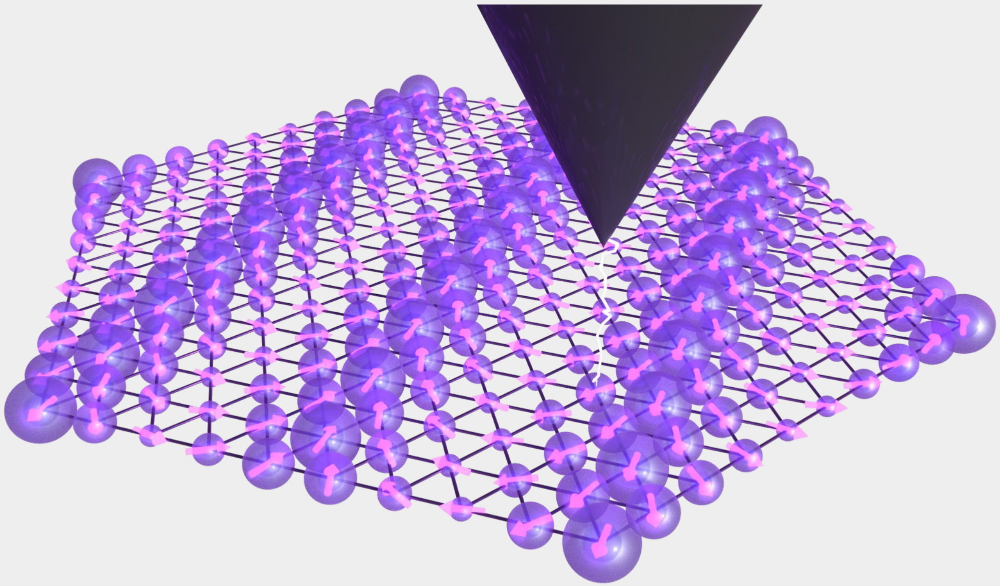
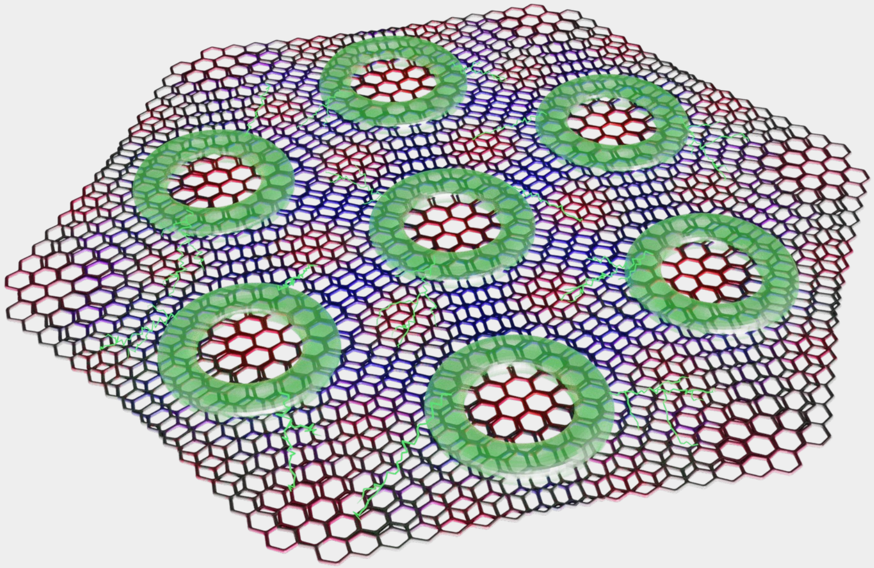
# Multiferroic van der Waals Materials





**Adolfo O Fumega**

Aalto University

ACADEMY OF FINLAND

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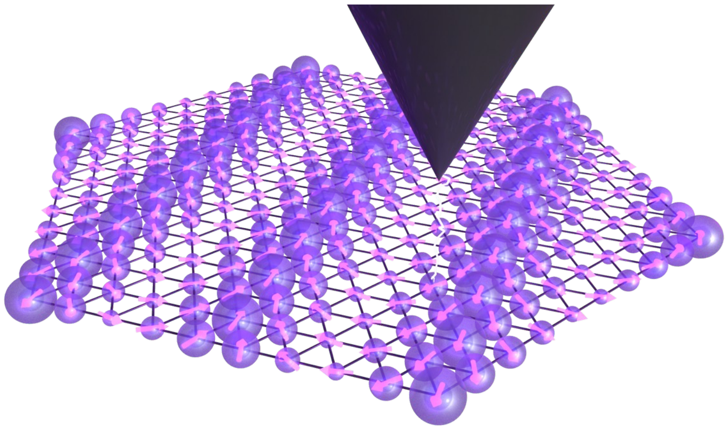
# Researchers

