

How to define hopping parameters in TB model Using Group Theory

Foundations of Group Theory

Tomoaki Kameda 7th Nov. 2024

Today's topic

The construction of a **multi-band tight binding model (TMDC)**

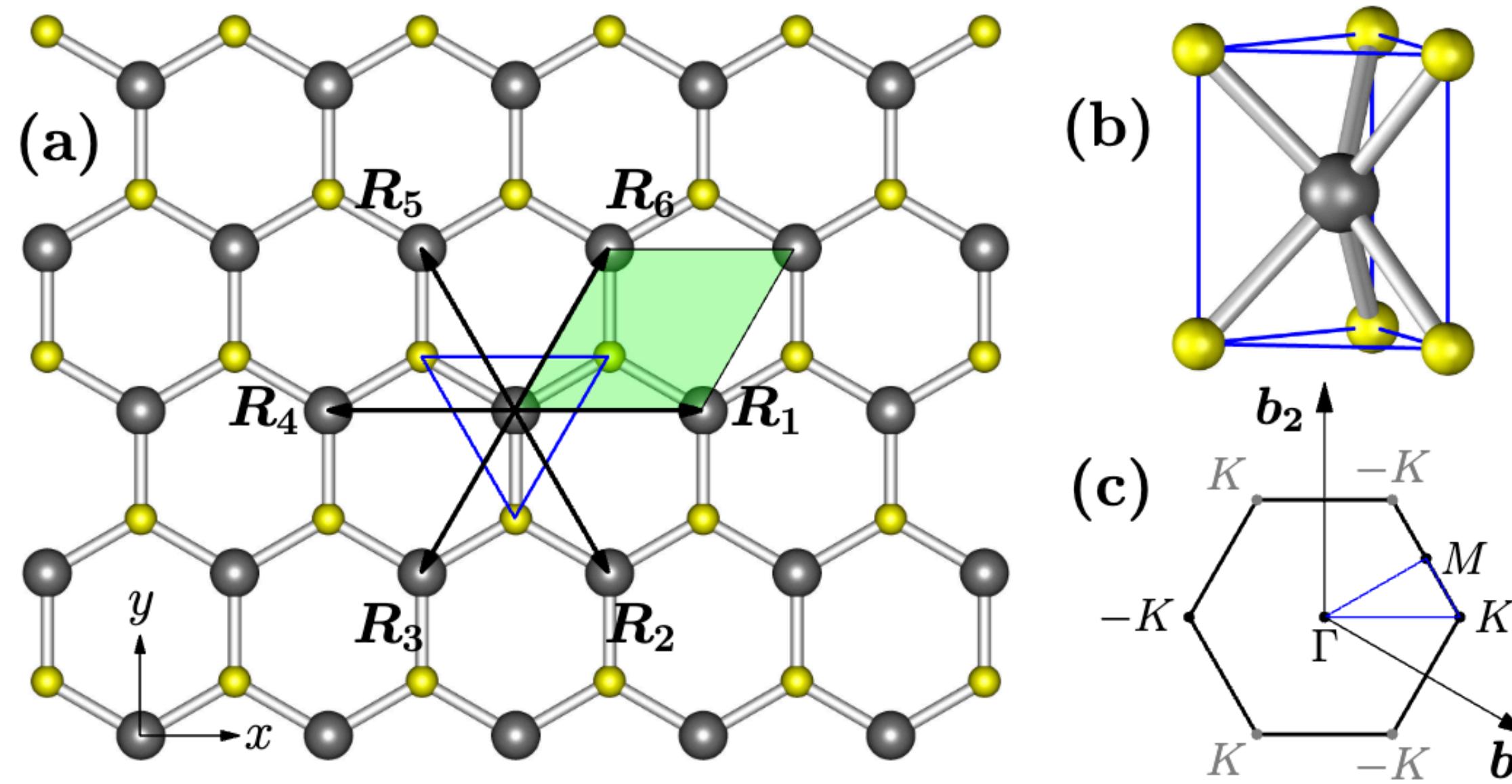
→ Using **group theory** to reduce independent hopping parameters

On the basics of **group theory** to understand the above

- Introduction to symmetry operations and group definitions
- Representations and Representation Matrices
- How to Interpret Character Tables
- Direct Product Representations and Selection Rules
- Formation of hybrid orbitals and symmetry conditions for orbital mixing.
- Overview of multi-band tight-binding model

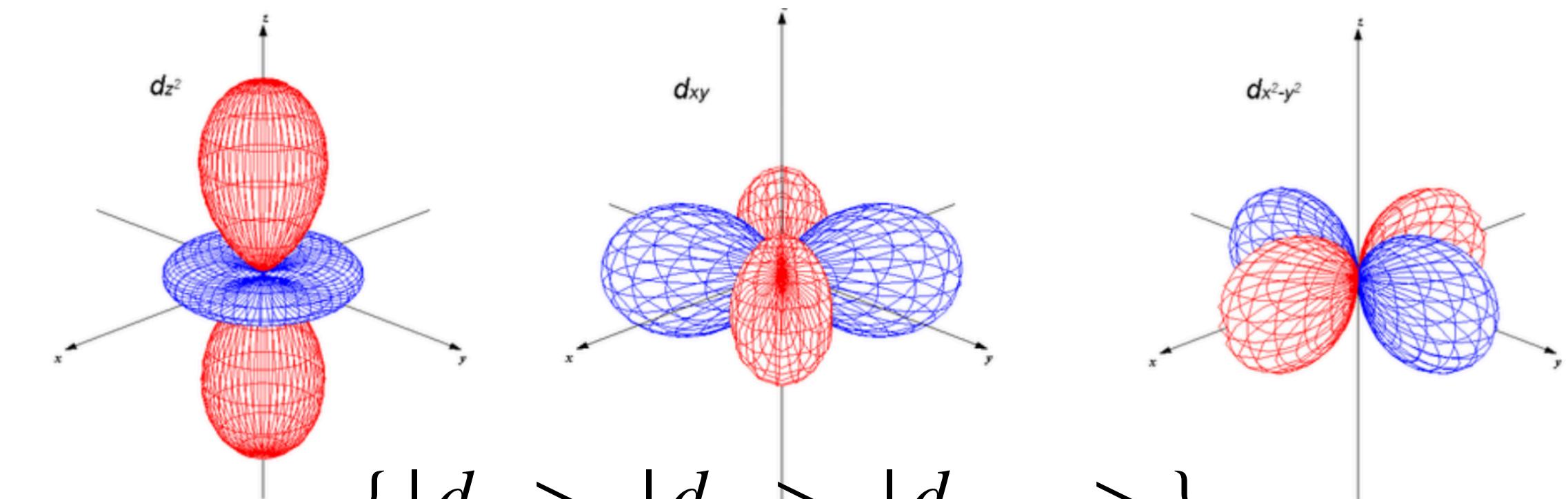
Three-Band Tight-Binding Model for TMDC

TMDC structure



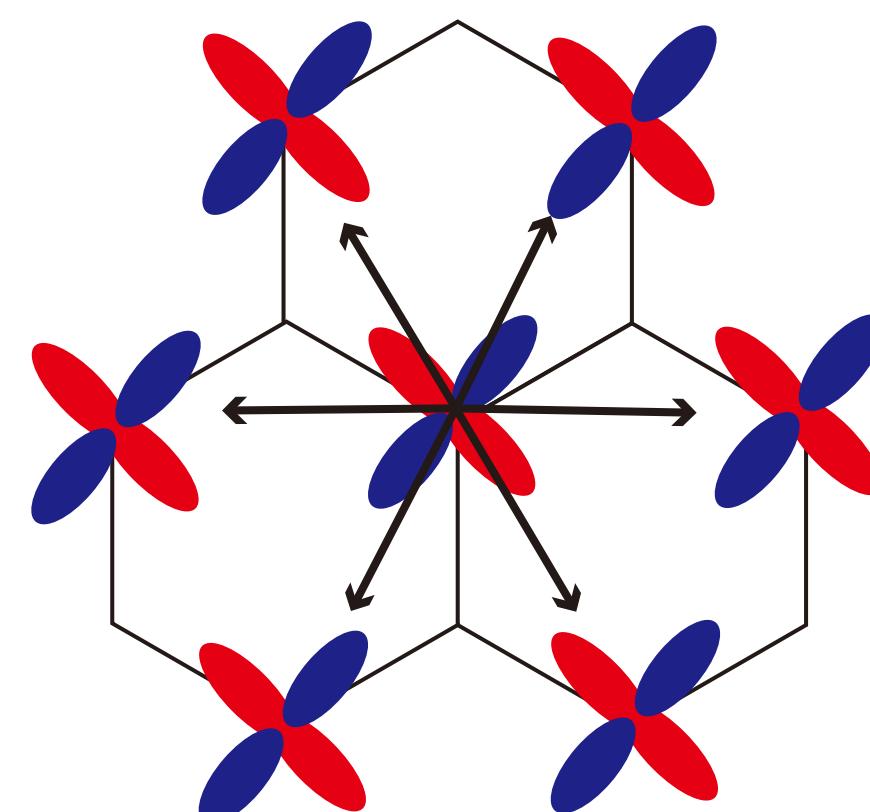
Why do the parameters increase?

- ① Multi atomic orbitals are considered.



