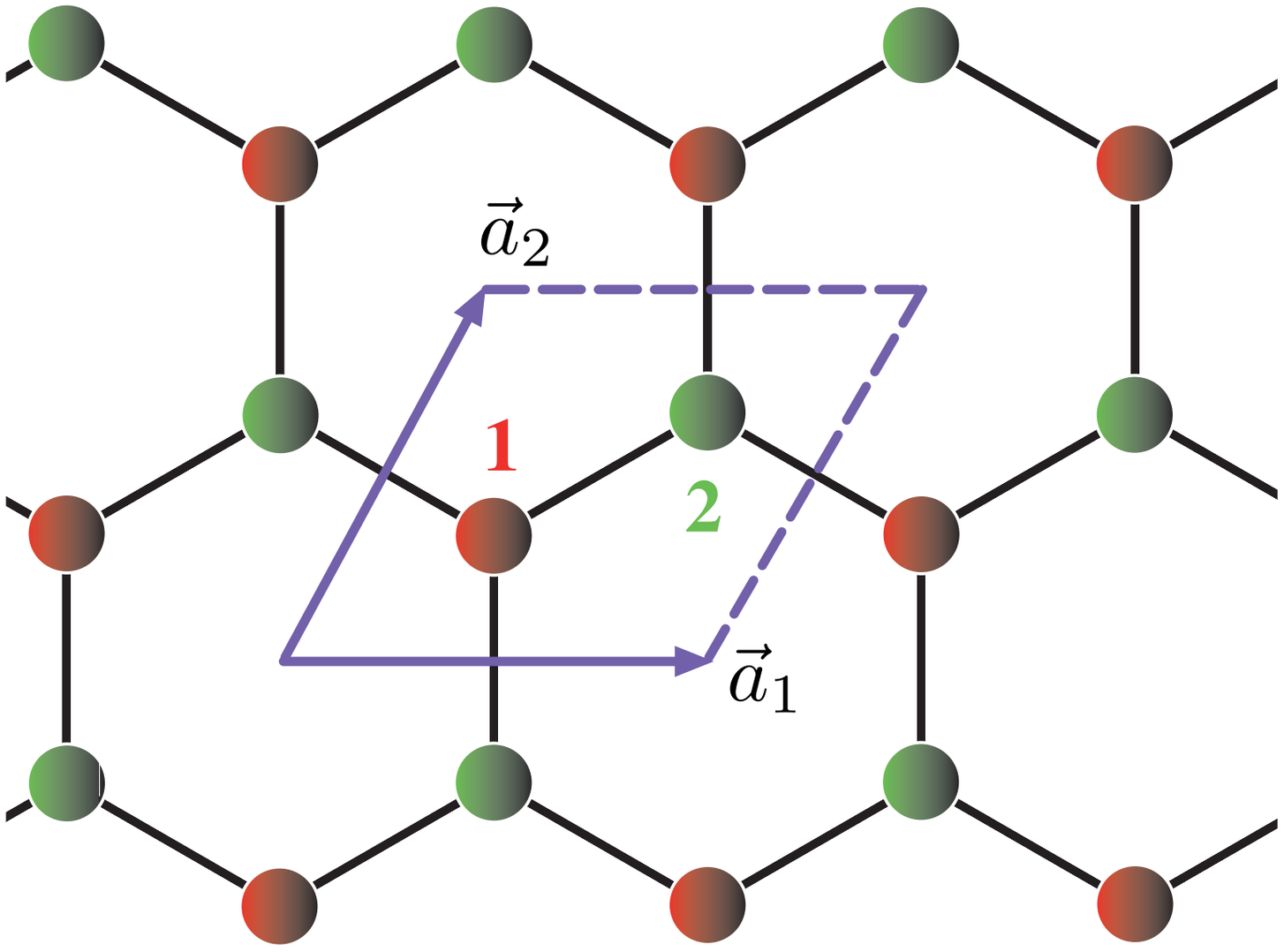
Tight binding bands for graphene



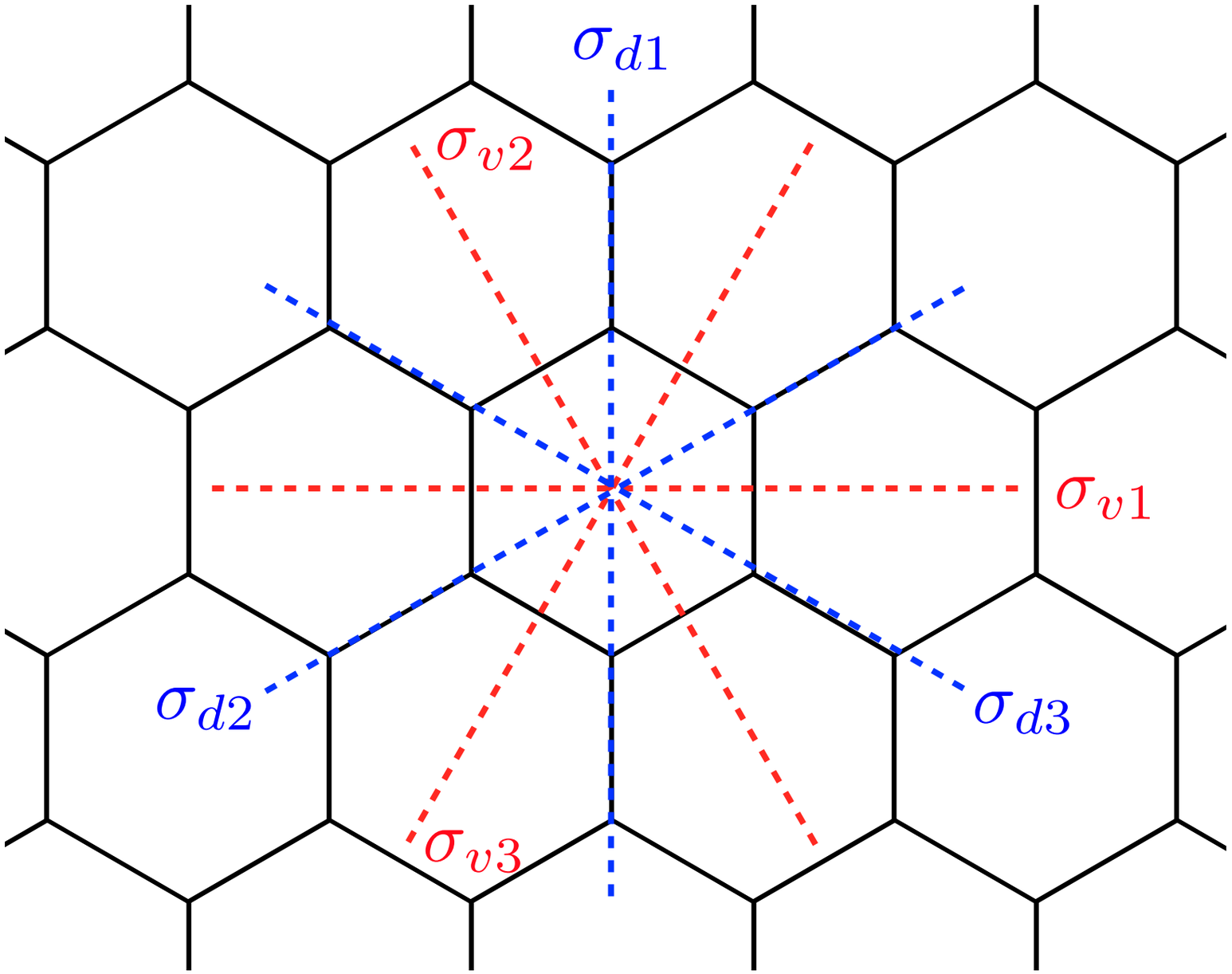


Beyond Bloch's theorem

The symmetries of graphene



C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{di}	σ_{vi}



C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{di}	σ_{vi}

Beyond Bloch's theorem

The symmetries of graphene

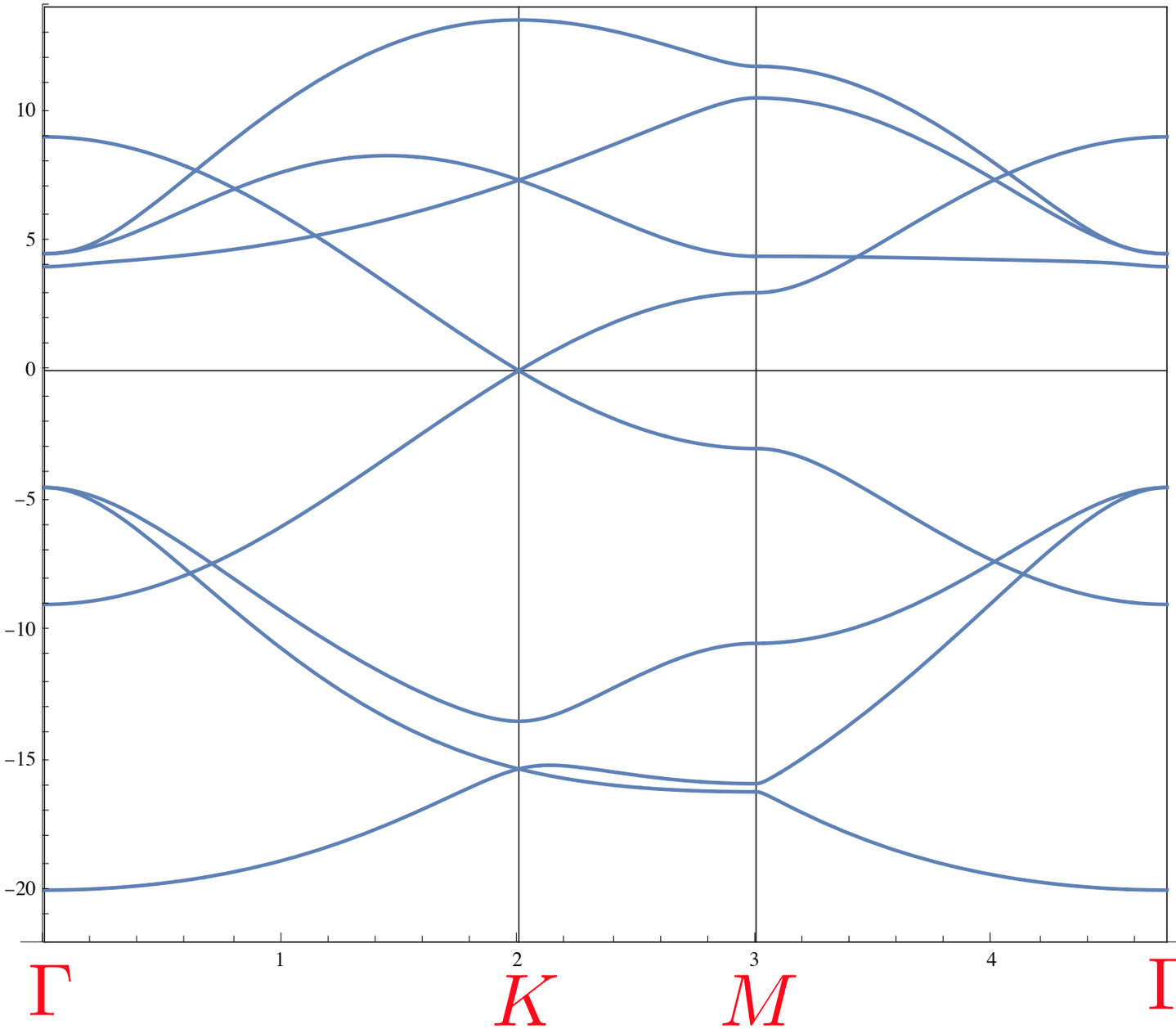