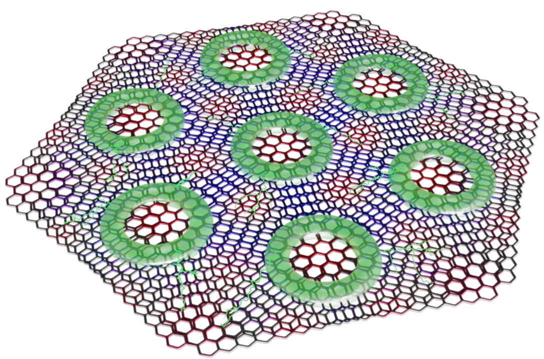
The first 2D Multiferroic



**Adolfo O. Fumega** and Jose L. Lado
2D Materials 9, 025010 (2022)

Mohammad Amini,* **Adolfo O Fumega**,*
Héctor González-Herrero,
Viliam Vaňo, Shawulienu Kezilebieke,
Jose L Lado+, Peter Liljeroth+
*Advanced Materials 2311342* (2024)

Artificial Moiré Multiferroics



**Adolfo O. Fumega** and Jose L. Lado
2D Materials 10, 025026 (2023)

# Researchers

**Adolfo O. Fumega** and Jose L. Lado
2D Materials 9, 025010 (2022)

Mohammad Amini,* **Adolfo O Fumega**,* Héctor González-Herrero, Viliam Vaňo, Shawulienu Kezilebieke, Jose L Lado⁺, Peter Liljeroth⁺
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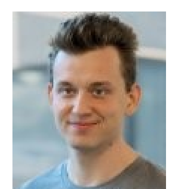
**Princeton University**



Viliam Vaňo

**Autonomous University of Madrid**

Héctor González Herrero

**University of Jyväskylä**

Shawulienu Kezilebieke

# Motivation

<u>Multiferroics</u>

↓

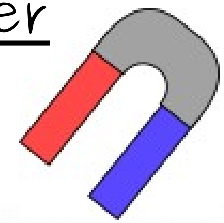
Materials with
**more than one**
**Ferroic** order

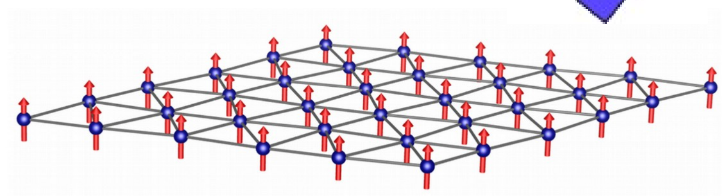
# Motivation

## Multiferroics

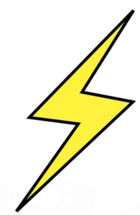
Materials with more than one Ferroic order

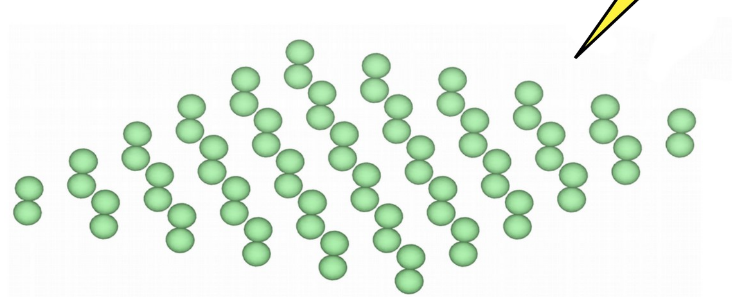
Magnetic order





Electric order



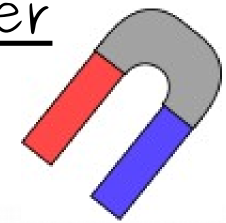


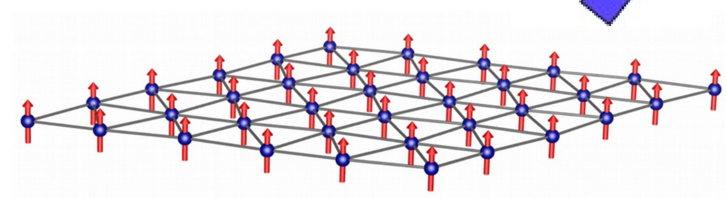
# Motivation

## Multiferroics

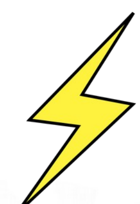
Materials with more than one Ferroic order