- ② Hopping magnitude depends on **hopping direction**

✗ $|d_{xy}\rangle$ Example $d_{xy} - d_{xy}$ hopping

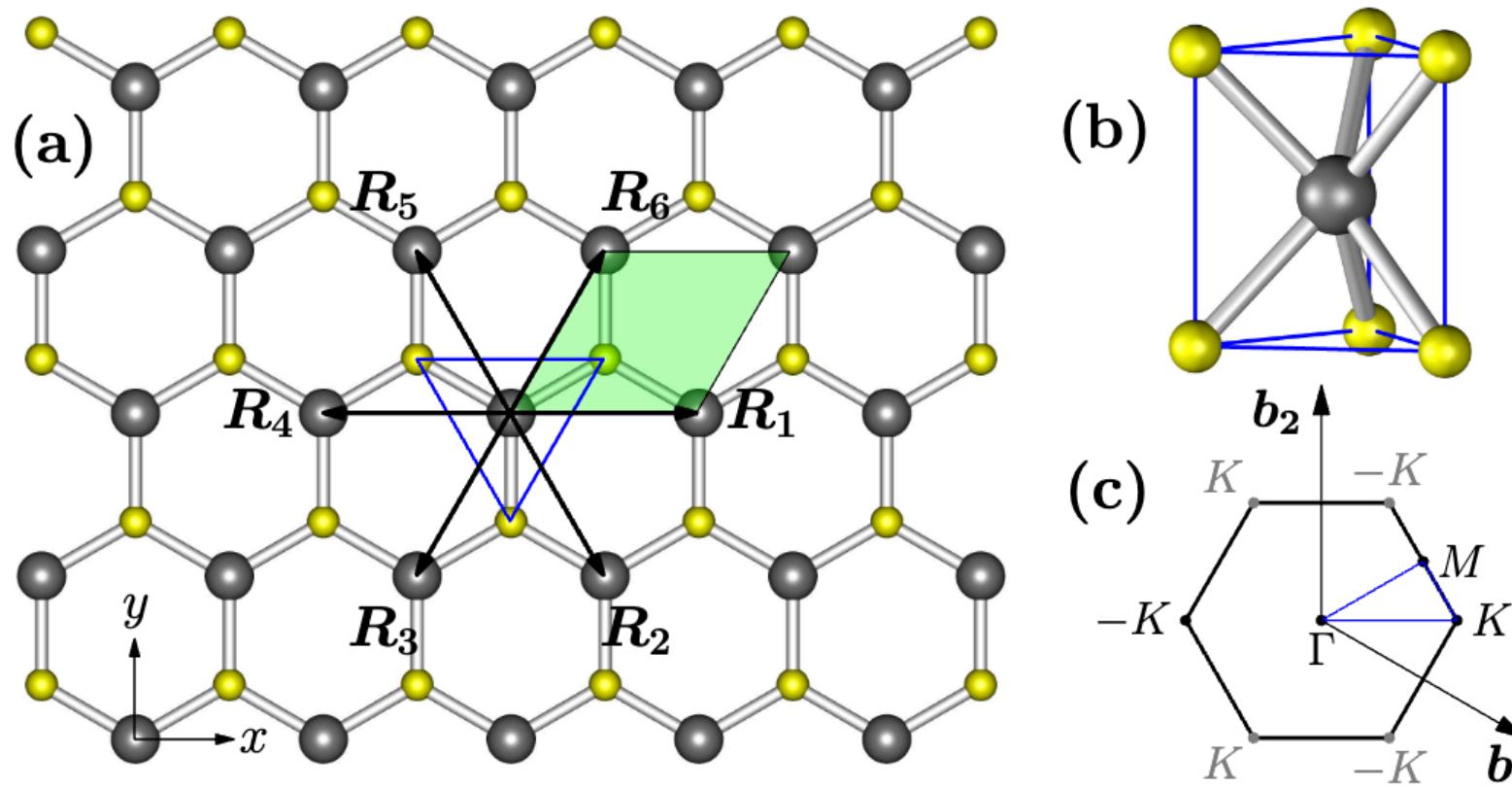


Three-Band Tight-Binding Model for TMDC

Model with nearest-neighbor hopping (not consider spin)

Consider 3 band in d orbital of transition atom

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$$\{ |d_{z^2}\rangle, |d_{xy}\rangle, |d_{x^2-y^2}\rangle \}$$

$$|\phi_\mu^j\rangle$$

μ -th basis belonging to the j -th IR

Mulliken symbol

$$A'_1 = \{d_{z^2}\}$$

$$E' = \{d_{xy}, d_{x^2-y^2}\}$$

Hamiltonian

$$H_{\mu\mu'}^{jj'}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} E_{\mu\mu'}^{jj'}(\mathbf{R}) \quad \mathbf{R} = \{R_1, \dots, R_6\}$$

Hopping parameter

$$E_{\mu\mu'}^{jj'}(\mathbf{R}) = \langle \phi_\mu^j(\mathbf{r}) | \hat{H} | \phi_{\mu'}^{j'}(\mathbf{r} - \mathbf{R}) \rangle$$

54 hopping parameters exist...!!

$ d_{z^2} $	H^{11}	H^{12}	0
$ d_{xy} $	H^{21}	H^{22}	0
$ d_{x^2-y^2} $	0		
$ d_{xz} $			
$ d_{yz} $			Not consider

Reduce the number of independent parameters by **considering the symmetry of matter!**

Group theory makes it easier!!

$$|\phi_1^1\rangle = d_{z^2}, \quad |\phi_1^2\rangle = d_{xy}, \quad |\phi_2^2\rangle = d_{x^2-y^2},$$

Symmetry Operation

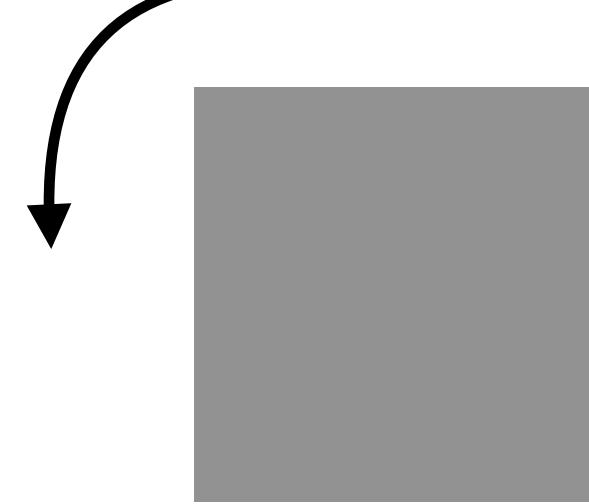
Symmetry operations are operations where the shape of an object or substance does not change.