Graphene is also invariant under reflections by the horizontal plane σ_h. Including σ_h enlarges the symmetry group from C_{6v} (*12* elements) to D_{6h} (*24* elements).

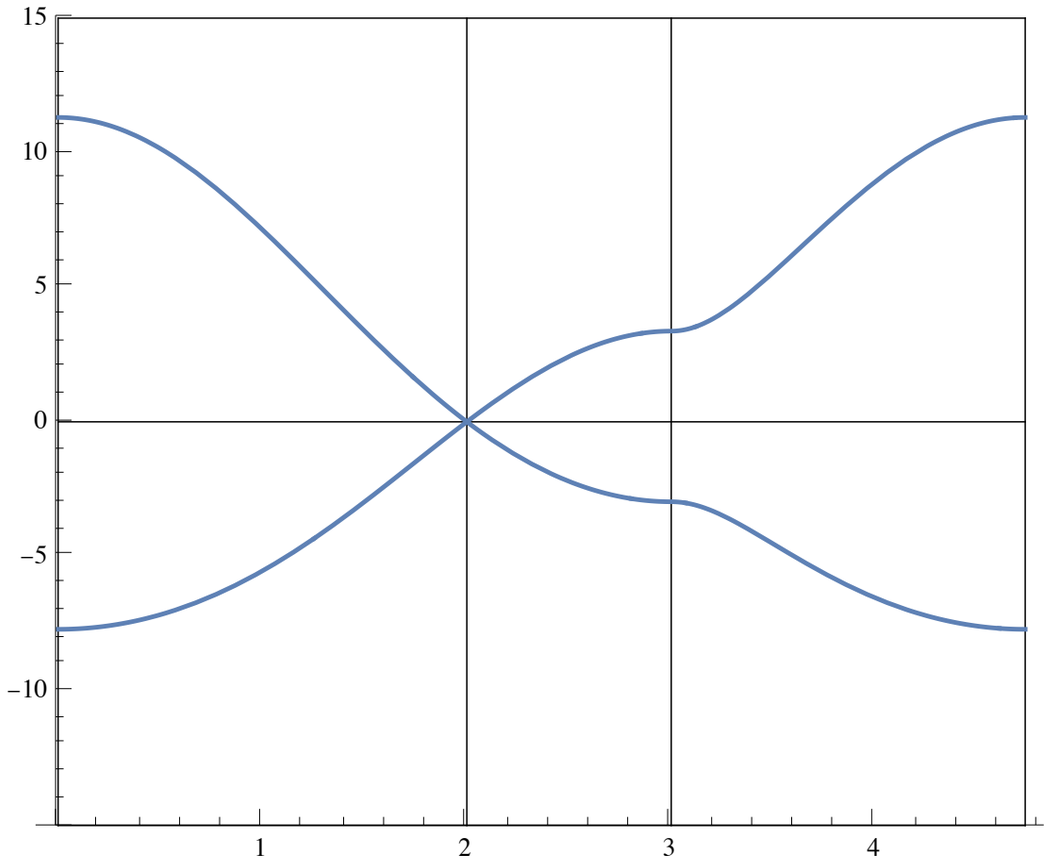
For the problem at hand this is unnecessary. We can keep to the simpler C_{6v} as long as we remember that:

The hamiltonian can not connect orbitals with different parities under σ_h.