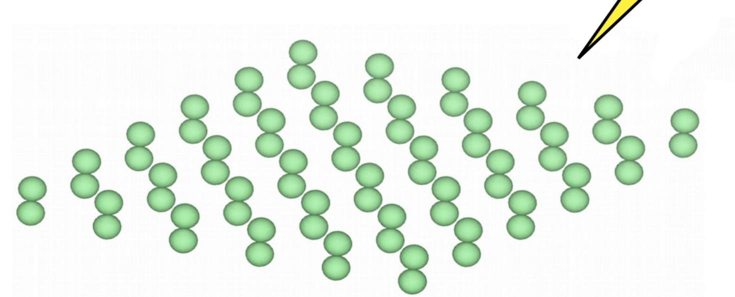
Magnetic order





Electric order

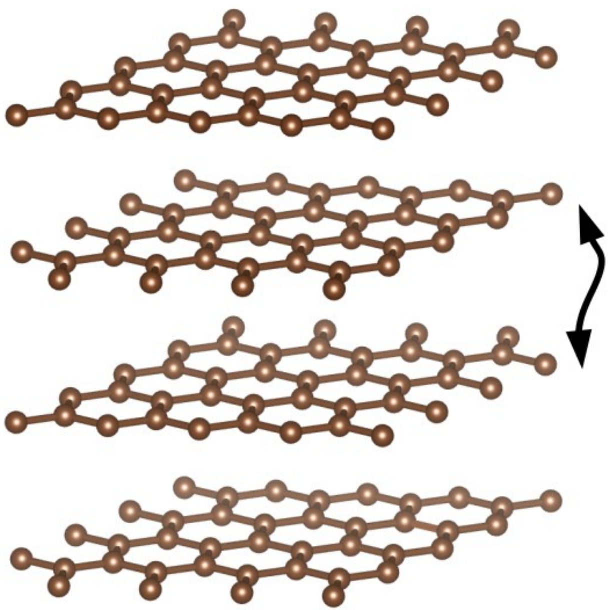




Magnetoelectric Coupling

# Motivation

## Layered van der Waals

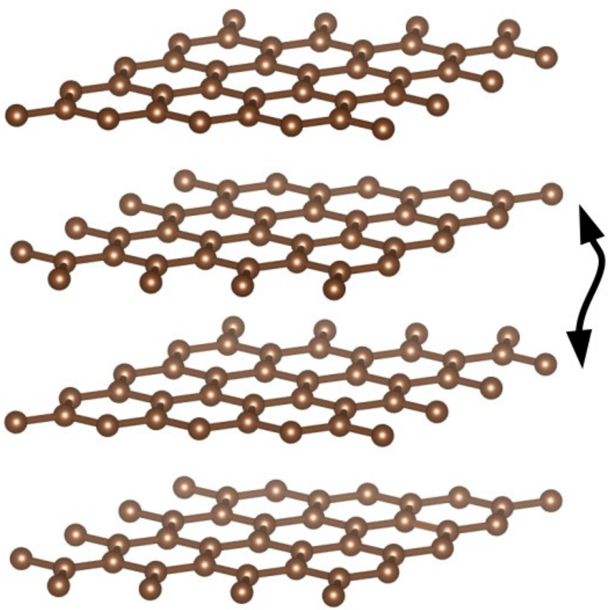


Graphite

Weak
van der Waals
bonding

# Motivation

Layered van der Waals



Graphite

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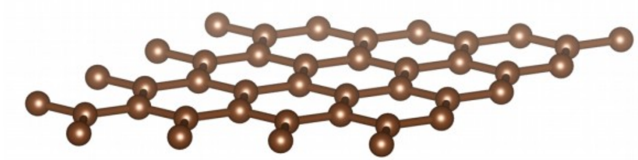

Graphene

Reach the
2D limit !!!

# Motivation

## Layered van der Waals

Monolayer

| Semimetal | Insulator | Superconductor | Ferromagnet | Ferroelectric | Multiferroic | ... |
| --- | --- | --- | --- | --- | --- | --- |
| Graphene | BN | $NbSe_2$ | $CrI_3$ | $MoTe_2$ | $NiI_2$ | |

# Motivation

Layered van der Waals

Monolayer

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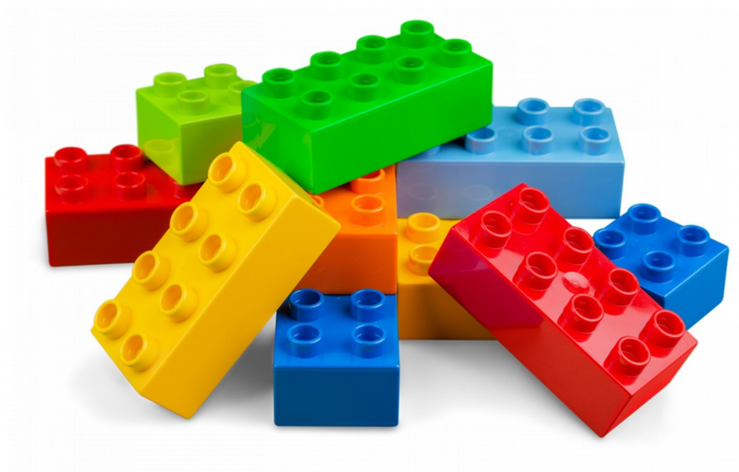
| Graphene | BN | $NbSe_2$ | $CrI_3$ | $MoTe_2$ | $NiI_2$ | |

