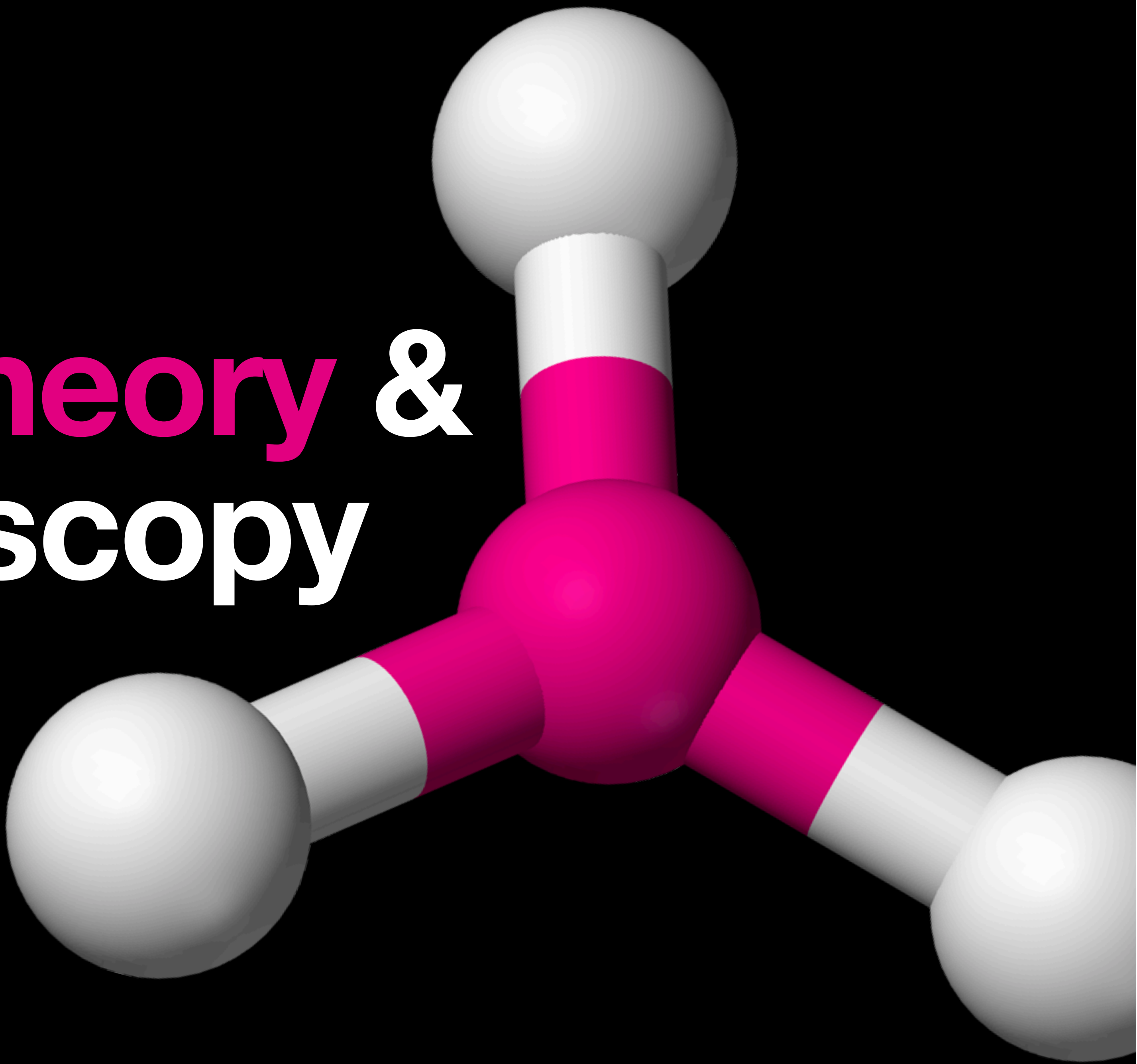
Group theory & spectroscopy

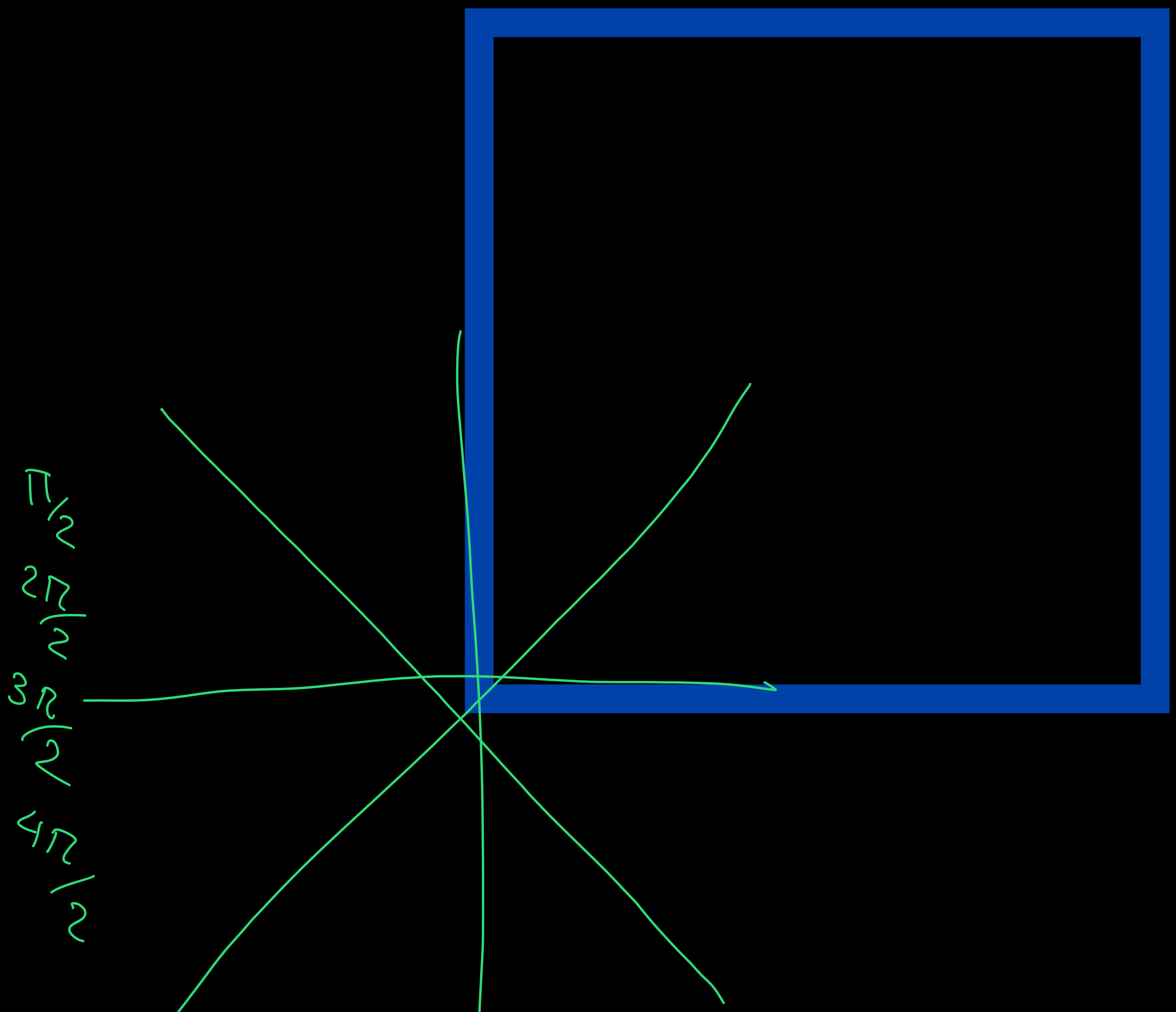
A brief intro.