(s, p_x, p_y) are **even**, whereas p_z is **odd** under σ_h.

Tight binding bands for graphene





“Pi-bands” (from *pz* orbitals)

(s, p_x, p_y) are **even**, whereas p_z is **odd** under σ_h .

Beyond Bloch's theorem

The little group

Given a vector $\vec{k}$, the little group $G_{\vec{k}}$ is the set of symmetries that leave $\vec{k}$ invariant

$$\boxed{\forall h \in G_{\vec{k}}\,, \quad h\vec{k} \equiv \vec{k}}$$

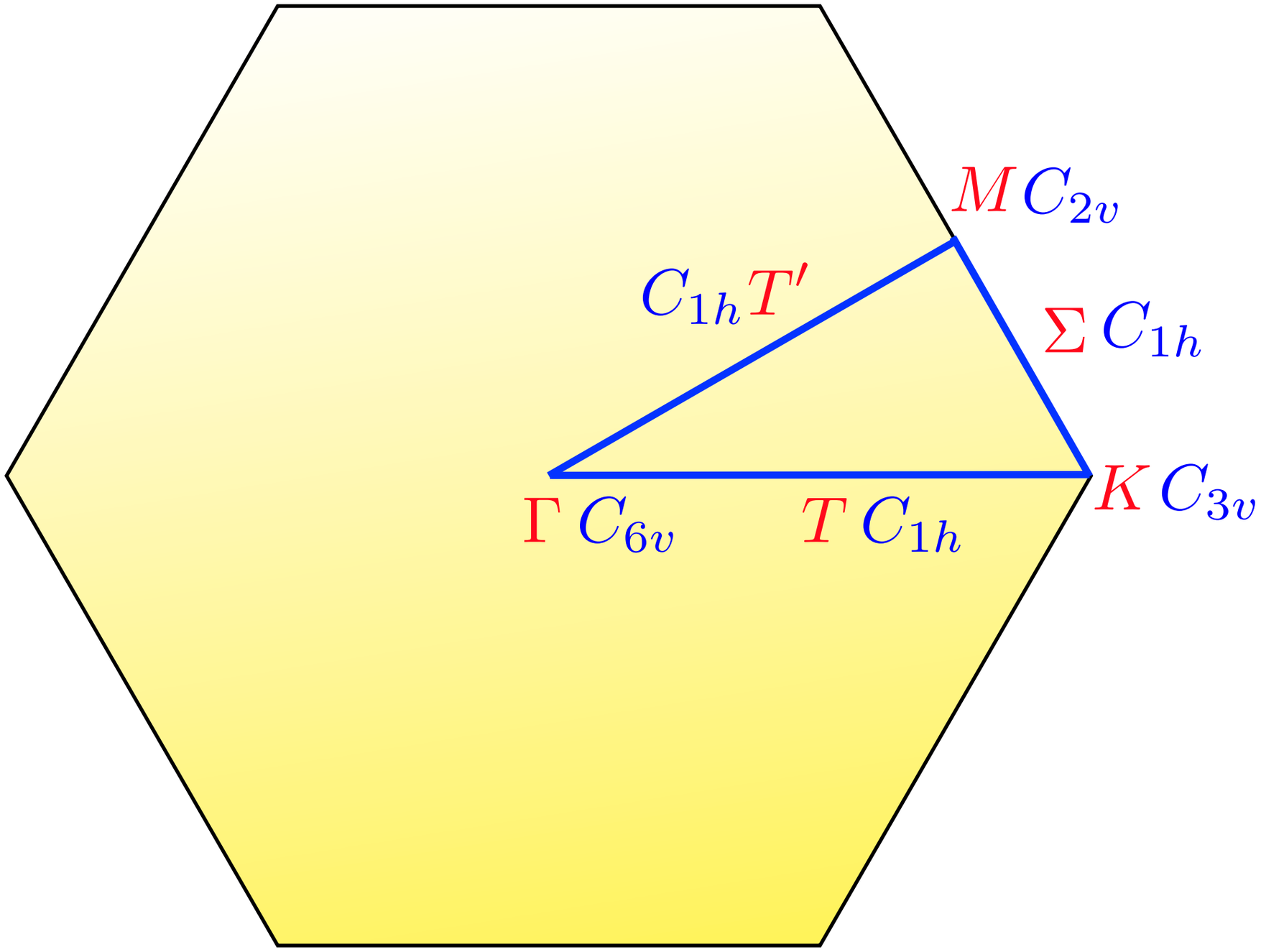
The Bloch waves $\{\psi^a_{\vec{k}}\}$ transform among themselves under the action of the *little group* $G_{\vec{k}}$.

This defines the *small representation* $T_{\vec{k}}$ of the little group $G_{\vec{k}}$

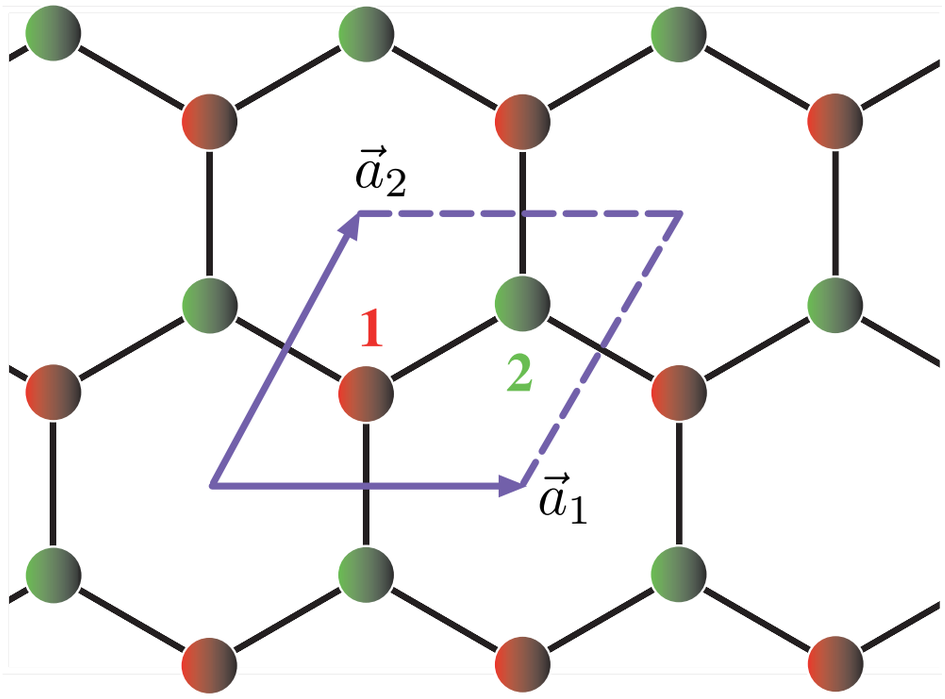
The hamiltonian $\mathcal{H}^{ab}(\vec{k})$ must be invariant under the little group $G_{\vec{k}}$