2D building blocks



# Motivation

**Layered van der Waals**

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|---|---|---|---|---|---|---|
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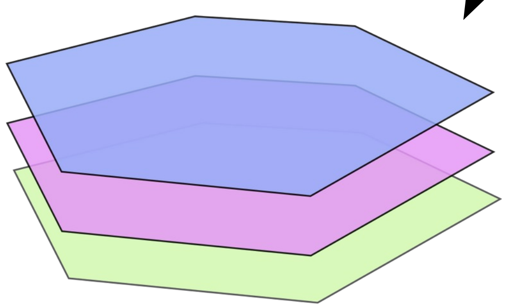
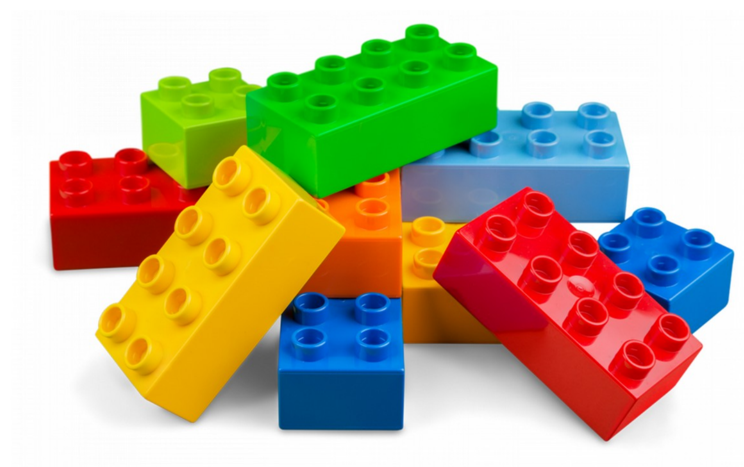
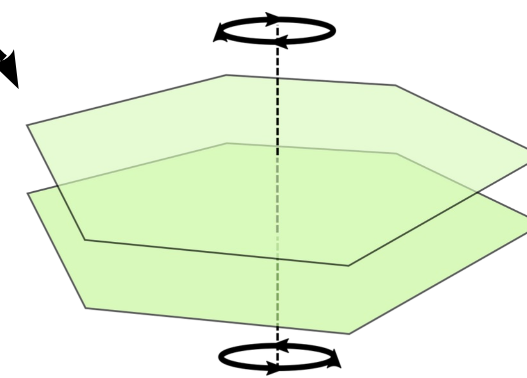
**2D building blocks**



Heterostructures





Twisted layers

# Motivation

## Layered van der Waals

Monolayer

| Semimetal | Insulator | Superconductor | Ferromagnet | Ferroelectric | Multiferroic | ... |
|---|---|---|---|---|---|---|
| Graphene | BN | $NbSe_2$ | $CrI_3$ | $MoTe_2$ | $NiI_2$ | |

The first 2D Multiferroic

Evidence for a single-layer van der Waals multiferroic
Song et al., Nature **602, 601-605 (2022)**

# Motivation

## Layered van der Waals

Monolayer

| Semimetal | Insulator | Superconductor | Ferromagnet | Ferroelectric | Multiferroic | ... |
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### The first 2D Multiferroic

Evidence for a single-layer van der Waals multiferroic
Song et al., Nature 602, 601-605 (2022)

→ Experimental evidence
Optical techniques

!

# Motivation

## Layered van der Waals

Monolayer

| Semimetal | Insulator | Superconductor | Ferromagnet | Ferroelectric | Multiferroic | ... |
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The first 2D Multiferroic

Evidence for a single-layer van der Waals multiferroic
Song et al., Nature **602, 601-605 (2022)**

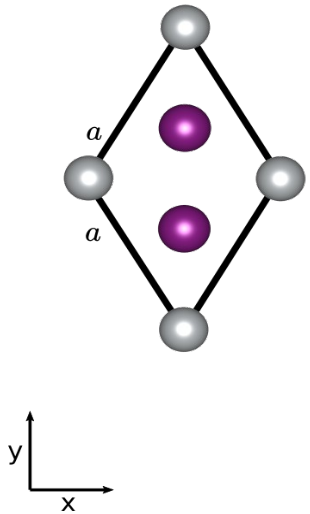
→ Experimental evidence
Optical techniques !

Origin of the multiferroic order in monolayer NiI2!

New methods to prove and characterize 2D multiferroics!