ZAHRA AKBARI
ERFAN RAHBARI

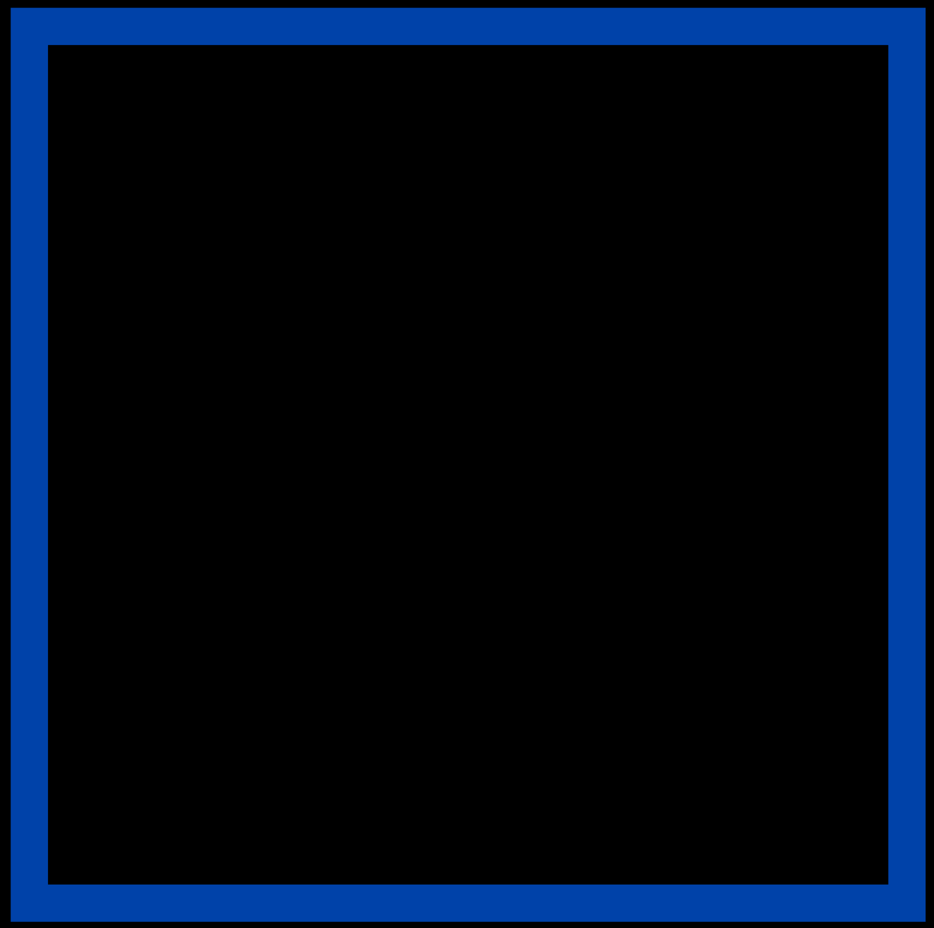
What is a group?

$0°$



What is a group?

90°

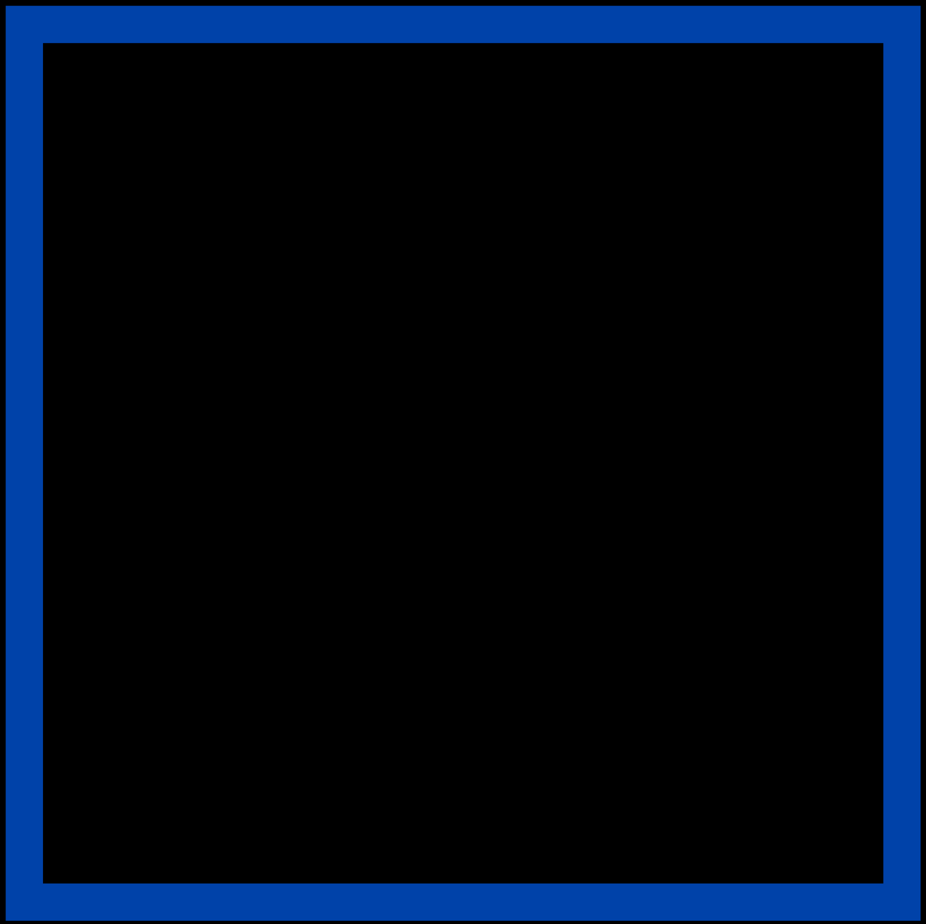


What is a group?