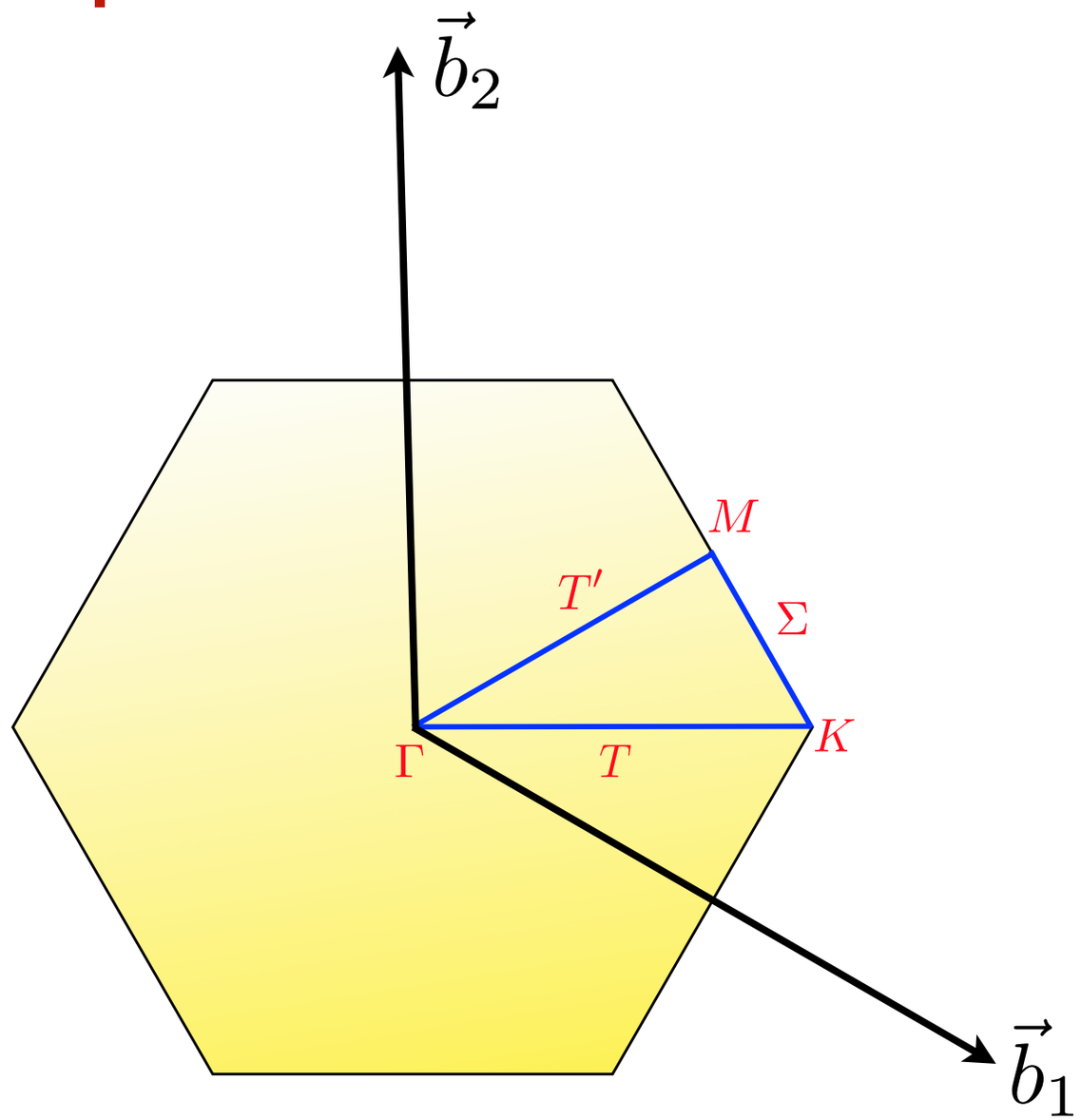
First Brillouin zone for graphene

Little groups



First Brillouin zone for graphene

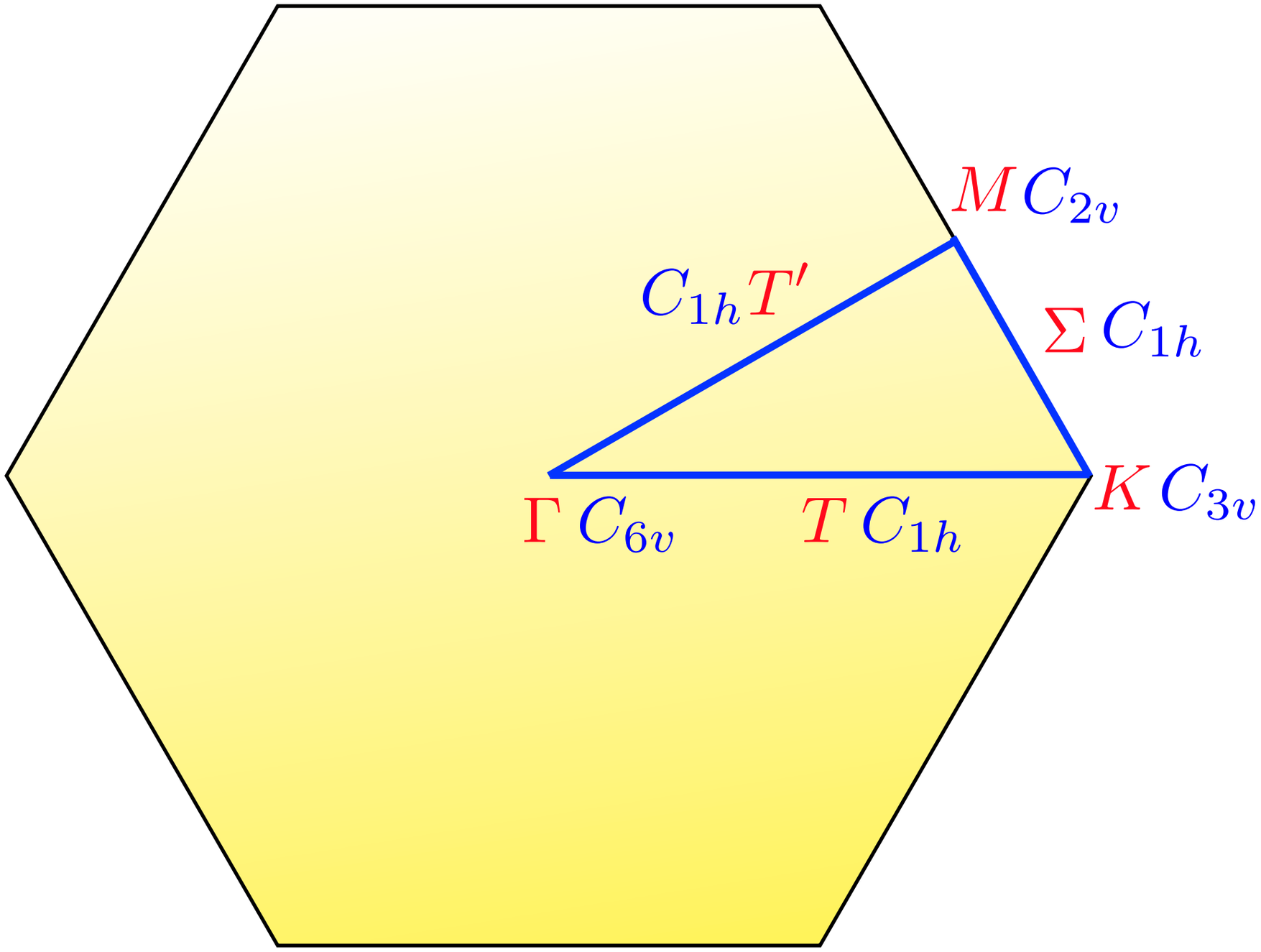


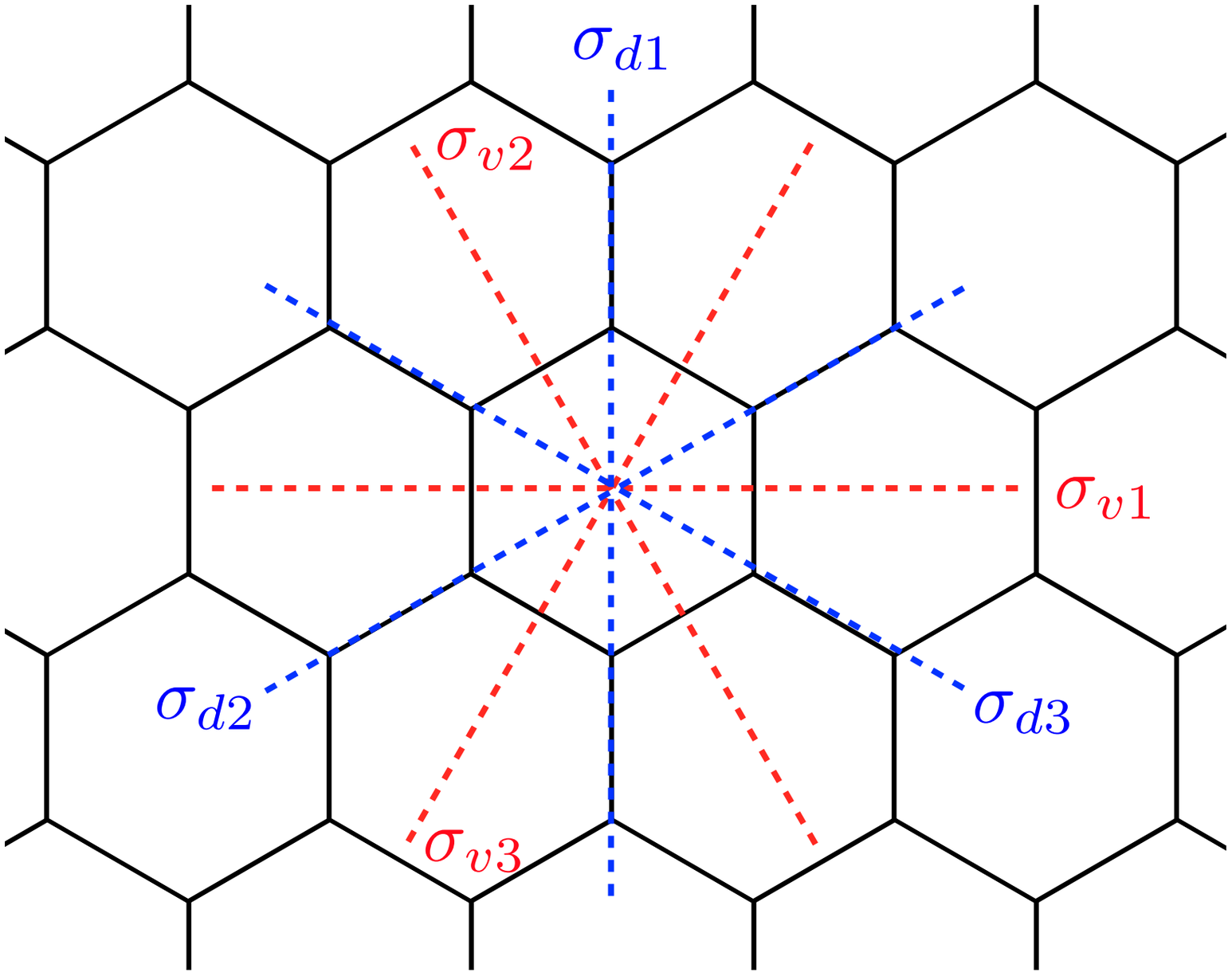


$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij}$$

First Brillouin zone for graphene

Little groups





C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{di}	σ_{vi}

First Brillouin zone for graphene

Little groups