# Multiferroicity in $NiI_2$

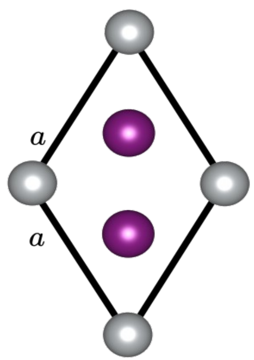
$NiI_2$



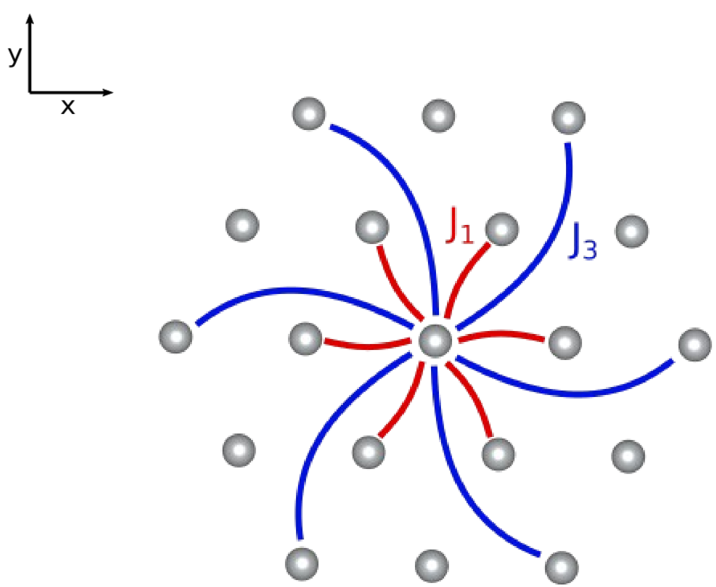

$Ni^{2+} \rightarrow S=1$

# Multiferroicity in $NiI_2$

$NiI_2$




$Ni^{2+}$ → S=1

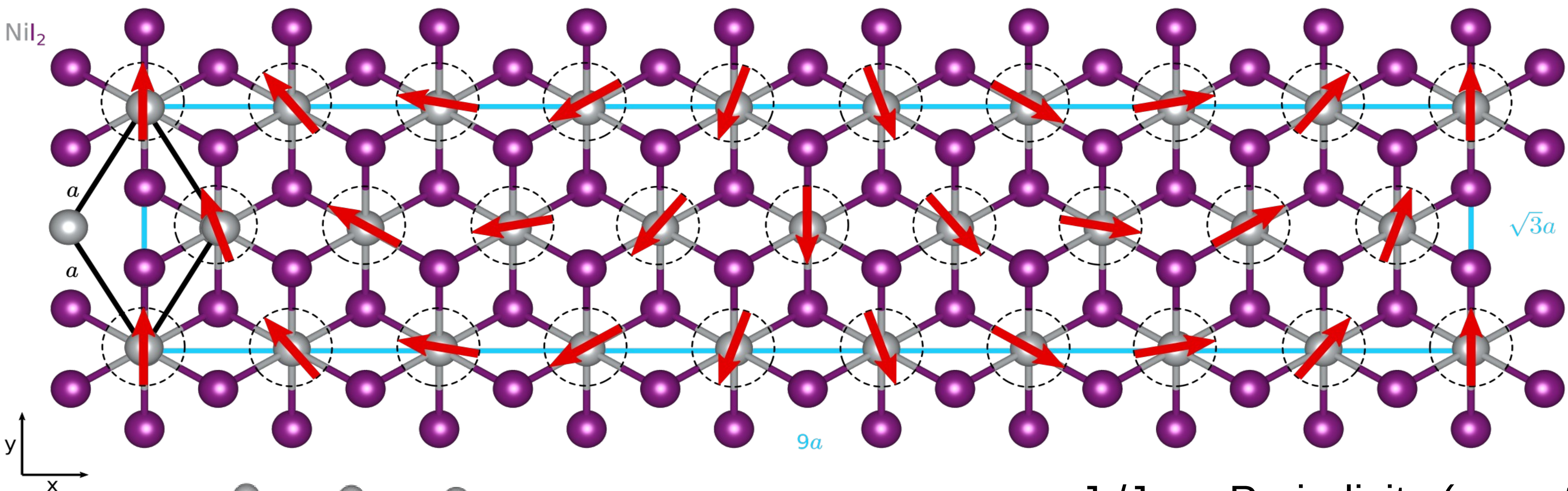


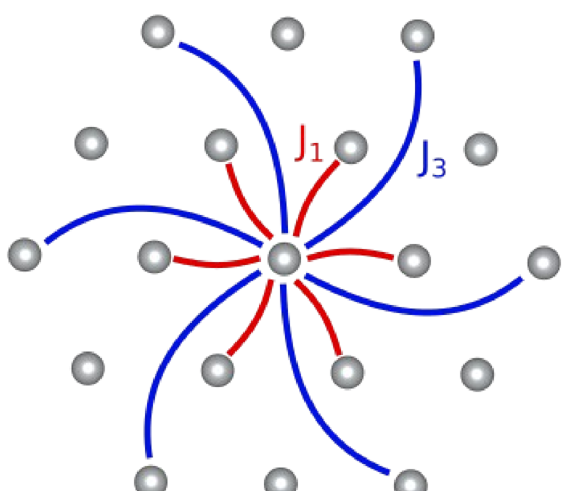

$J_1$ → Ferromagnetic exchange

Competing

$J_3$ → Antiferromagnetic exchange

# Multiferroicity in $NiI_2$



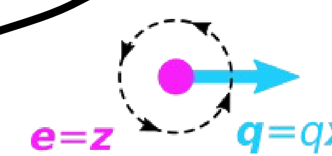

$J_3/J_1$ → Periodicity (**q**-vector)