$A(BC) = (AB)C$

90°

- G should be closed under multiplication



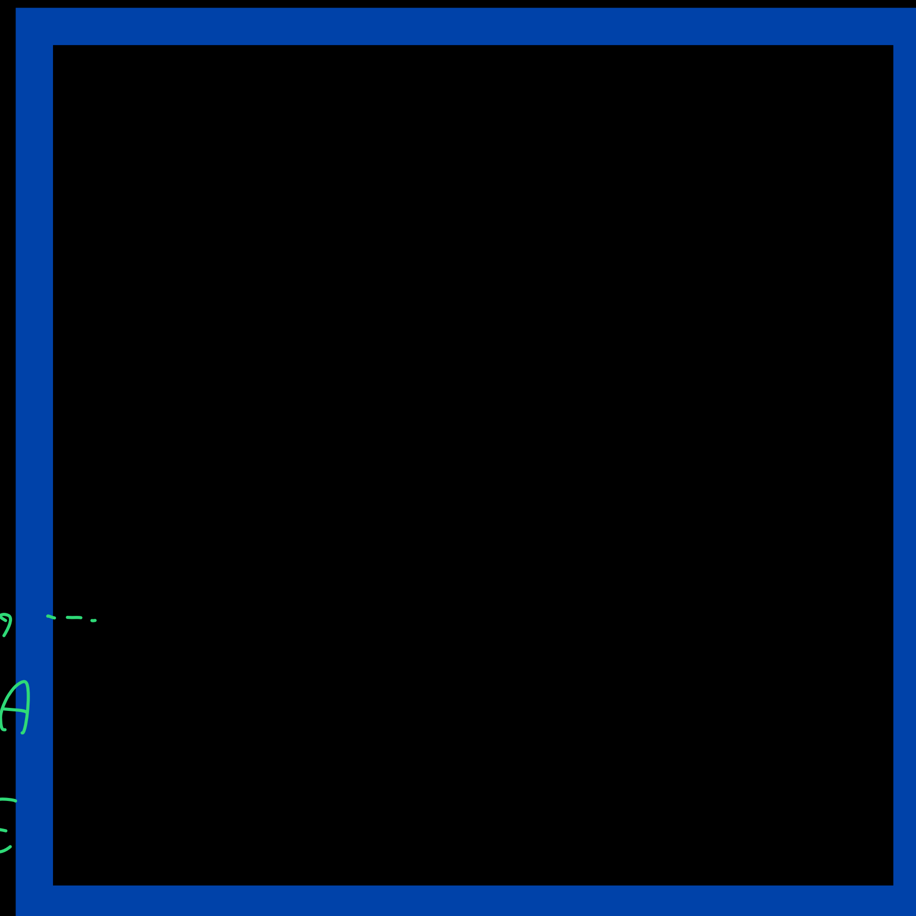
$I, E \quad aE = Ea = a$

What is a group?

90°

- G should be closed under multiplication

- Multiplication must be associative



$I, a, a^2, \ldots$

$AB = BA$

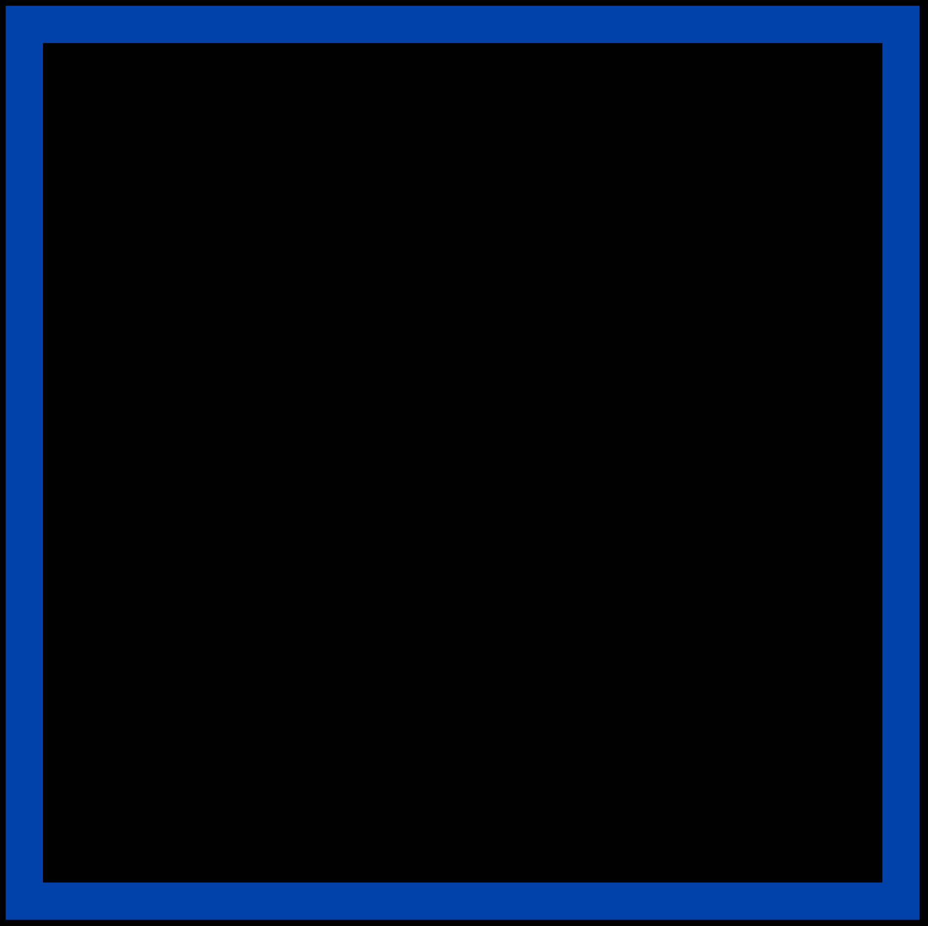
$a^{-1}a = E$

ab

What is a group?

90°

- G should be closed under multiplication
- Multiplication must be associative
- There must be an identity operator in the group



$G = \{I, r_4, r_4^2, r_4^3, t_x, t_y, t_{d_1}, t_{d_2}\}$

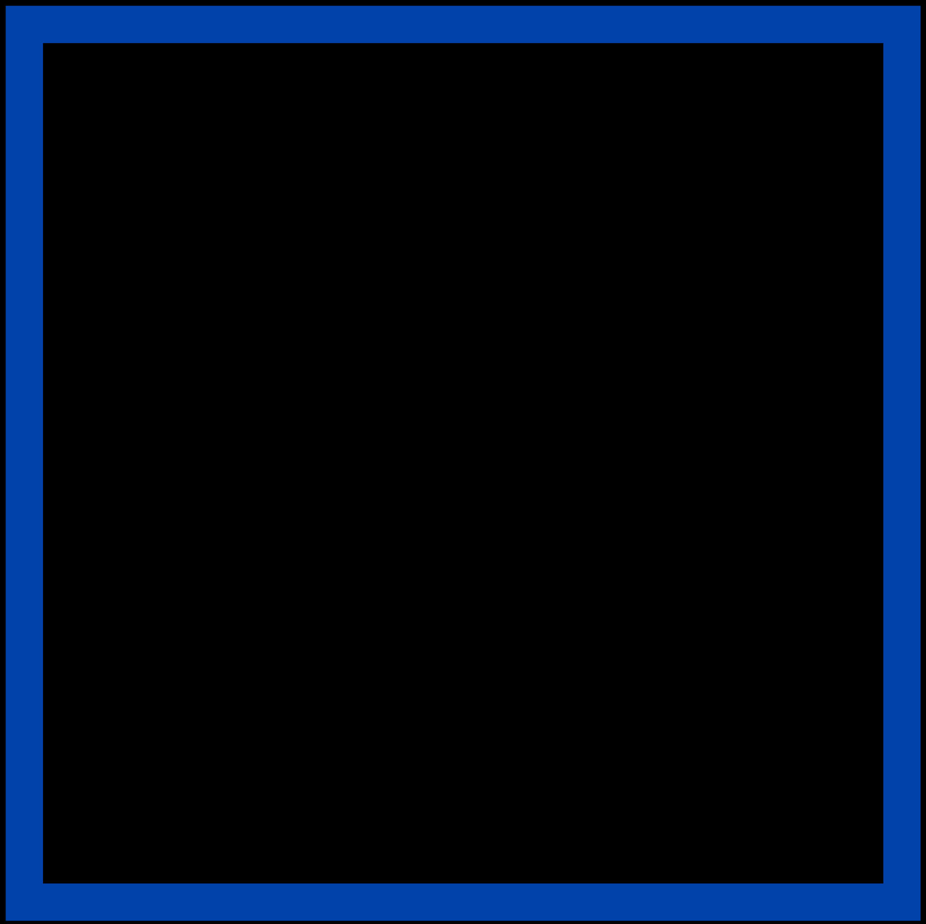
What is a group?

90°

- G should be closed under multiplication
- Multiplication must be associative
- There must be an identity operator in the group

I (e)

- For each element of the group must be an inverse



What is a group?