Γ	C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{d_i}	σ_{v_i}
T	C_{1h}	E					σ_{v_1}
K	C_{3v}	E		$C_3^{\pm}$			σ_{v_i}

$T(\Gamma, K)$

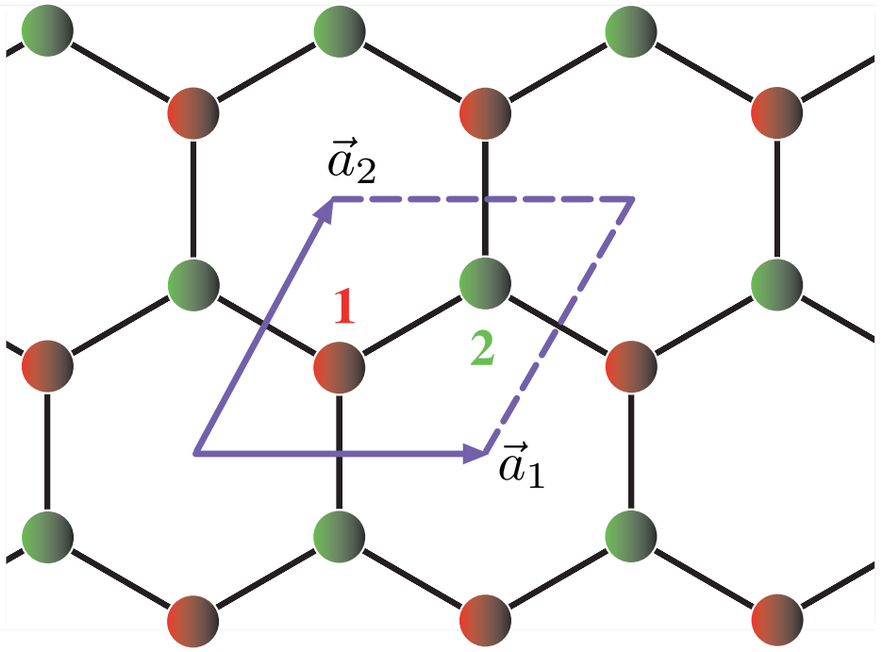
Γ	C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{d_i}	σ_{v_i}
Σ	C_{1h}	E				σ_{d_2}	
M	C_{2v}	E	C_2			σ_{d_2}	σ_{v_2}

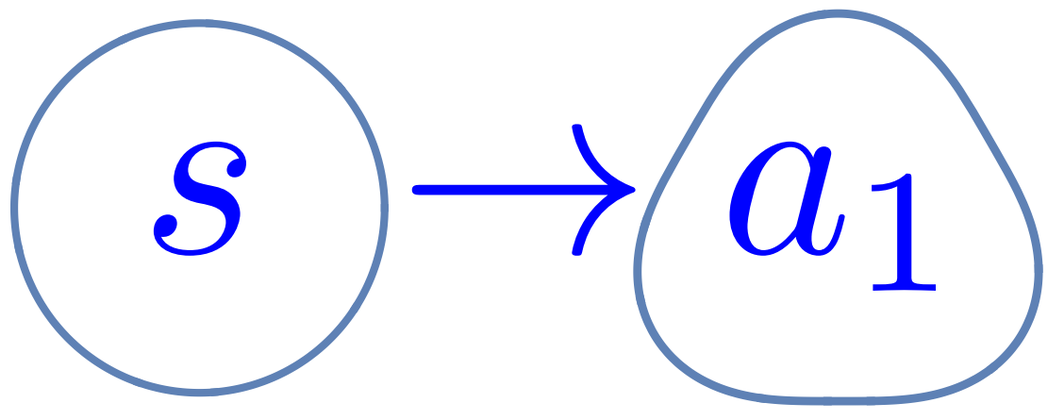
$\Sigma(\Gamma, M)$

K	C_{3v}	E	$C_3^{\pm}$	σ_{v_i}
T'	C_{1h}	E		σ_{v_2}
M	C_{2v}	E	C_2	σ_{d_2} σ_{v_2}