Let's consider TMDC symmetry operation

Rotation

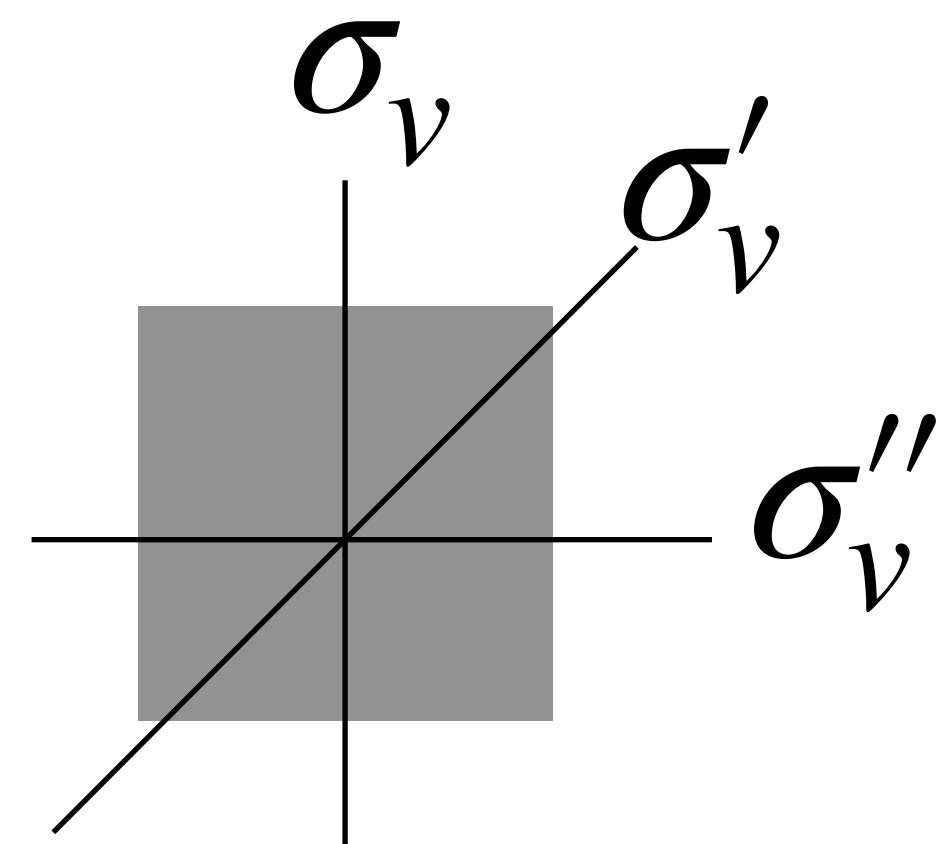
C_n

C_4 90° rotate

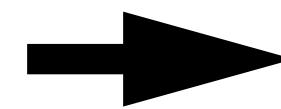


Reflection

σ_v

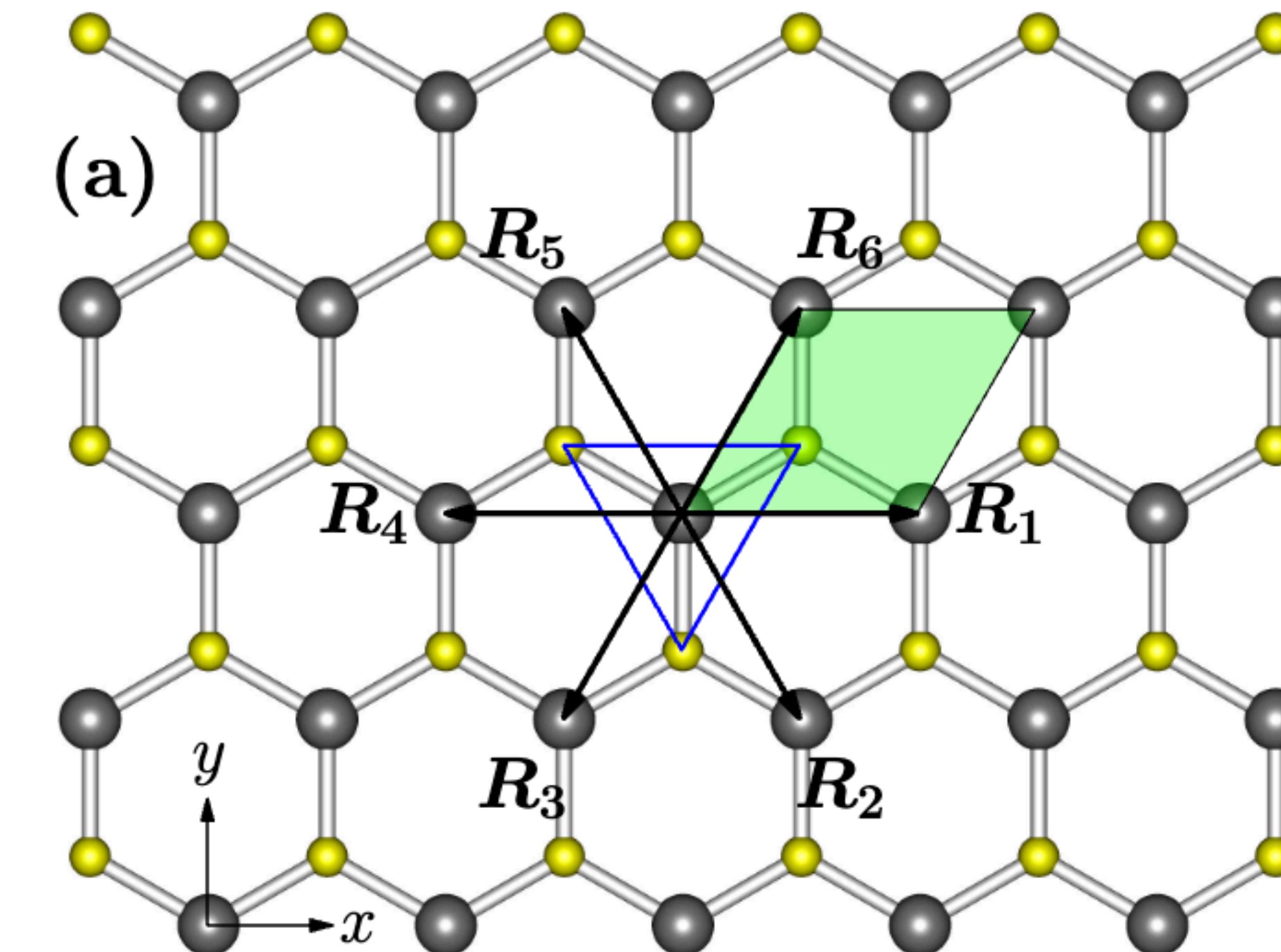


A set of symmetry operations forms a group.



Point group

$D_{3h}, \{\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_v, \hat{\sigma}'_v, \hat{\sigma}''_v\},$



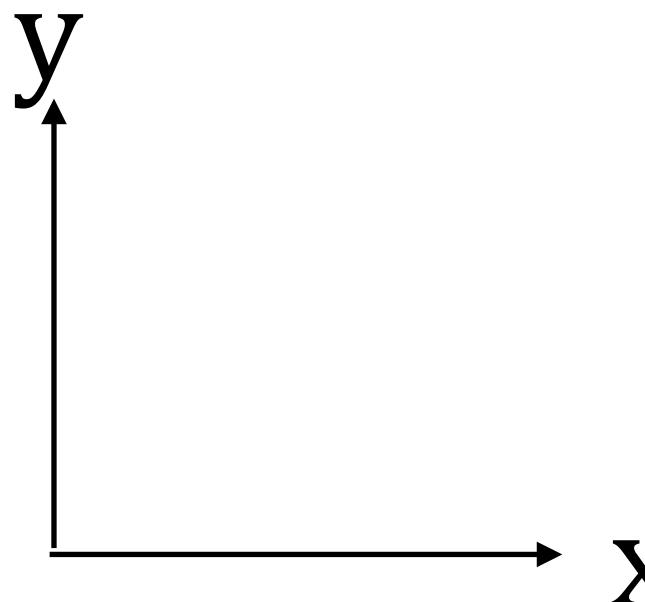
Representation of Symmetry Operations

The form of a symmetry operation depends on the choice of **basis**.

Rotation

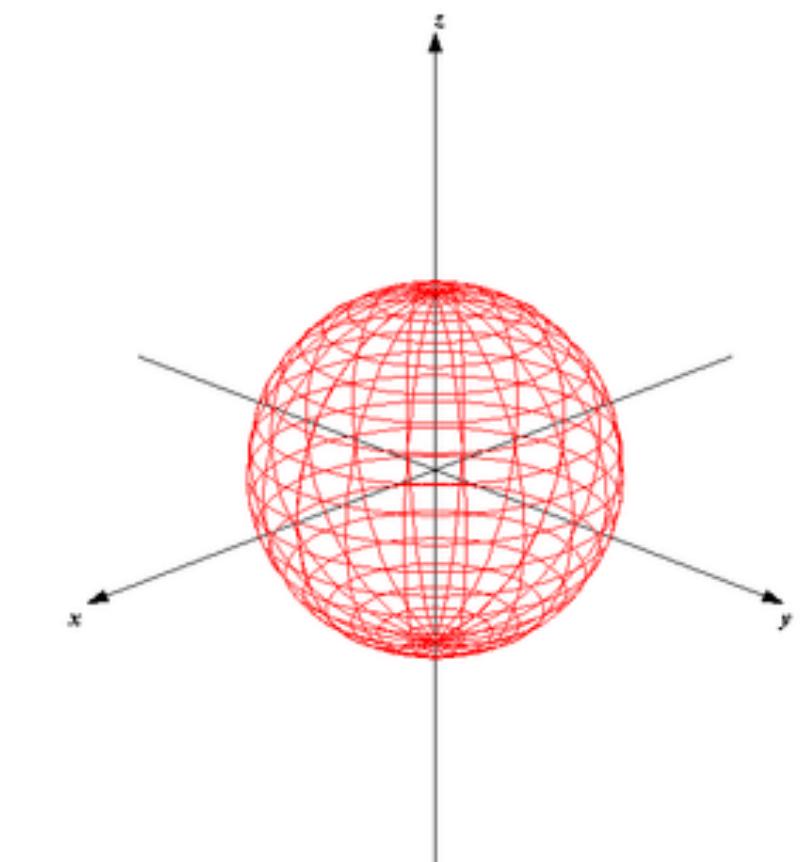
Basis is {x,y}

$$C_3 \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$



Basis is {s-orbital}

$$C_3(s) = 1 \cdot (s)$$



There are **multiple representations** to describe a symmetry operation.

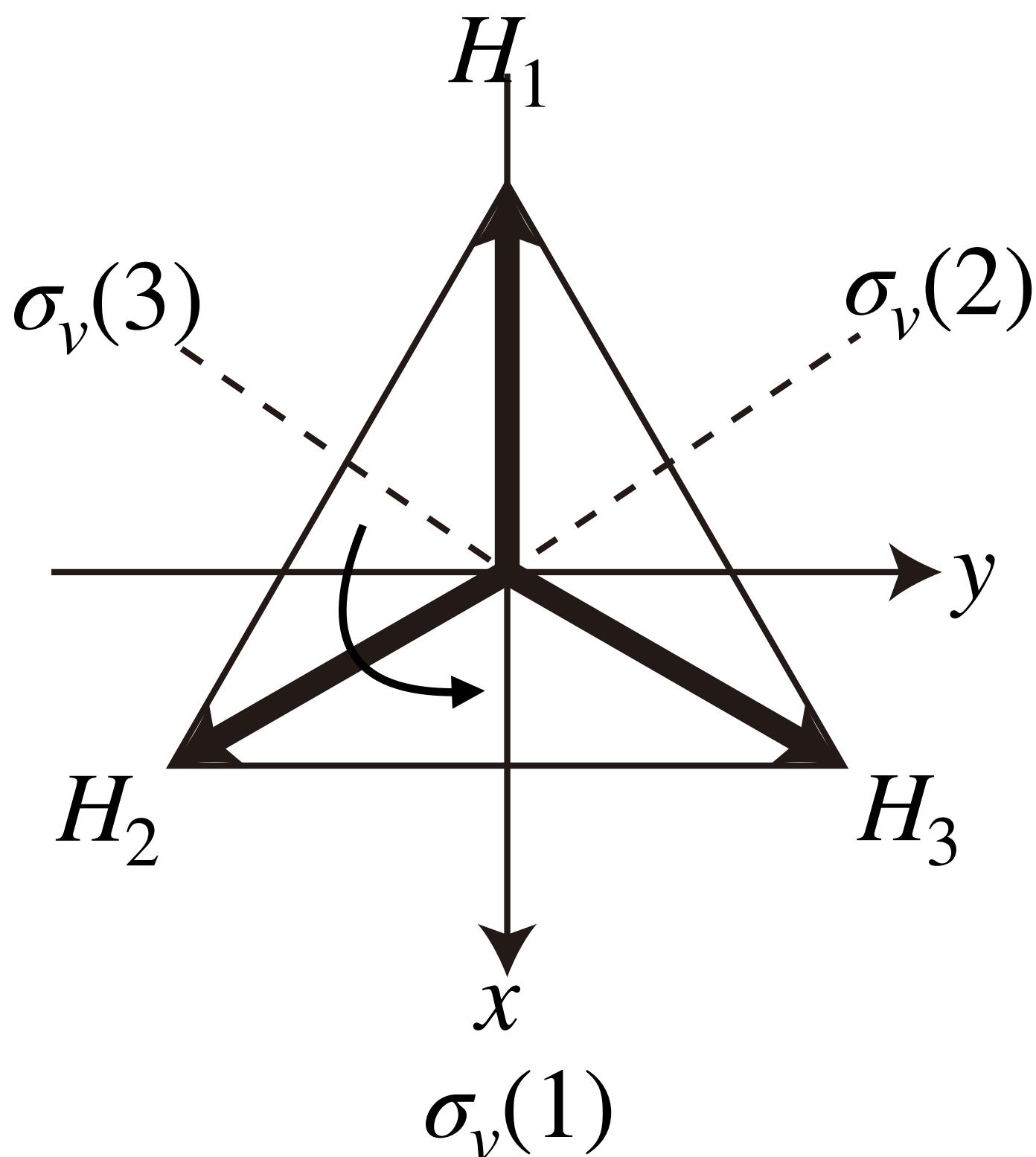
Representation of Symmetry Operations

Irreducible and Reducible Representations of the C_{3v} Point Group

Create a representation matrix with $2s, 2p_x, 2p_y, 2p_z$ as the basis.