$J_1$ → Ferromagnetic exchange

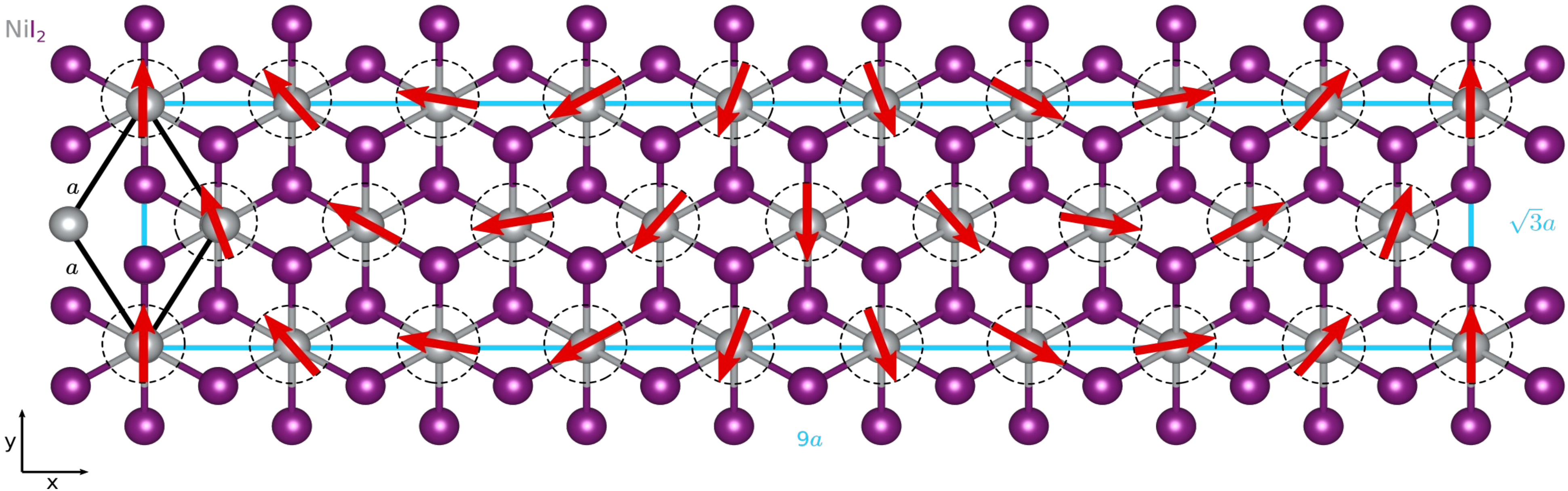
Competing

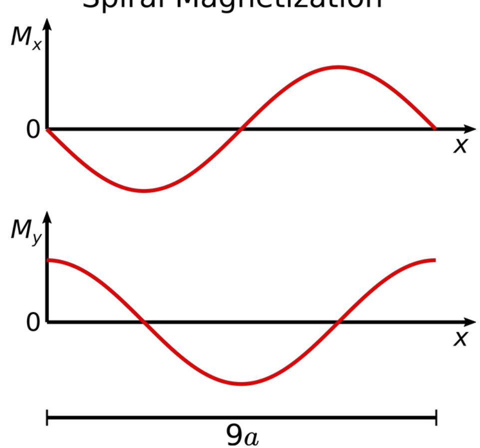
Spin Spiral

$J_3$ → Antiferromagnetic exchange



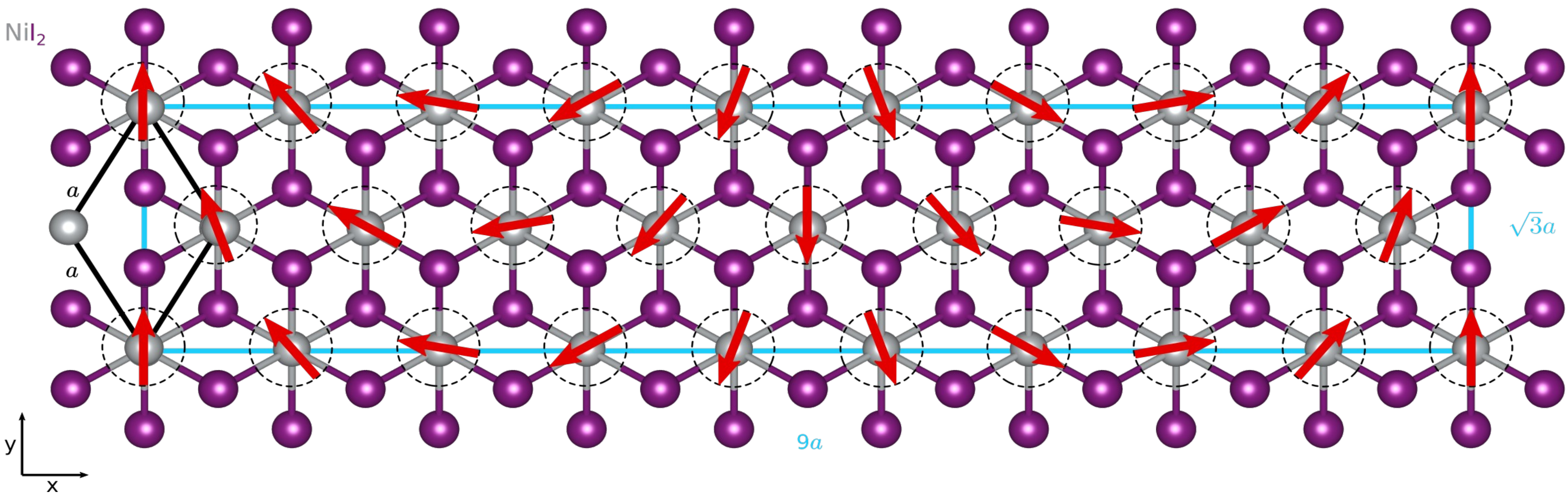
# Multiferroicity in $NiI_2$

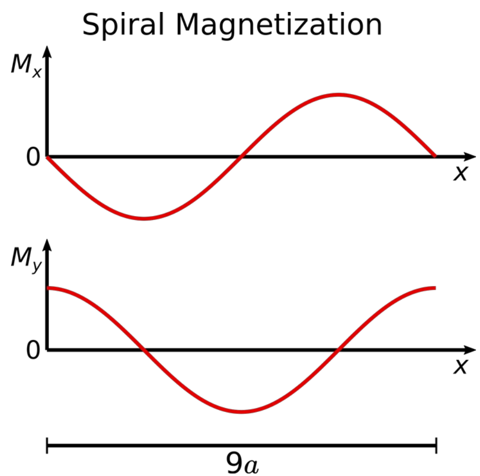



$$\mathbf{M} = \mathrm{M}(-\sin(\mathbf{qr}), \cos(\mathbf{qr}), 0)$$