$T'(K, M)$

The site symmetry group





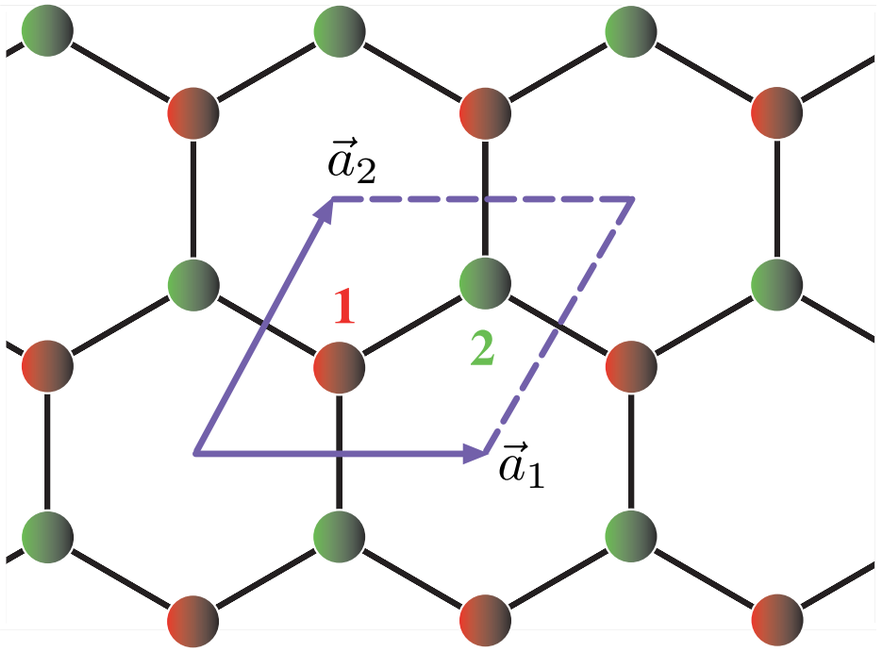
The site symmetry group for orbitals in atoms **1** and **2** is

$$C_{3v} = \{E, C_3^{\pm}, \sigma_{di}\}$$

Atomic orbitals are distorted by the crystal field and their symmetry may be lowered. For instance, for an *s* orbital at atom **1**:

$$D_0^+ = A_1 \Longrightarrow s \rightarrow a_1$$

The site symmetry group



$$s \to a_1$$

$$p \to a_1 + e$$

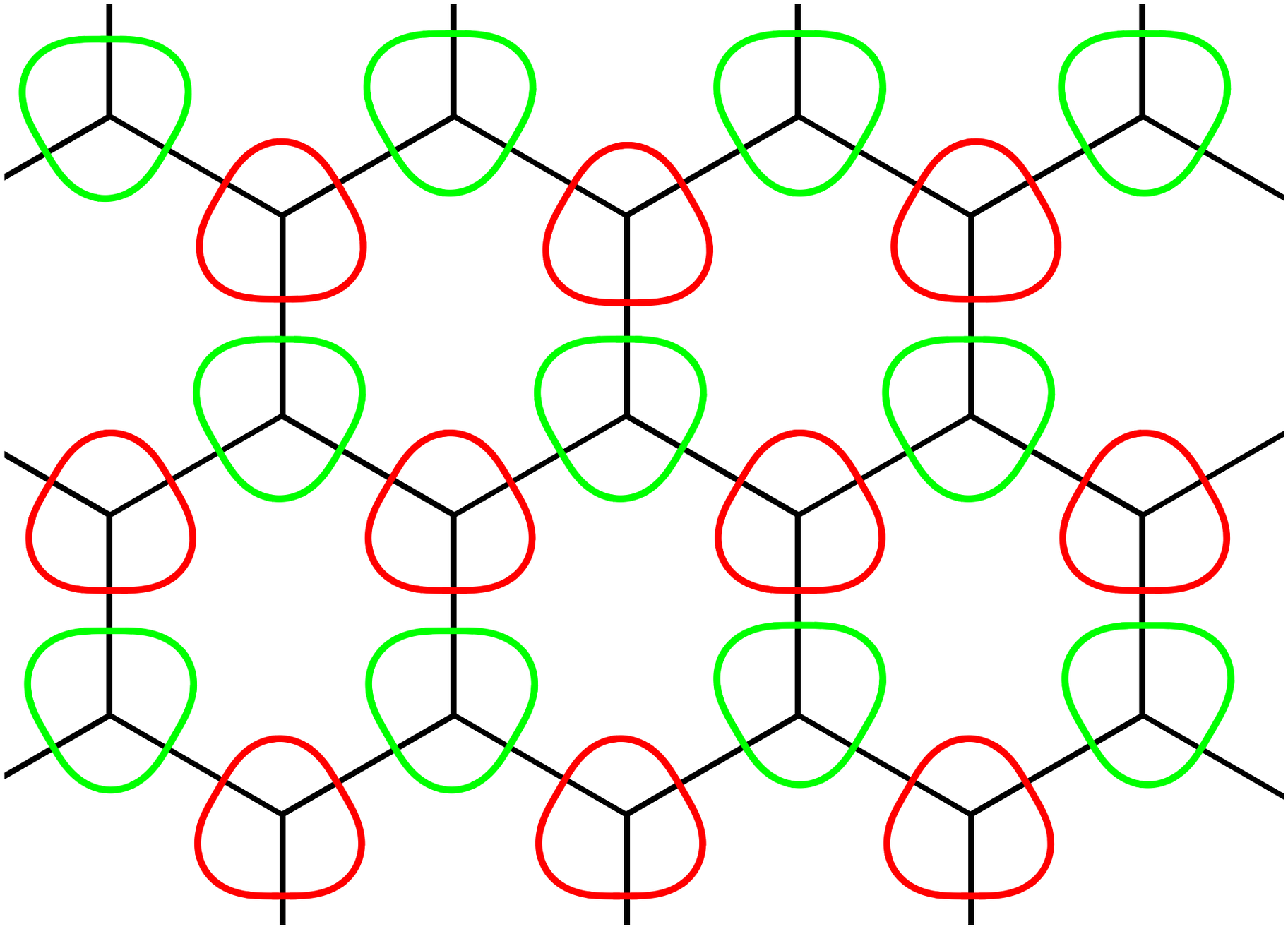
$$d \to a_1 + 2e$$

$$f \to 2a_1 + a_2 + 2e$$

In what follows we will study the two bands arising from the p_z orbitals for *"spinless"* electrons. We begin by placing one p_z orbital at each atom in the crystal.

$$D_1^- = A_1(p_z) + E(p_x, p_y) \Longrightarrow \boxed{p_z \to a_1}$$

Bands from pz-orbitals



Bands from pz-orbitals

Next, we exploit the translation invariance of the crystal by forming two Bloch waves

$$\psi^a_{\vec{k}}(\vec{r}) = \sum_{\vec{t}\in\mathcal{T}} \phi_{a_1}(\vec{r} - \vec{r}_a - \vec{t})\, e^{i\vec{k}\cdot\vec{t}}$$

where $a = 1, 2$, and ϕ_{a_1} is a (distorted) p_z -orbital.

The two Bloch waves $(\psi^1_{\vec{k}},\ \psi^2_{\vec{k}})$ at a point of the first Brillouin zone trasform under the little group $G_{\vec{k}}$. The matrices of the transformations define the 2-dimensional representation $T_{\vec{k}}$.

In order to decompose $T_{\vec{k}}$, we must compute its character.