Example: NH₃

$$C_{3v} = \{E, 2C_3, C_3, 3\sigma_v\}$$



$$C_3(s) = (1)s + (0)p_x + (0)p_y + (0)p_z$$

$$C_3(p_x) = (0)s + \left(-\frac{1}{2}\right)p_x + \left(-\frac{\sqrt{3}}{2}\right)p_y + (0)p_z$$

$$C_3(p_y) = (0)s + \left(\frac{\sqrt{3}}{2}\right)p_x + \left(-\frac{1}{2}\right)p_y + (0)p_z$$

$$C_3(p_z) = (0)s + (0)p_x + (0)p_y + (1)p_z$$

$$\rightarrow C_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

Representation of Symmetry Operations

Create a representation matrix with $2s, 2p_x, 2p_y, 2p_z$ as the basis.

$$\begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix}$$

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$C_3 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

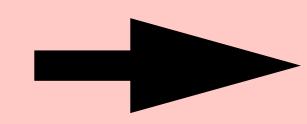
$$C_3^2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v(1) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v(2) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$\sigma_v(3) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

This 4x4 matrix is block-out matrix



Reducible Representations.

Representation of Symmetry Operations

Create a representation matrix with $2s, 2p_x, 2p_y, 2p_z$ as the basis.

irreducible representations(IR)

	E	C_3	C_3^2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$	
s	1	1	1	1	1	1	$\Gamma_1 \rightarrow$ IR
p_z	1	1	1	1	1	1	$(\Gamma_1) \rightarrow$ IR
p_x	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix}$	$\Gamma_3 \rightarrow$ IR
p_y							

Character \rightarrow Trace of the Representation Matrix

The character is essential for identifying irreducible representations within a reducible representation.

Hybrid Orbital Formation

Symmetry Considerations and Atomic Orbitals

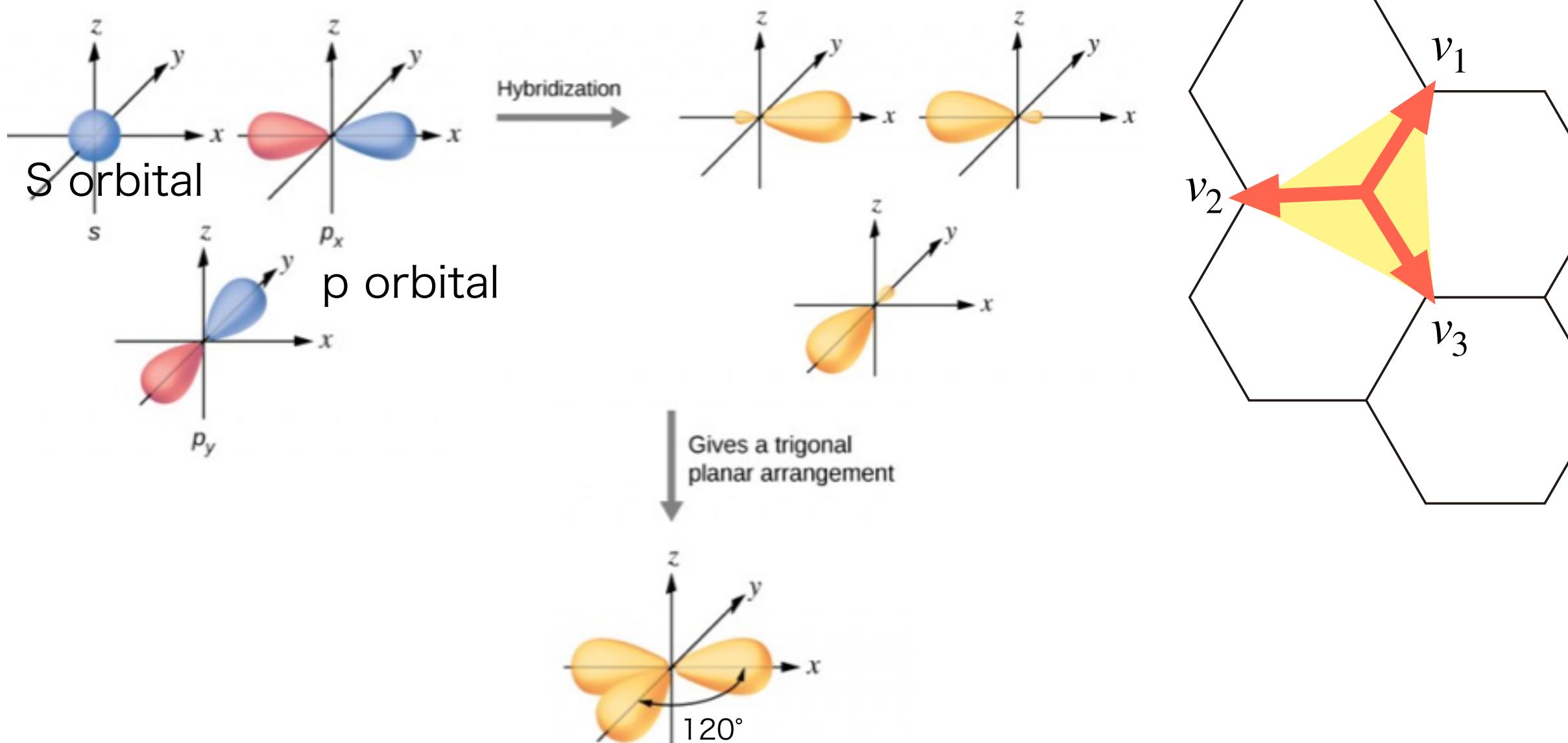
Which atomic orbitals are allowed to be mixed?

procedure

- ① Assume vectors that is representative of the hybrid orbital.
- ② Find out which representation they belong to. (Creating an character table)
- ③ Simplify to irreducible representation

graphene C_{6v} For simplicity, think C_{3v}

sp^2 hybridization



② Create an character table

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(v_1v_2v_3)$	3	0	1

③ Simplify to irreducible representation

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	s orbital
A_2	1	1	-1	pz orbital
E	2	-1	0	px, py orbital
$\Gamma(v_1v_2v_3)$	3	0	1	

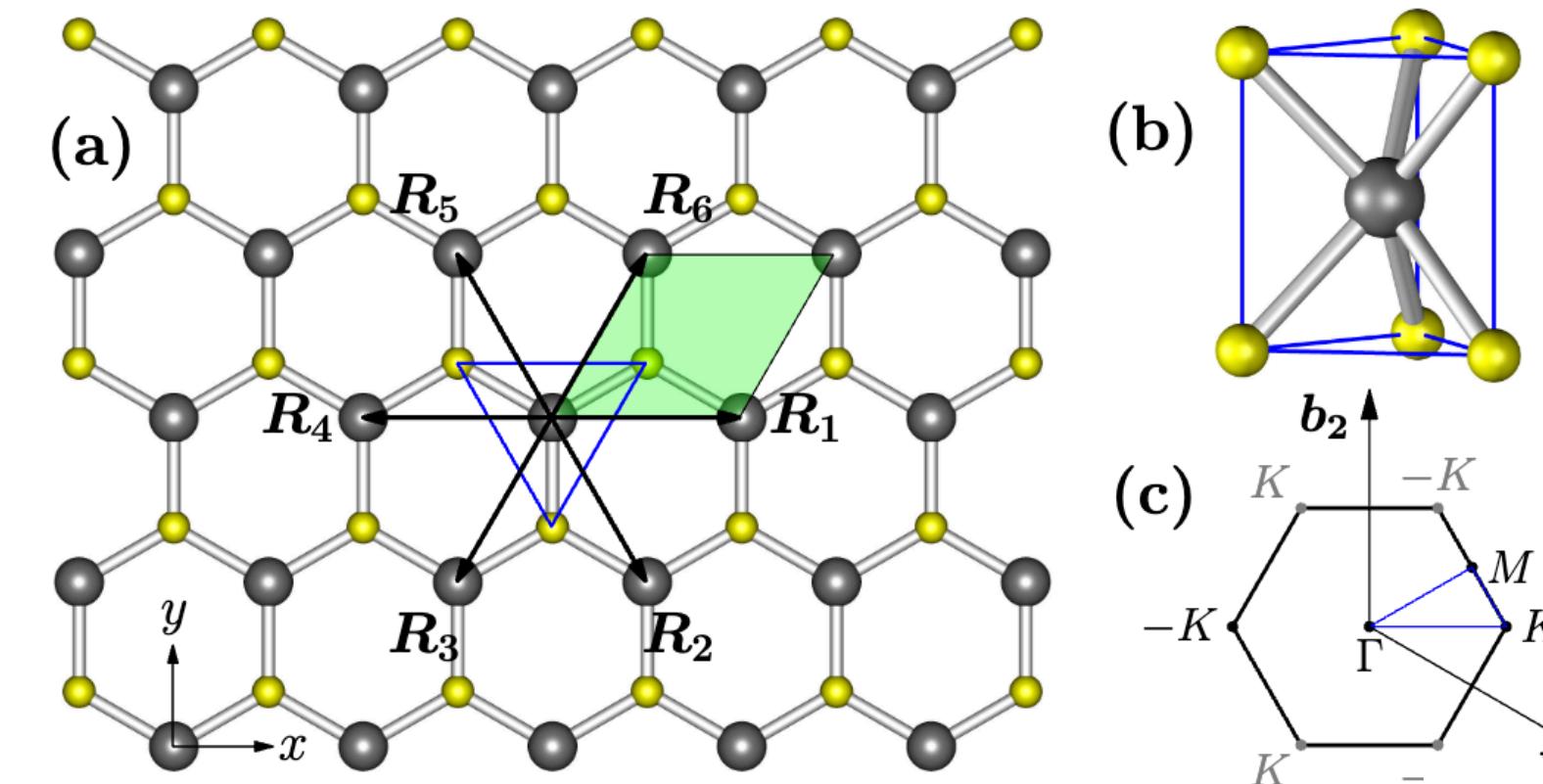
$$\rightarrow \Gamma(v_1v_2v_3) = A_1 + E$$