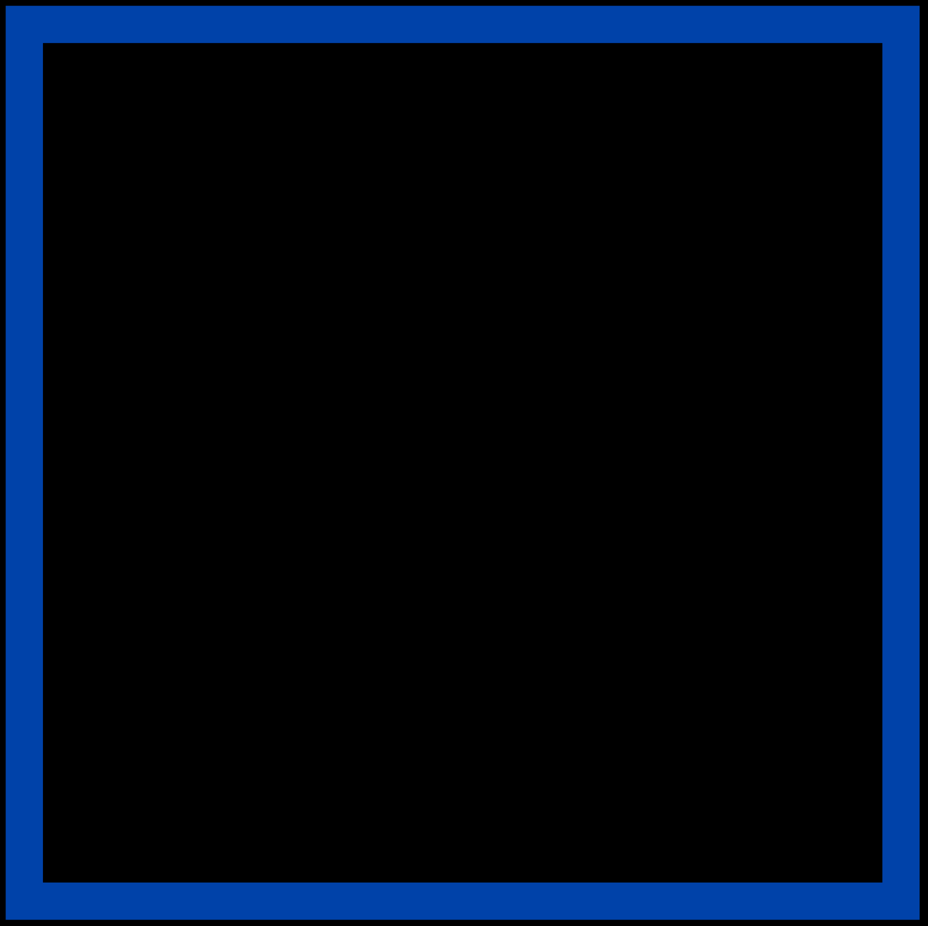
90°

- G should be closed under multiplication

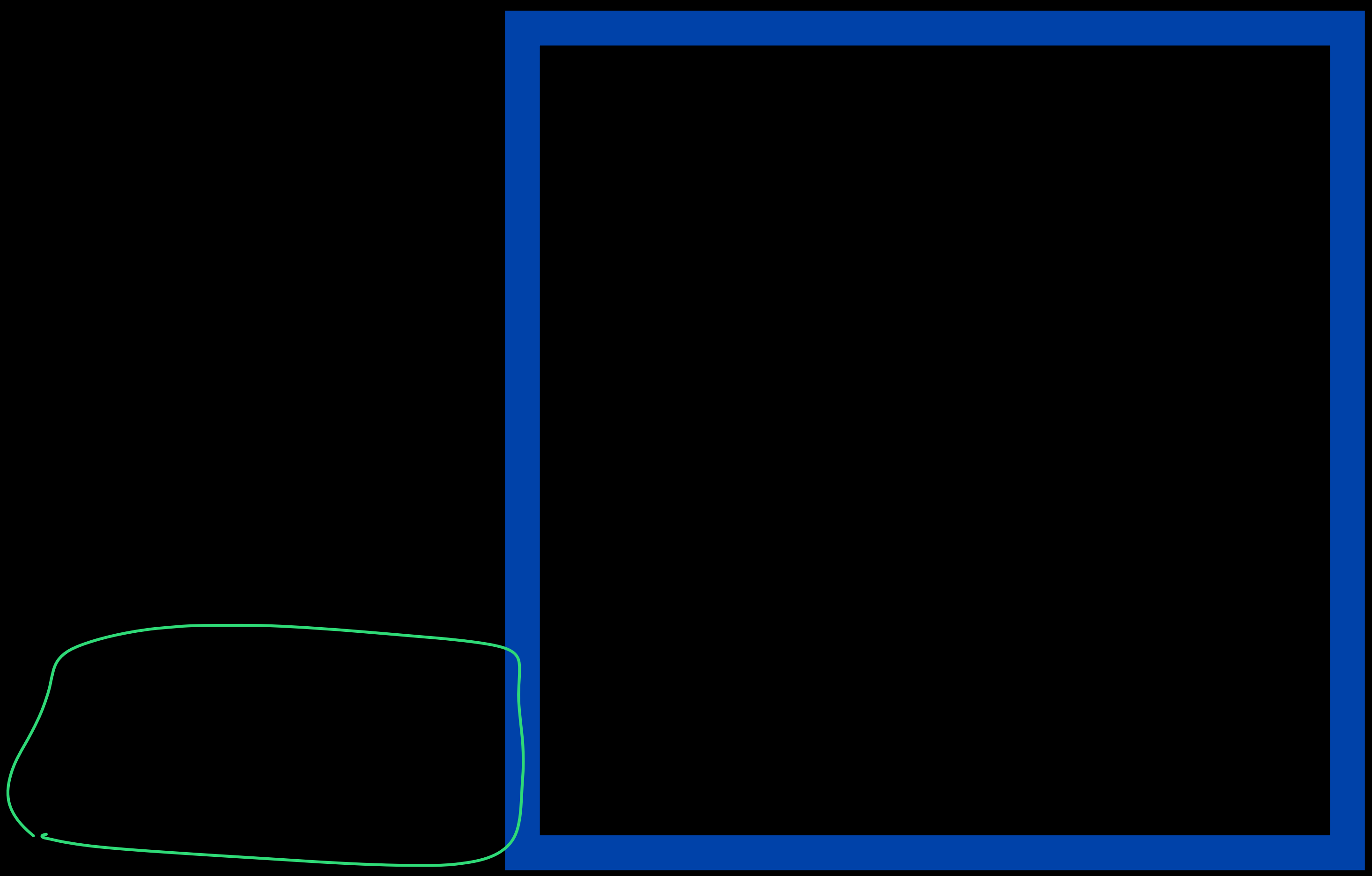
C_n $\frac{2\pi}{n}$

- Multiplication must be associative
- There must be an identity operator in the group
- For each element of the group must be an inverse