Bands from pz-orbitals

The character can be obtained by using the following general formula

$$\chi_T(g,\vec{k}) = \sum_{i=1}^{A} \varphi_i(g,\vec{k})\theta_i(g)\chi_\tau(g)$$

where the sum is over the *A* atoms in the primitive cell, *A*=2 in our case.

$\theta_i(g)$ is equal to *1* if the atom *i* is invariant under *g*, zero otherwise.

The phase $\varphi_i(g,\vec{k})$ may arise due to the fact that we are rotating (transforming) Bloch waves that carry phases.

Finally, $\chi_\tau(g)$ is the character of the IR of the orbitals. In our case, $\chi_{A_1}(g) = 1$

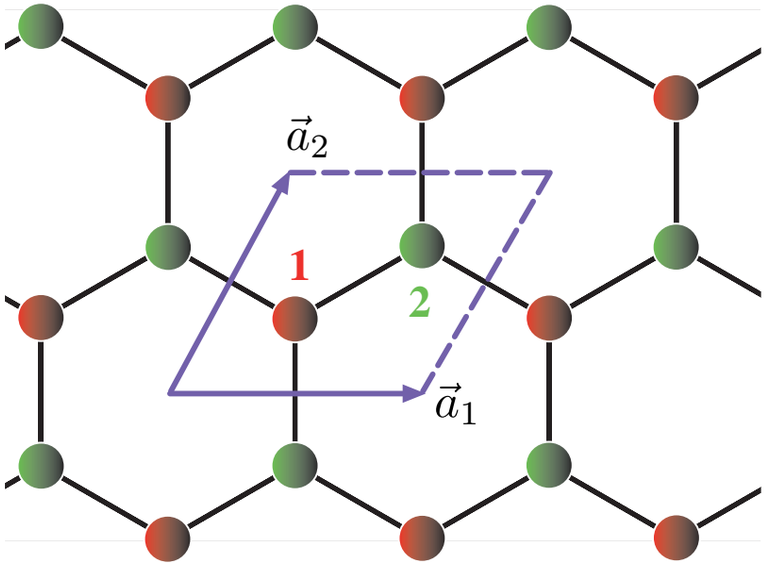
Bands from pz-orbitals

The Gamma point

There are no phases at the Gamma point, and the general formula reduces to

$$\chi_\Gamma(g) = \sum_{i=1}^{2} \theta_i(g)\chi_{A_1}(g) = n_{inv}(g)$$

where n_{inv} is the number of atoms invariant under g. This gives



C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{d_i}	σ_{v_i}
χ_Γ	2	0	2	0	2	0

Bands from pz-orbitals

The Gamma point

C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{d_i}	σ_{v_i}
χ_Γ	2	0	2	0	2	0

Using the magic formula gives

$$T_\Gamma = A_1 + B_2 = \boxed{\Gamma_1 + \Gamma_3}$$

$622\ (D_6)$		$6mm\ (C_{6v})$		$\bar{6}2m\ (D_{3h})$		E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	C'_{2i}	C''_{2i}
						E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{di}	σ_{vi}
						E	σ_h	$C_3^{\pm}$	$S_3^{\pm}$	C'_{2i}	σ_{vi}
A_1	Γ_1	A_1	Γ_1	A'_1	Γ_1	1	1	1	1	1	1
A_2	Γ_2	A_2	Γ_2	A'_2	Γ_2	1	1	1	1	−1	−1
B_1	Γ_3	B_2	Γ_3	A''_1	Γ_3	1	−1	1	−1	1	−1
B_2	Γ_4	B_1	Γ_4	A''_2	Γ_4	1	−1	1	−1	−1	1
E_2	Γ_6	E_2	Γ_6	E'	Γ_6	2	2	−1	−1	0	0
E_1	Γ_5	E_1	Γ_5	E''	Γ_5	2	−2	−1	1	0	0

$6/mmm = 622 \otimes \bar{1}\ (D_{6h} = D_6 \otimes C_i)$

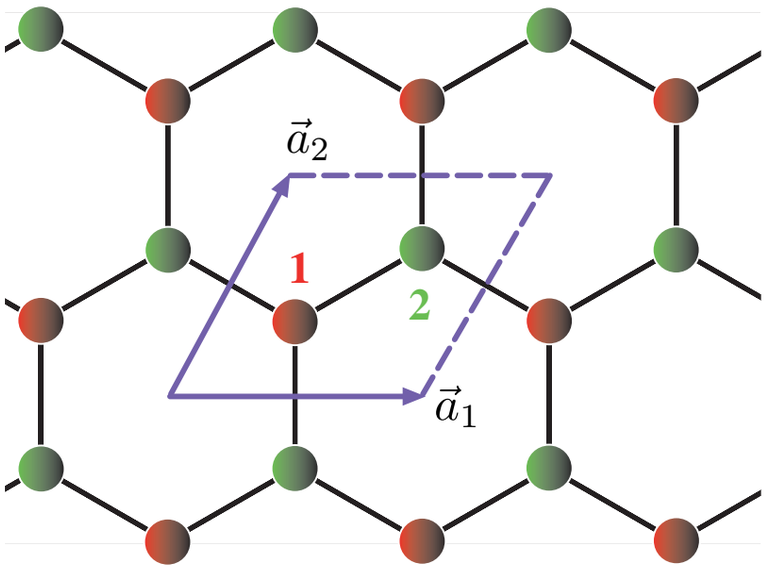
Bands from pz-orbitals

The K point

In this case we have to use the general formula with $\chi_{A_1} = 1$

$$\chi_K(g) = \sum_{i=1}^{2} \varphi_i(g, \vec{K})\theta_i(g)$$

The phases are actually different for the two atoms and we get



C_{3v}	E	$C_3^{\pm}$	σ_{v_i}
$\varphi_1\theta_1$	1	ω^*	0
$\varphi_2\theta_2$	1	ω	0
χ_K	2	-1	0

$$\omega = e^{\frac{2\pi i}{3}}$$

Bands from pz-orbitals

The K point

C_{3v}	E	$C_3^{\pm}$	σ_{v_i}
$\varphi_1\theta_1$	1	ω^*	0
$\varphi_2\theta_2$	1	ω	0
χ_K	2	-1	0

$$T_K = K_3$$

$32\ (D_3)$		$3m\ (C_{3v})$		E E	$C_3^{\pm}$ $C_3^{\pm}$	C'_{2i} σ_{di}
A_1	Γ_1	A_1	Γ_1	1	1	1
A_2	Γ_2	A_2	Γ_2	1	1	-1
E	Γ_3	E	Γ_3	2	-1	0

$\bar{3}m = 32 \otimes \bar{1}\ (D_{3d} = D_3 \otimes C_i)$

The fact that K_3 is *2*-dimensional implies the *degeneracy of the two bands* at the *K*-point.

Bands from pz-orbitals

The M point

C_{2v}	E	C_2	σ_{d_2}	σ_{v_2}
$\varphi_1\theta_1$	1	0	1	0
$\varphi_2\theta_2$	1	0	1	0
χ_M	2	0	2	0

$$T_M = M_1 + M_2$$

$mm2\ (C_{2v})$		$222\ (D_2)$		E E	C_{2z} C_{2z}	σ_y C_{2y}	σ_x C_{2x}
A_1	Γ_1	A	Γ_1	1	1	1	1
B_2	Γ_4	B_3	Γ_4	1	−1	−1	1
A_2	Γ_3	B_1	Γ_3	1	1	−1	−1
B_1	Γ_2	B_2	Γ_2	1	−1	1	−1

$mmm = 222 \otimes \bar{1}\ (D_{2h} = D_2 \otimes C_i)$

Bands from pz-orbitals

The symmetry lines

We know that the little group $G_{\vec{k}}$ for $\vec{k}$ on a symmetry line is always a subgroup of the little groups for the endpoints.