Mixture of S orbital and px, py orbital allowed

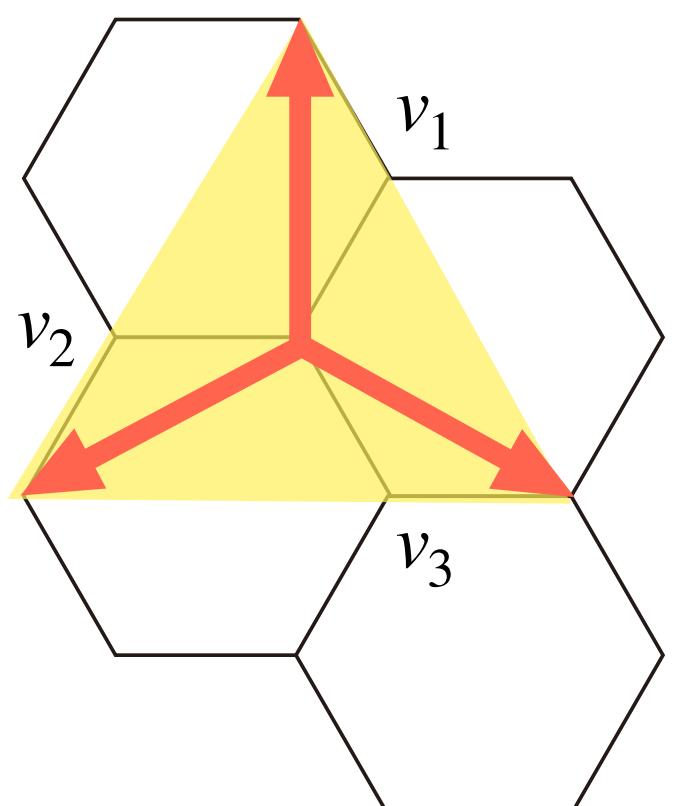
Hybrid Orbital Formation

Symmetry Considerations and Atomic Orbitals

TMDC D_{3h}



① Assume hybrid orbital



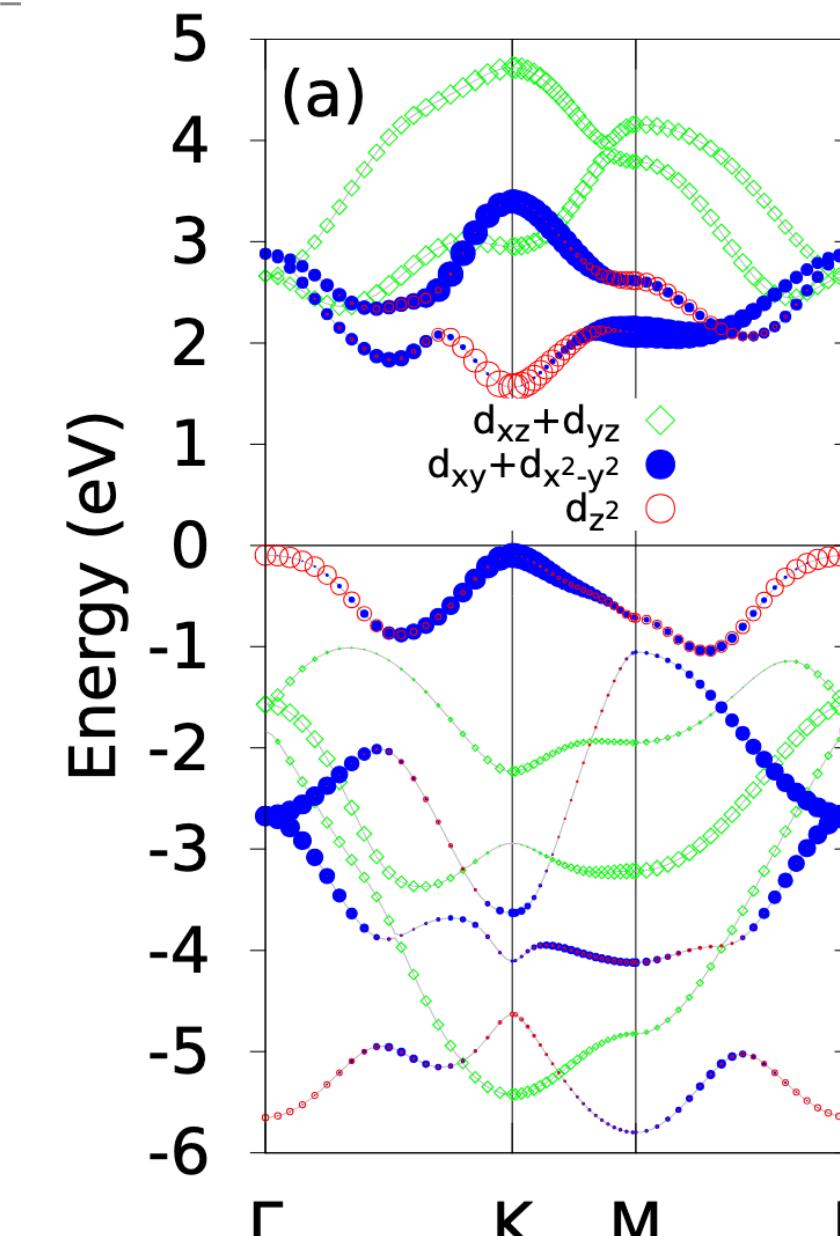
- ② Create an character table
- ③ Simplify to irreducible representation

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$3\sigma_v$	
A'_1	1		1	1	1	$\{d_{z^2}\}$
E'	2	-1	0	2	0	$\{d_{xy}, d_{x^2-y^2}\}$
E''	2	-1	0	-2	0	$\{d_{yz}, d_{xz}\}$
$\Gamma(v_1v_2v_3)$	3	0	1	3	1	

$\rightarrow \Gamma(v_1v_2v_3) = A'_1 + E'$

Mixture of $\{d_{z^2}\}$ orbital and $\{d_{xy}, d_{x^2-y^2}\}$ orbitals allowed

$\{d_{xz}, d_{yz}\}$ do not mix with other orbits

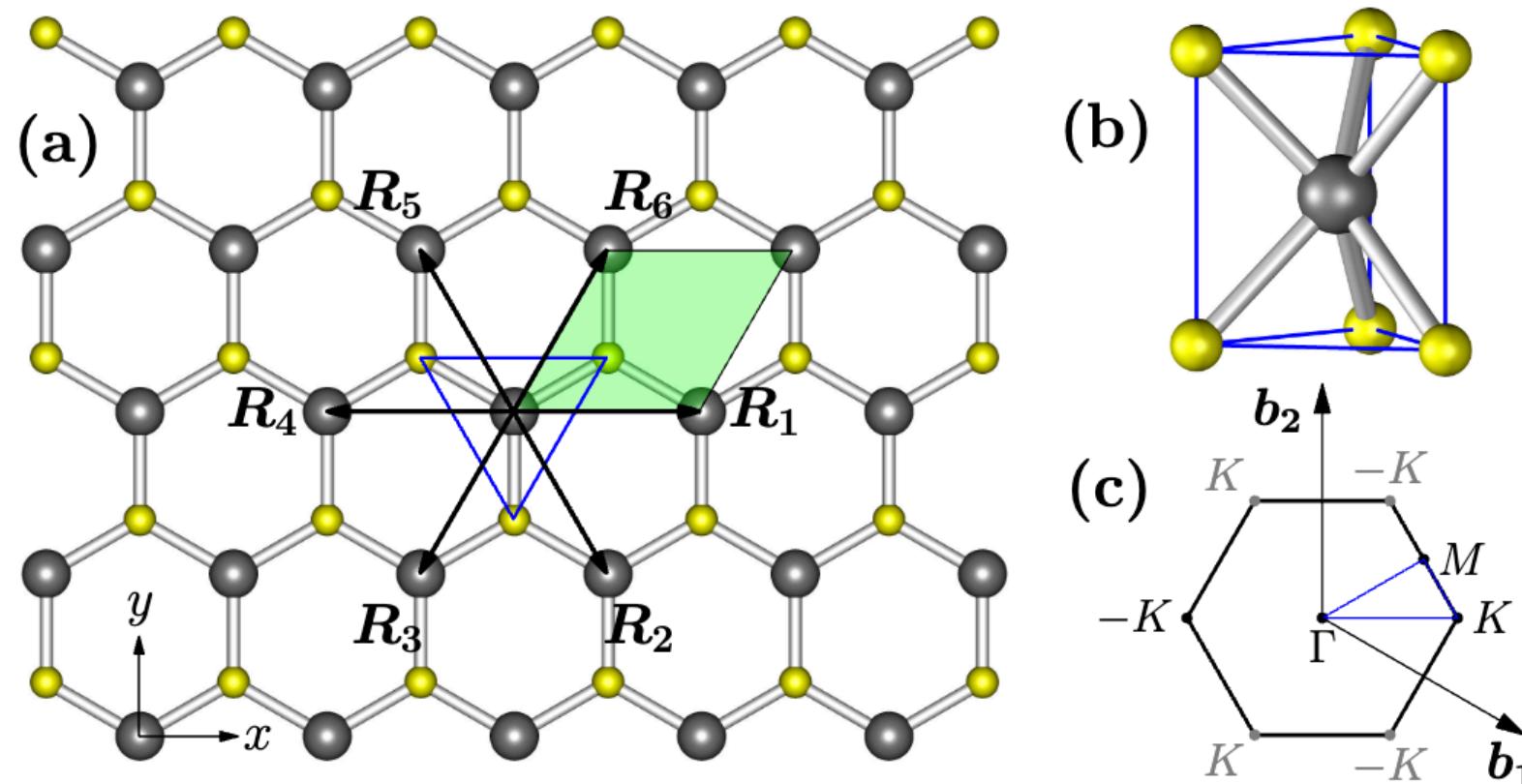


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$ d_{xy} $	H^{21}	H^{22}	0
$ d_{x^2-y^2} $	0	0	0
$ d_{xz} $	0	0	0
$ d_{yz} $	0	0	0

Not consider
Hybrid orbital is not exist

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Consider 3 band in d orbital of transition atom