rotation

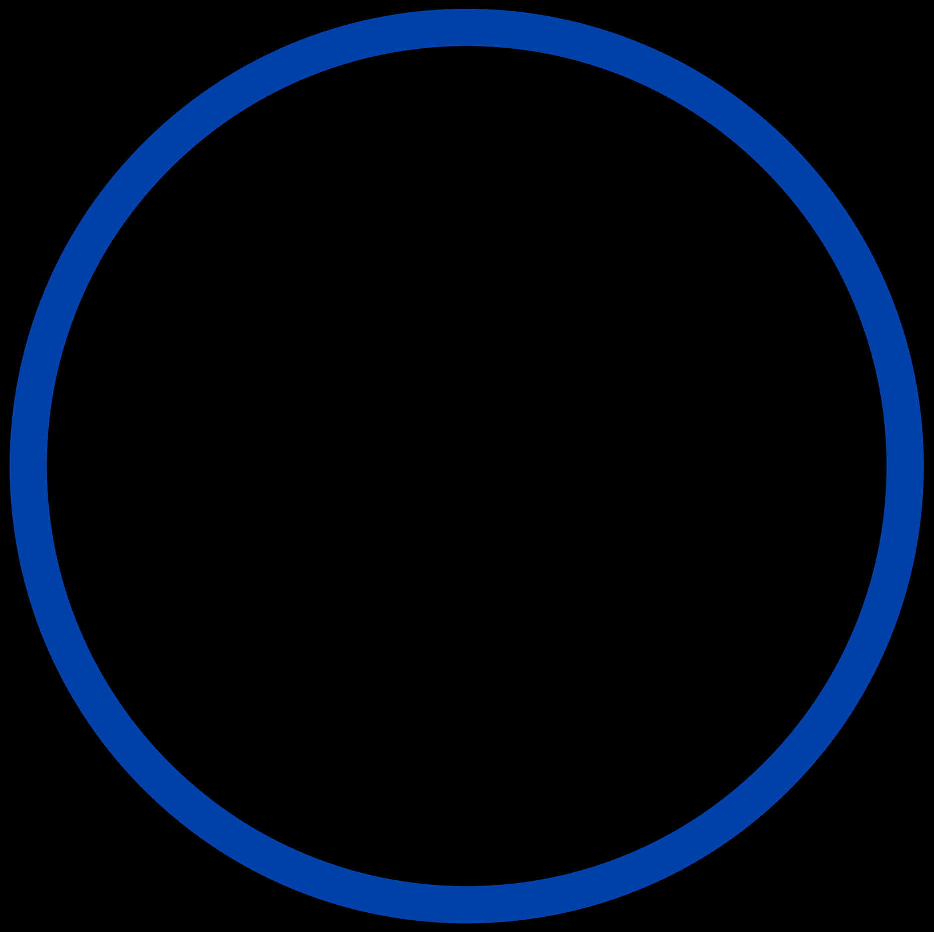


E.G.



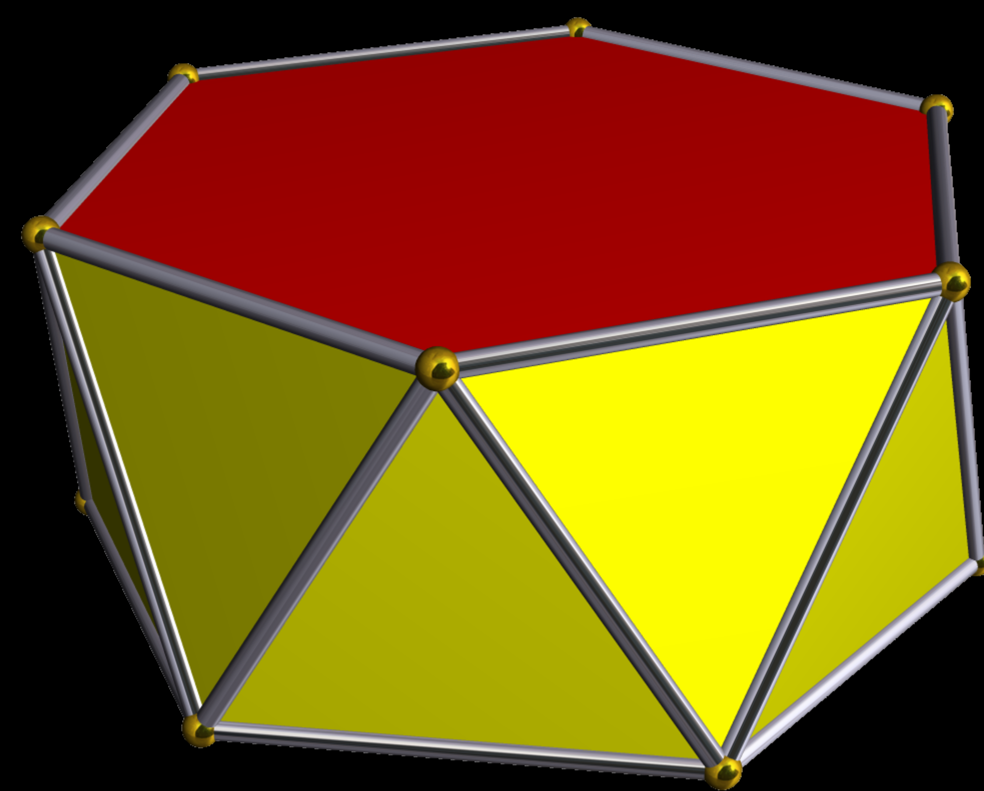
E.G.

CO_2



Symmetric operators

- $I \quad (E)$: Identity
- C_n: Propper rotation
- σ : Plane symmetry
- i : Inversion symmetry
- S_n : Improper symmetry



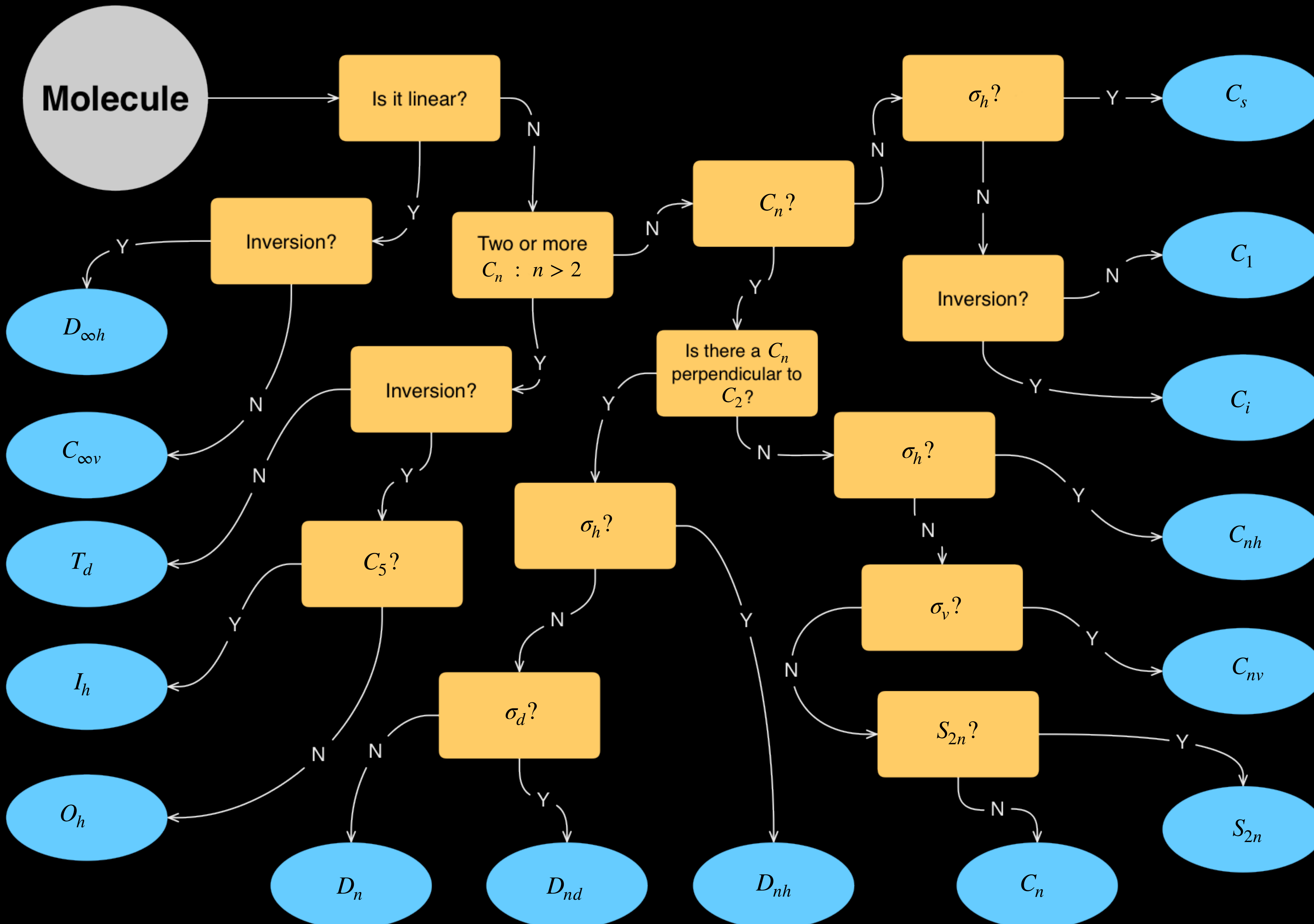
What does it have to with us?