For instance, the group-subgroup relations for the $T(\Gamma, k)$ line are

Γ	C_{6v}	E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{d_i}	σ_{v_i}
T	C_{1h}	E					σ_{v_1}
K	C_{3v}	E		$C_3^{\pm}$			σ_{v_i}

Then we can use subduction to obtain T_T either from T_Γ or from T_K.

Bands from pz-orbitals

The symmetry lines

To proceed from the Gamma point, we have to compare the character tables for C_{6v} and C_{1h}

$622\ (D_6)$		$6mm\ (C_{6v})$		$\bar{6}2m\ (D_{3h})$		E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	C'_{2i}	C''_{2i}
						E	C_2	$C_3^{\pm}$	$C_6^{\pm}$	σ_{di}	σ_{vi}
						E	σ_h	$C_3^{\pm}$	$S_3^{\pm}$	C'_{2i}	σ_{vi}
A_1	Γ_1	A_1	Γ_1	A'_1	Γ_1	1	1	1	1	1	1
A_2	Γ_2	A_2	Γ_2	A'_2	Γ_2	1	1	1	1	−1	−1
B_1	Γ_3	B_2	Γ_3	A''_1	Γ_3	1	−1	1	−1	1	−1
B_2	Γ_4	B_1	Γ_4	A''_2	Γ_4	1	−1	1	−1	−1	1
E_2	Γ_6	E_2	Γ_6	E'	Γ_6	2	2	−1	−1	0	0
E_1	Γ_5	E_1	Γ_5	E''	Γ_5	2	−2	−1	1	0	0

$6/mmm = 622 \otimes \bar{1}\ (D_{6h} = D_6 \otimes C_i)$

$\bar{1}\ (C_i)$		$2\ (C_2)$		$m\ (C_{1h})$		E	I
						E	C_{2z}
						E	σ_z
A_g	Γ_1^+	A	Γ_1	A'	Γ_1	1	1
A_u	Γ_1^-	B	Γ_2	A''	Γ_2	1	−1

$2/m = 2 \otimes \bar{1}\ (C_{2h} = C_2 \otimes C_i)$

C_{6v}	E	σ_{v_i}
C_{1h}	E	σ_{v_1}
Γ_1	1	1
Γ_3	1	−1

$$\Gamma_1 \to T_1$$
$$\Gamma_3 \to T_2$$

Compatibility relations

$$T_\Gamma = \Gamma_1 + \Gamma_3 \longrightarrow T_T = T_1 + T_2$$

Bands from pz-orbitals

The symmetry lines

The remaining compatibility relations are obtained in the same way

$$\Gamma_1 \to T_1$$
$$\Gamma_3 \to T_2$$

$$\Gamma_1 \to \Sigma_1$$
$$\Gamma_3 \to \Sigma_1$$

$$M_1 \to T_1'$$
$$M_2 \to T_2'$$

$$K_3 \to T_1 + T_2$$

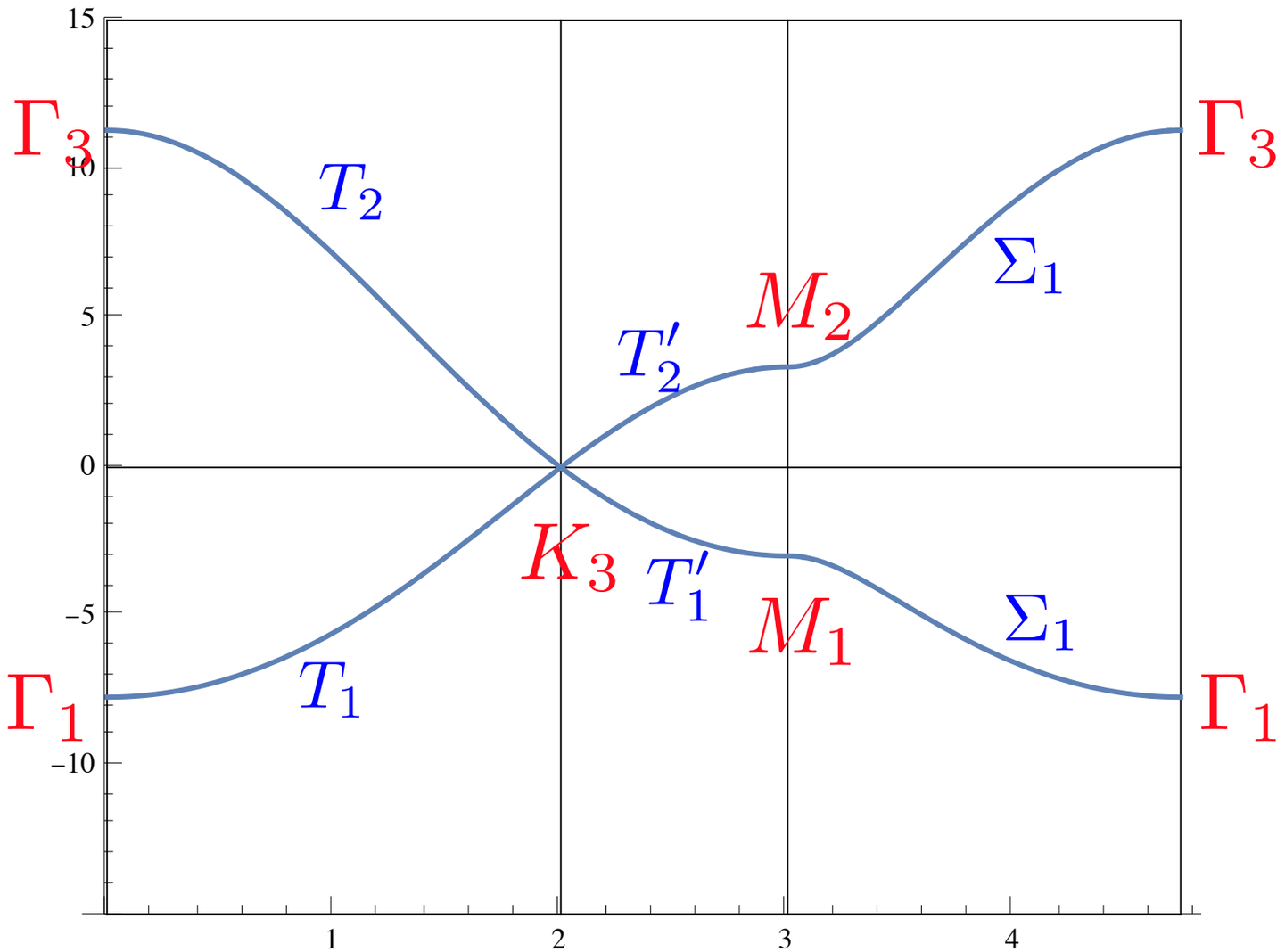
$$M_1 \to \Sigma_1$$
$$M_2 \to \Sigma_1$$

$$K_3 \to T_1' + T_2'$$

$$T_\Gamma = \Gamma_1 + \Gamma_3$$
$$T_K = K_3$$
$$T_M = M_1 + M_2$$

$$T_T = T_1 + T_2$$
$$T_\Sigma = 2\Sigma_1$$
$$T_{T'} = T_1' + T_2'$$

Bands from pz-orbitals



“Pi-bands” (from *pz* orbitals)