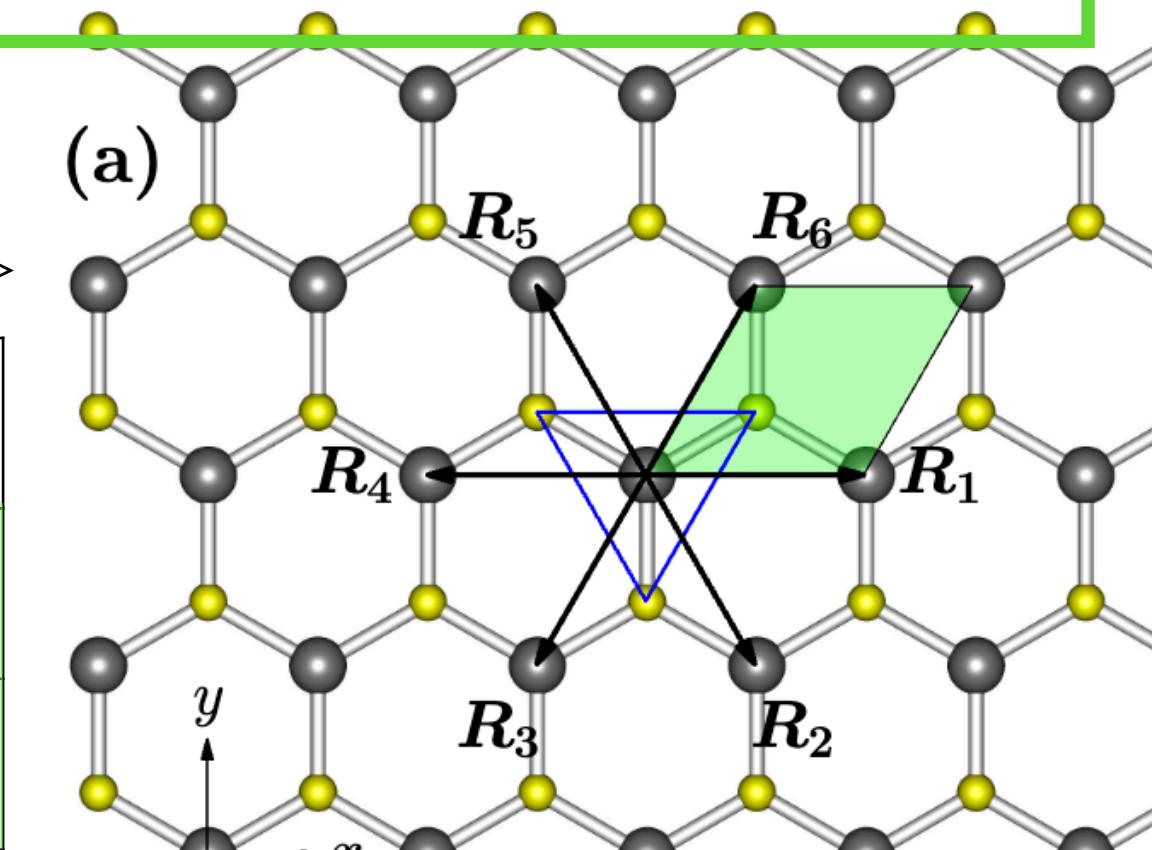
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Formula for hopping integrals to all neighboring sites

$$E^{jj'}(\hat{g}_n \mathbf{R}) = D^j(\hat{g}_n) E^{jj'}(\mathbf{R}) [D^{j'}(\hat{g}_n)]^\dagger,$$

Hopping matrix

$ d_{z^2}\rangle$	$ d_{xy}\rangle$	$ d_{x^2-y^2}\rangle$
E^{11}	E^{12}	
E^{21}	E^{22}	



$$E^{11} = E_{11}^{11}(\mathbf{R})$$

$$E^{12} = (E_{11}^{12}(\mathbf{R}), E_{12}^{12}(\mathbf{R}))$$

$$E^{21} = \begin{pmatrix} E_{11}^{21}(\mathbf{R}) \\ E_{21}^{21}(\mathbf{R}) \end{pmatrix} \quad E^{22} = \begin{pmatrix} E_{11}^{22}(\mathbf{R}) & E_{12}^{22}(\mathbf{R}) \\ E_{21}^{22}(\mathbf{R}) & E_{22}^{22}(\mathbf{R}) \end{pmatrix}$$

\hat{g}_n are a subset of the symmetry operations of D_{3h} , $\{\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_v, \hat{\sigma}'_v, \hat{\sigma}''_v\}$, $D^j(\hat{g}_n)$ is the matrix of the j-th IR.

D_{3h}	E	C_3	C_3^2	σ_v	σ'_v	σ''_v
A'_1	1	1	1	1	1	1
E'	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$

Ex.

$$E^{11}(R_5) = D^1(C_3) E^{11}(R1) [D^1(C_3)]^\dagger$$

$$E^{12}(R_4) = D^1(\sigma'_v) E^{12}(R1) [D^2(\sigma'_v)]^\dagger$$

Three-Band Tight-Binding Model for TMDC

Model with nearest-neighbor hoping (not consider spin)

Consider 3 band in d orbital of transition atom

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Elements of Hamiltonian

$$H^{\text{NN}}(\mathbf{k}) = \begin{bmatrix} h_0 & h_1 & h_2 \\ h_1^* & h_{11} & h_{12} \\ h_2^* & h_{12}^* & h_{22} \end{bmatrix}, \quad \boxed{\begin{aligned} h_0 &= 2t_0(\cos 2\alpha + 2 \cos \alpha \cos \beta) + \epsilon_1, & h_{11} &= 2t_{11} \cos 2\alpha + (t_{11} + 3t_{22}) \cos \alpha \cos \beta + \epsilon_2, \\ h_1 &= -2\sqrt{3}t_2 \sin \alpha \sin \beta + 2it_1(\sin 2\alpha + \sin \alpha \cos \beta), & h_{22} &= 2t_{22} \cos 2\alpha + (3t_{11} + t_{22}) \cos \alpha \cos \beta + \epsilon_2, \\ h_2 &= 2t_2(\cos 2\alpha - \cos \alpha \cos \beta) + 2\sqrt{3}it_1 \cos \alpha \sin \beta, & h_{12} &= \sqrt{3}(t_{22} - t_{11}) \sin \alpha \sin \beta \\ &&&+ 4it_{12} \sin \alpha (\cos \alpha - \cos \beta), \end{aligned}}$$

$$(\alpha, \beta) = \left(\frac{1}{2}k_x a, \frac{\sqrt{3}}{2}k_y a \right), \quad \epsilon_j \text{ is the on-site energy}$$

$$\begin{aligned} t_0 &= E_{11}^{11}(\mathbf{R}_1), & t_1 &= E_{11}^{12}(\mathbf{R}_1), & t_2 &= E_{12}^{12}(\mathbf{R}_1), \\ t_{11} &= E_{11}^{22}(\mathbf{R}_1), & t_{12} &= E_{12}^{22}(\mathbf{R}_1), & t_{22} &= E_{22}^{22}(\mathbf{R}_1), \end{aligned}$$

6 hopping parameters !

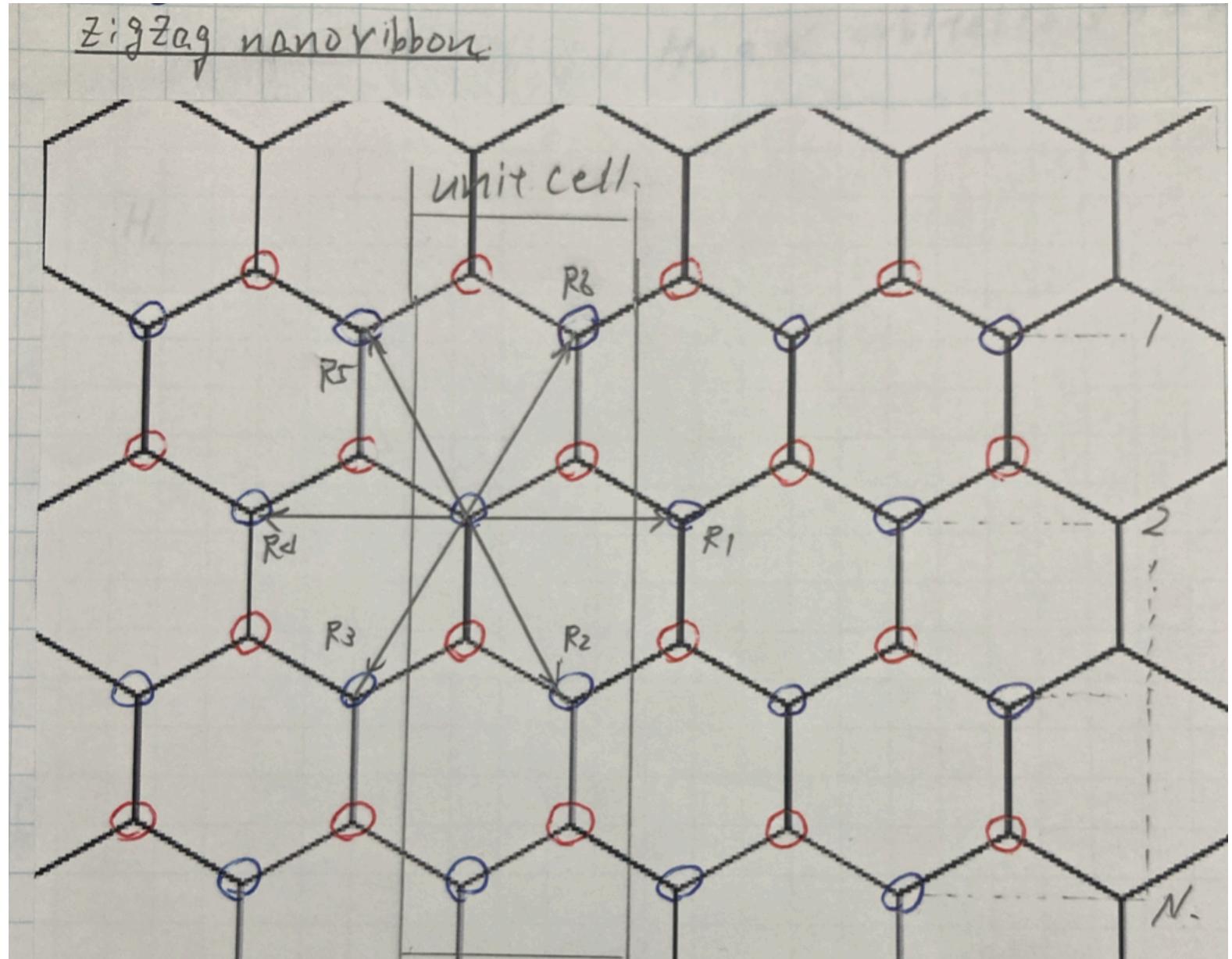
Energy band of Graphene

Not yet

Zigzag TMDC Nano-ribbon

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Elements of Hamiltonian



$$H_{n\gamma,n\gamma'}^{\text{ribbon}} = \delta_{\gamma\gamma'} e_\gamma + e^{i\mathbf{k}\cdot\mathbf{R}_1} E_{\gamma\gamma'}(\mathbf{R}_1) + e^{i\mathbf{k}\cdot\mathbf{R}_4} E_{\gamma\gamma'}(\mathbf{R}_4), \quad (n = 1, \dots, W); \quad (\text{A1})$$