$$\hat{H}$$

What does it have to with us?

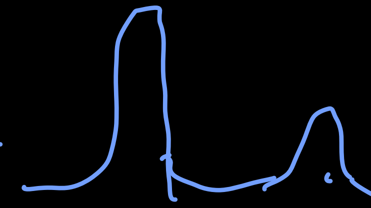
$$[\hat{O}, \hat{H}] = 0$$

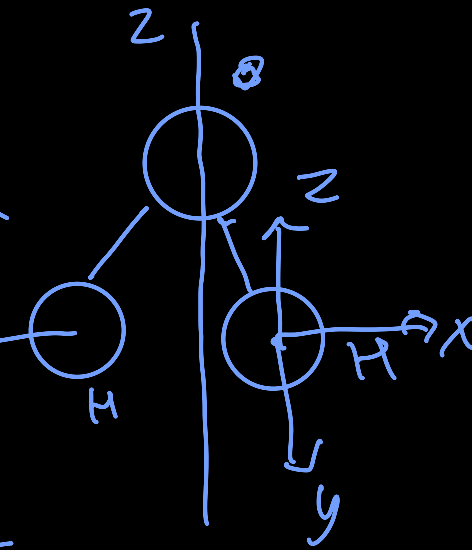
How to determine what's what?



Character table

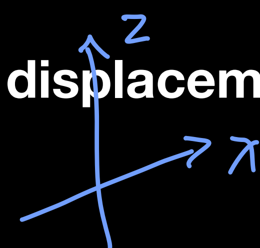
x, y, z





Representation for atom displacement: H_2O as an example

The C_{2v} character table



$2C_2$

	E	C_2	σ_{zx}	σ_{yz}	h=4	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yx
Γ	9	-1	1	3		

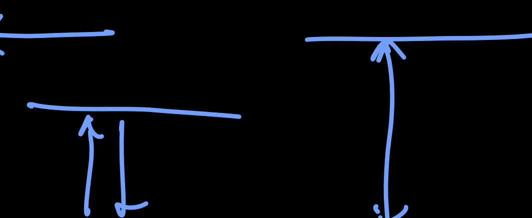
+1 +1 −1 0

3

9

IR →

raman



Reducing representation formula

$$\text{\# of irreducible representations of a given group} = \frac{1}{order} \sum \underbrace{\text{\# of operations in the class}}_{2} \times \underbrace{\text{characters of reducible rep.}} \times \underbrace{\text{char. of irr. rep.}}_{1}$$

Calculation of vib. Modes of water

3 ← 3N – 6 ← 3

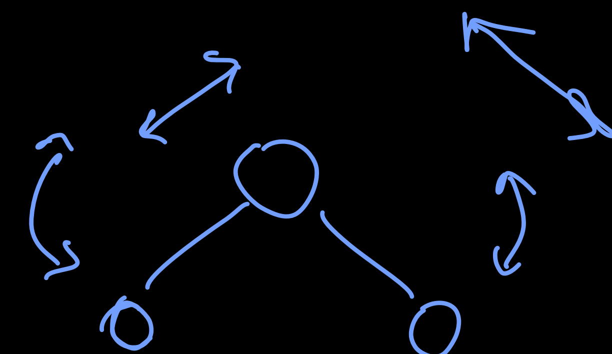
3N – 5 ← خطي

$$\Gamma_{total} = 3A_1 + A_2 + 2B_1 + 3B_2$$

$$-\Gamma_{translational} = A_1 \qquad + B_1 + B_2$$

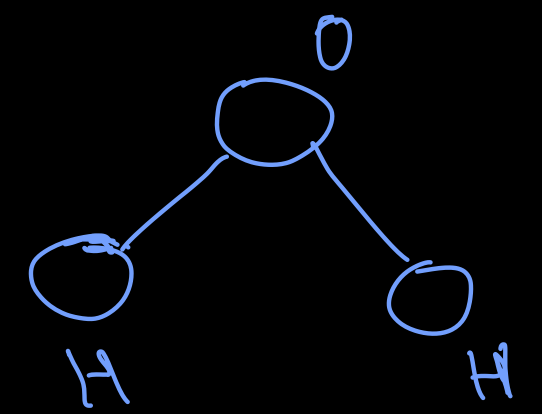
$$\Gamma_{rotational} = \qquad + A_2 + B_1 + B_2$$