# Multiferroicity in $NiI_2$




$$\mathbf{M} = \mathrm{M}(-\sin(\mathbf{qr}), \cos(\mathbf{qr}), 0)$$

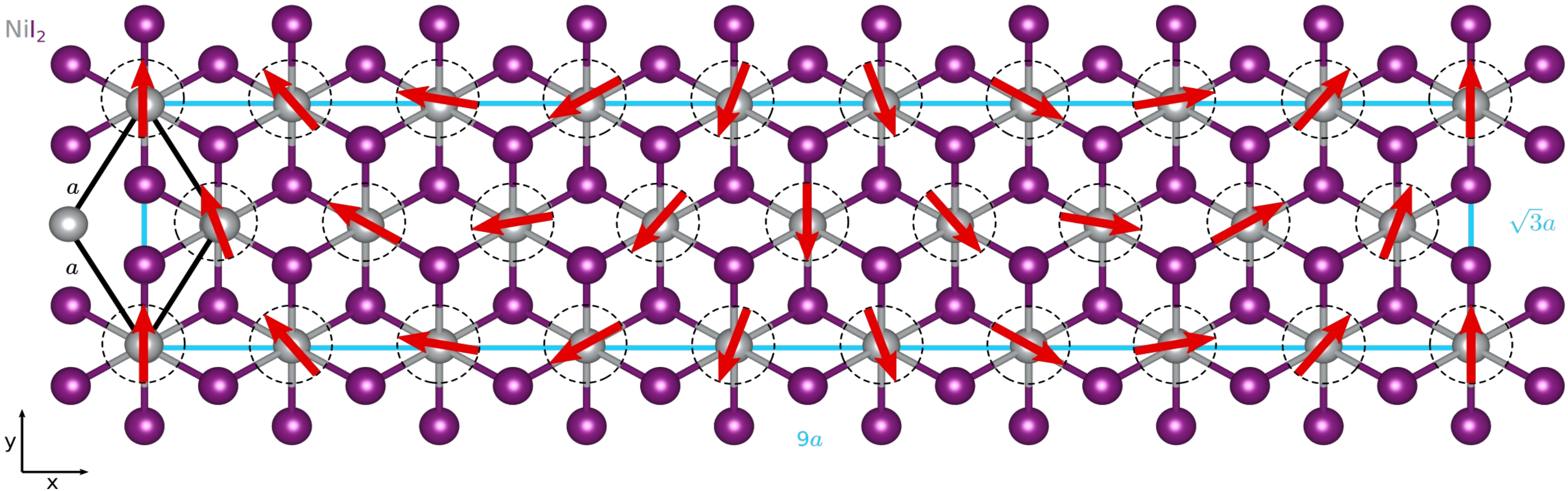
$$\mathbf{P} = \Lambda \frac{\mathbf{M} \times (\nabla \times \mathbf{M})}{\mathrm{M}^2}$$

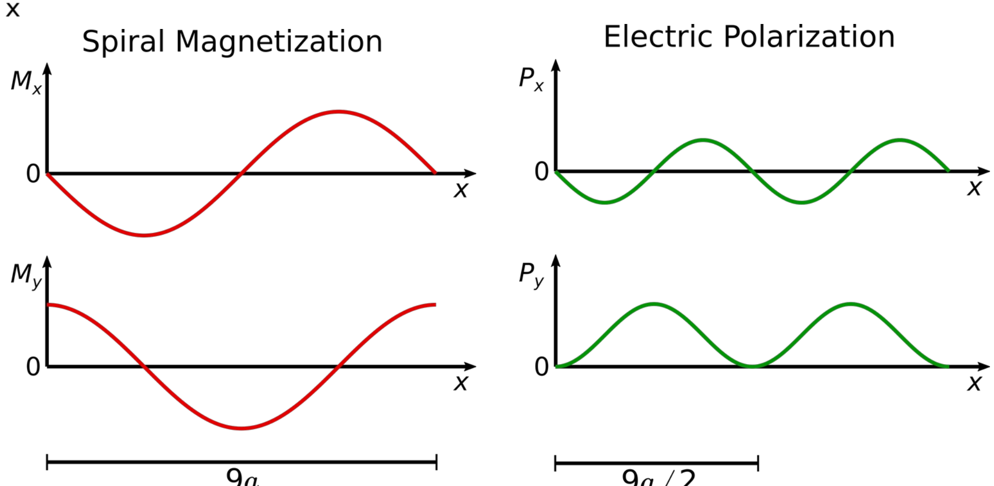
Spin-orbit coupling from I atoms

Mostovoy, Phys. Rev. Lett. 96, 067601 (2006)