$$H_{n\gamma,(n-1)\gamma'}^{\text{ribbon}} = e^{i\mathbf{k}\cdot\mathbf{R}_2} E_{\gamma\gamma'}(\mathbf{R}_2) + e^{i\mathbf{k}\cdot\mathbf{R}_3} E_{\gamma\gamma'}(\mathbf{R}_3), \quad (n = 2, \dots, W); \quad (\text{A2})$$

$$H_{n\gamma,(n+1)\gamma'}^{\text{ribbon}} = e^{i\mathbf{k}\cdot\mathbf{R}_5} E_{\gamma\gamma'}(\mathbf{R}_5) + e^{i\mathbf{k}\cdot\mathbf{R}_6} E_{\gamma\gamma'}(\mathbf{R}_6), \quad (n = 1, \dots, W - 1); \quad (\text{A3})$$

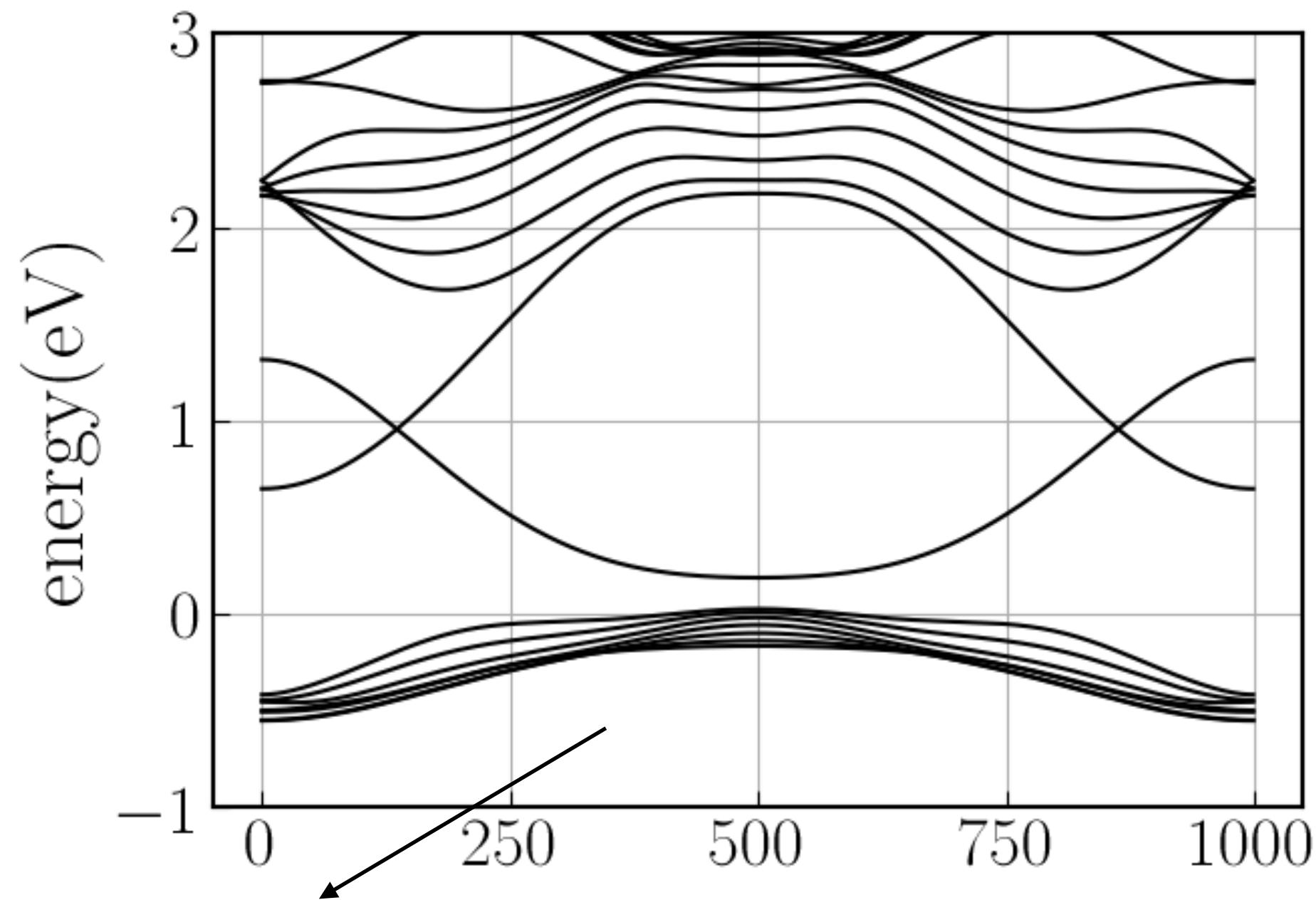
$$h'_1 \equiv H_{nn}^{\text{ribbon}}, h'_2 \equiv H_{n,n-1}^{\text{ribbon}}$$

$$h'_1 = \begin{bmatrix} \epsilon_1 + 2\cos(k_x a)t_0 & 2i\sin(k_x a)t_1 & 2\cos(k_x a)t_2 \\ -2i\sin(k_x a)t_1 & \epsilon_2 + 2\cos(k_x a)t_{11} & 2i\sin(k_x a)t_{12} \\ 2\cos(k_x a)t_2 & -2i\sin(k_x a)t_{12} & \epsilon_2 + 2\cos(k_x a)t_{22} \end{bmatrix}, \quad (\text{A5})$$

$$h'_2 = \begin{bmatrix} 2\cos(\frac{1}{2}k_x a)t_0 & i\sin(\frac{1}{2}k_x a)(t_1 - \sqrt{3}t_2) & -\frac{1}{2}\cos(\frac{1}{2}k_x a)(\sqrt{3}t_1 + t_2) \\ -i\sin(\frac{1}{2}k_x a)(t_1 + \sqrt{3}t_2) & \frac{1}{2}\cos(\frac{1}{2}k_x a)(t_{11} + 3t_{22}) & -i\sin(\frac{1}{2}k_x a)(\frac{\sqrt{3}}{2}t_{11} + 2t_{12} - \frac{\sqrt{3}}{2}t_{22}) \\ \cos(\frac{1}{2}k_x a)(\sqrt{3}t_1 - t_2) & -i\sin(\frac{1}{2}k_x a)(\frac{\sqrt{3}}{2}t_{11} - 2t_{12} - \frac{\sqrt{3}}{2}t_{22}) & \frac{1}{2}\cos(\frac{1}{2}k_x a)(3t_{11} + t_{22}) \end{bmatrix}. \quad (\text{A6})$$

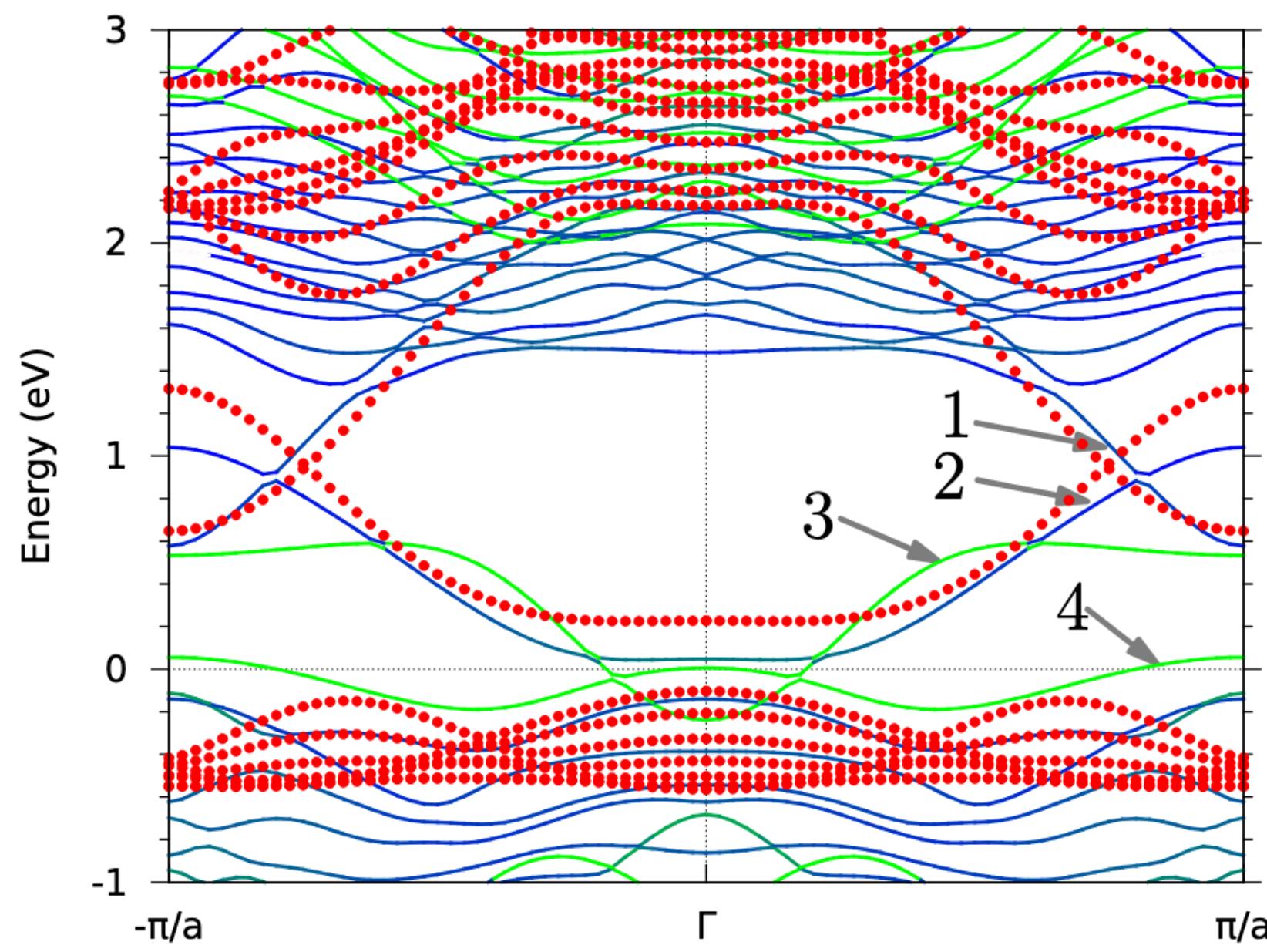
$$H^{\text{ribbon}}(k_x) = \begin{bmatrix} h'_1 & h'^\dagger_2 \\ h'_2 & h'_1 & h'^\dagger_2 \\ & h'_2 & h'_1 & \ddots \\ & \ddots & \ddots & h'^\dagger_2 \\ & & h'_2 & h'_1 \end{bmatrix}, \quad (\text{A4})$$