$$\Gamma_{vibrational} = 2A_1 + B_2$$



Representation for single orbitals

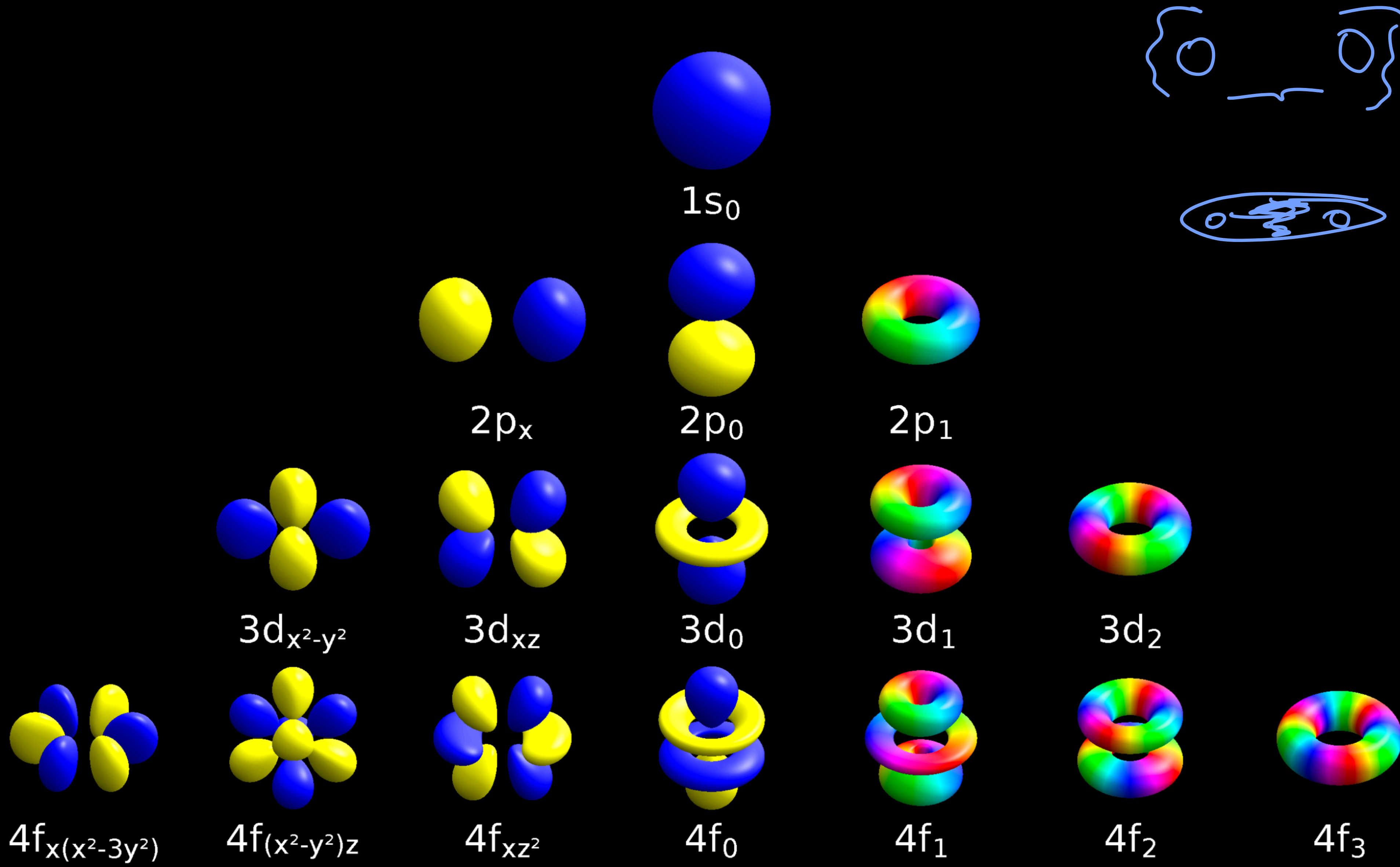
H2o as an example

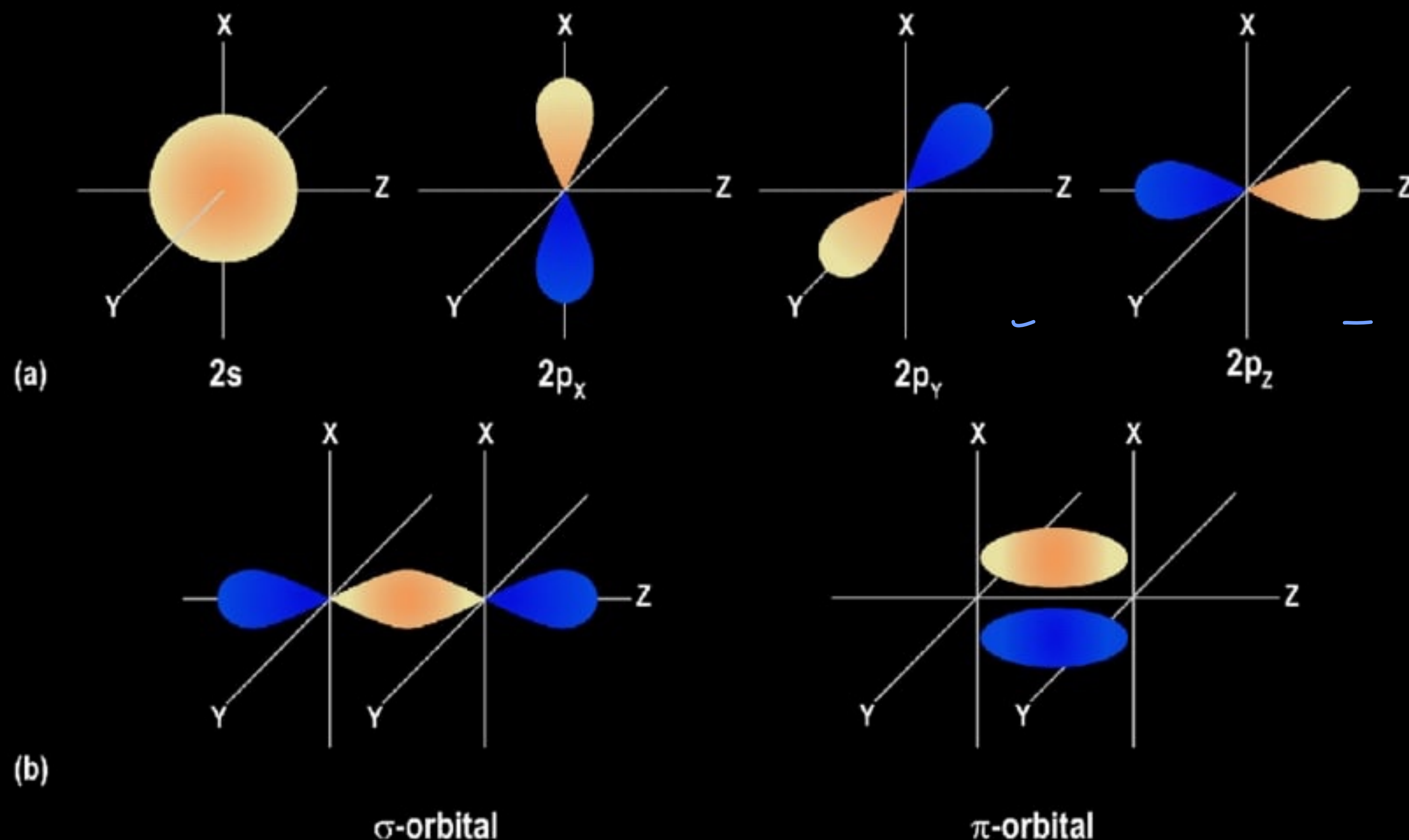


	E	C_2	σ_{zx}	σ_{yz}
$\Gamma(P_z)$	1	1	1	1
$\Gamma(P_x)$	1	-1	1	-1
$\Gamma(P_y)$	1	-1	-1	1
$\Gamma(red)$	2	0	0	2