My calclation



Valence band is different. (Check now)

Liu. 2013



Mo atoms at the two edges of the ribbon, band 3 is from the Mo- d_{yz} orbital at the Mo-terminated edge, and band 4 is from the S- p_y and p_z orbitals at the S-terminated edge. Due to the

Edge modes in zigzag and armchair ribbons of monolayer MoS₂

Habib Rostami^{1,2}, Reza Asgari^{2,3} and Francisco Guinea^{4,5}

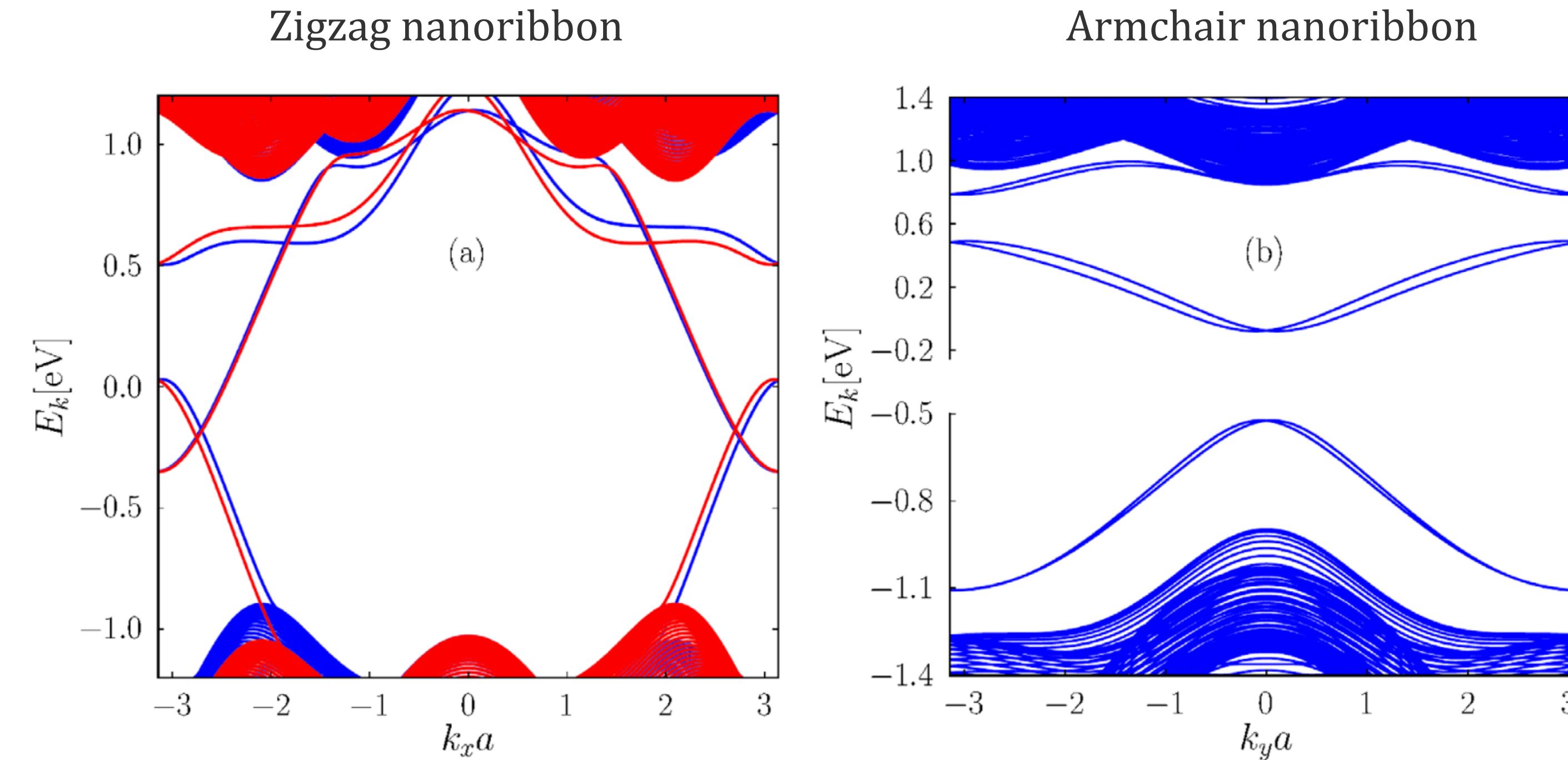


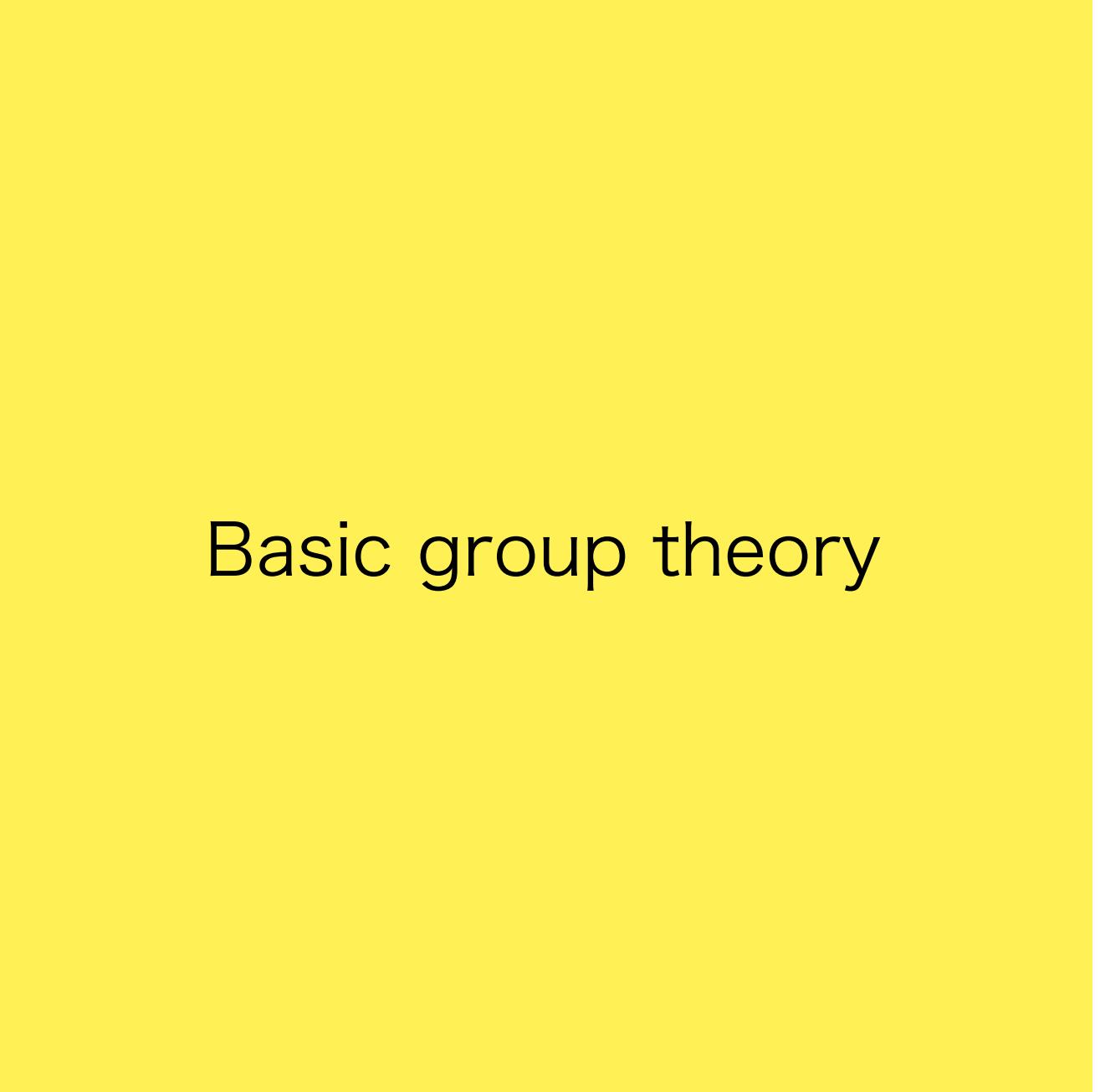
Figure 4. Energy dispersion of MoS₂ ribbons. (a) Zigzag ribbon $N = 100$. (b) Armchair ribbon $N = 101$. Red and blue colors indicate spin components. Owing to the spin degeneracy in the armchair ribbon just spin up component is plotted. The definition of N for both zigzag and armchair ribbons is depicted on the figure 1.

Edge Nonlinear Optics on a MoS₂ Atomic Monolayer

The broken inversion symmetry of the atomically thin monolayer shows strong second-harmonic generation (SHG)

Group Theory

Details of the mathematical definition of a group are omitted.



Basic group theory