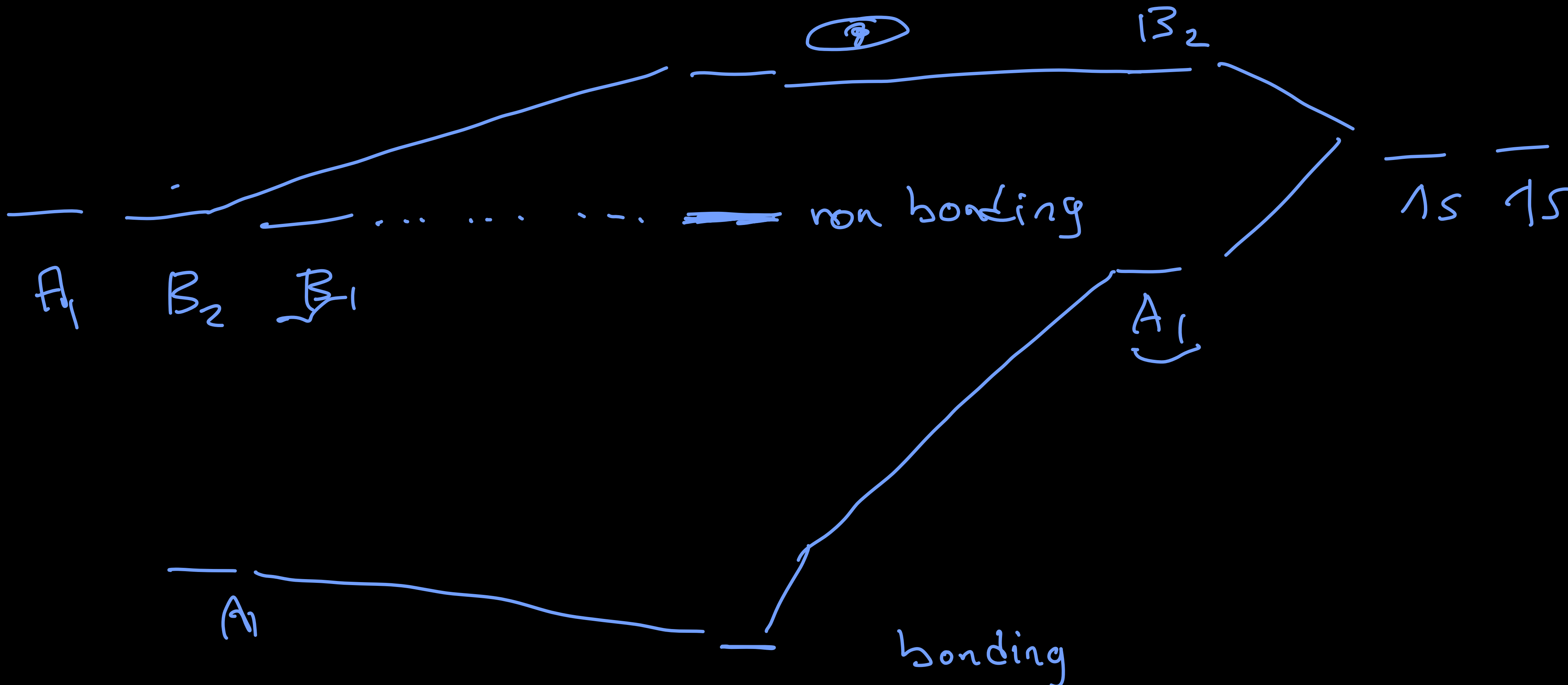
P

$$\Gamma(A_1) = 1$$
$$\Gamma(B_1) = 1$$
$$\Gamma(B_2) = 1$$


$1s_0$
$2p_x$
$2p_0$
$2p_1$
$3d_{x^2-y^2}$
$3d_{xz}$
$3d_0$
$3d_1$
$3d_2$
$4f_{x(x^2-3y^2)}$
$4f_{(x^2-y^2)z}$
$4f_{xz^2}$
$4f_0$
$4f_1$
$4f_2$
$4f_3$


X
Z
Y
(a)
2s
$2p_X$
$2p_Y$
$2p_Z$
(b)
σ-orbital
π-orbital

Constructing a MO Diagram for water



Transition moment

$$\overrightarrow{M}_{21} = \int \Psi_2 \overrightarrow{\mu} \Psi_1 \, d\tau$$

$= 0$ مجاز X

$=$ مجاز

$$\left\langle \Gamma_2 \otimes \Gamma\mu_{xyz} \otimes \Gamma_1 \right\rangle$$

	Ag	Au	
Ag	1	1	1
Au			

For an electric transition to be allowed the integral must be non-zero

If the result of the direct product does not contain the totally irreducible rep. then the transition is forbidden

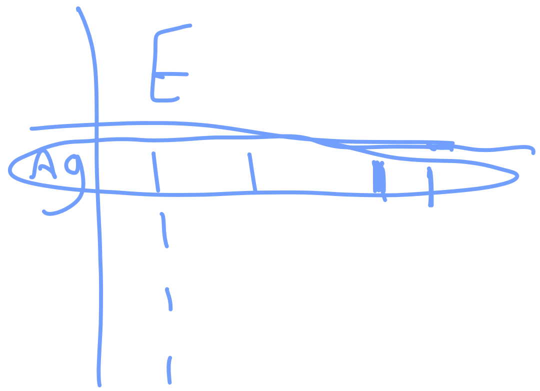
X

iR

$$\langle \psi_2 | x | \psi_1 \rangle^2$$

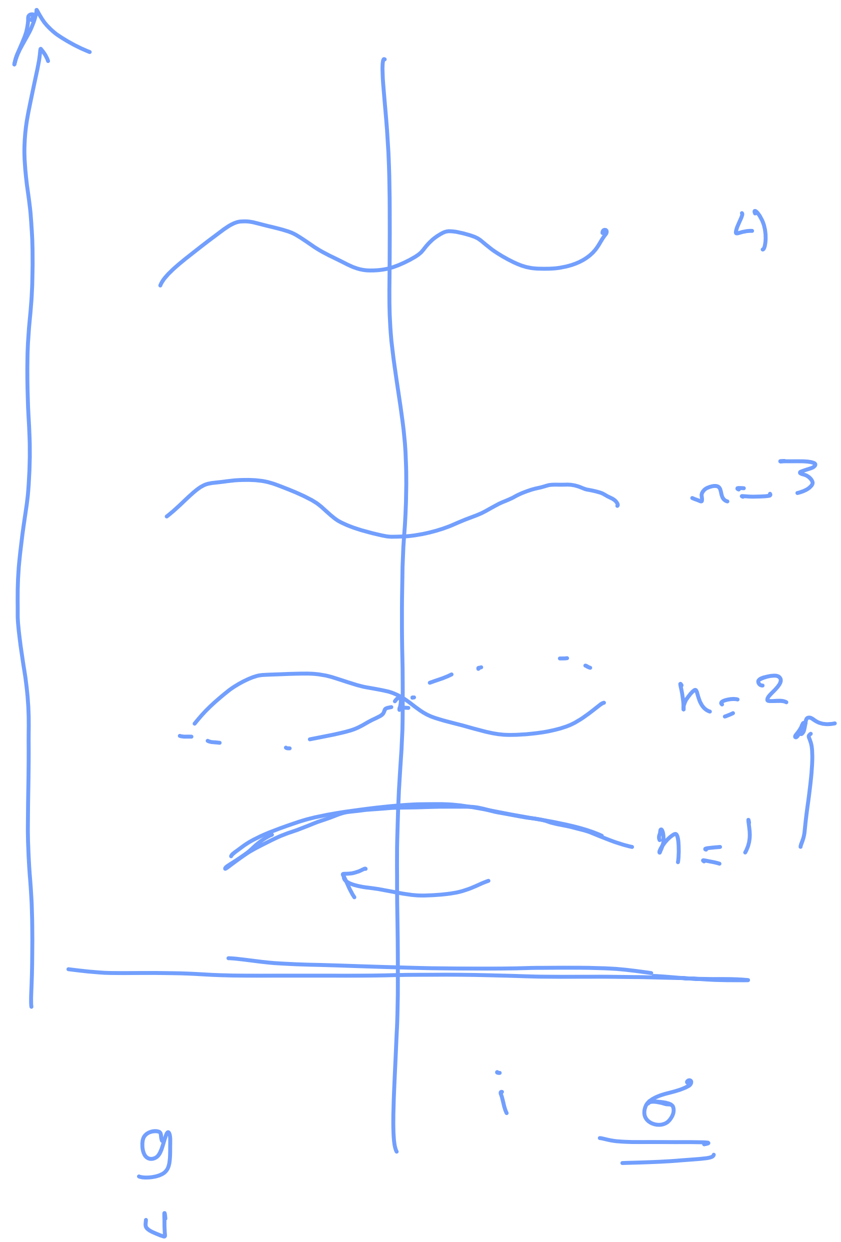
$$\langle A_u | A_u | A_g \rangle$$

$$\langle A_g \rangle^2 \neq 0$$



✓

	Ag	Au
Ag	g	
Au		



N تا مهره داریم

m تا ظرف

از ظرف iام n_i تا

$$\sum_{i=1}^{m} n_i = N$$

l تا می‌خوام انتخاب کنیم

$$0 \leq \quad <$$

$$\binom{l+1}{m+1} \qquad \binom{l+1}{m+1}$$