AOF and Jose Lado, 2D Materials 9 (2), 025010 (2022)

# Multiferroicity in $NiI_2$



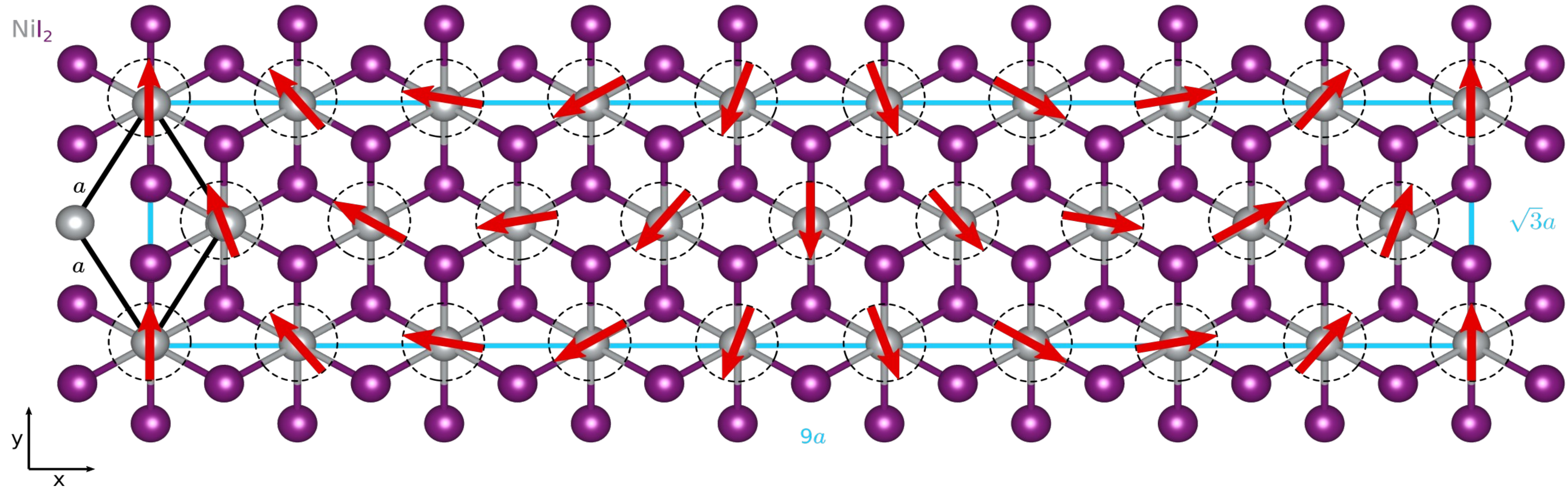



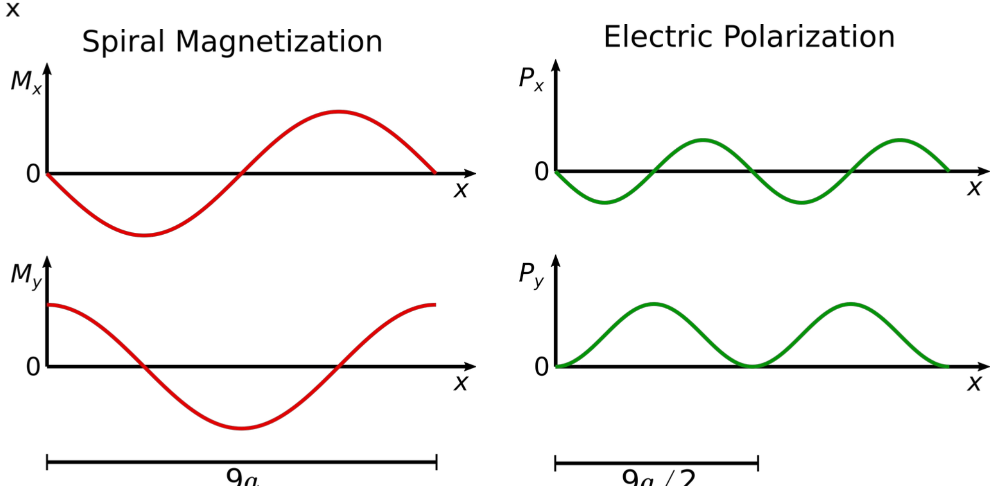

$$\mathbf{M} = \mathrm{M}(-\sin(\mathbf{qr}), \cos(\mathbf{qr}), 0)$$

Half the periodicity

$$\mathbf{P} = \Lambda \mathrm{q}(-\sin(2\mathbf{q}\cdot\mathbf{r})/2, \sin^2(\mathbf{q}\cdot\mathbf{r}), 0)$$

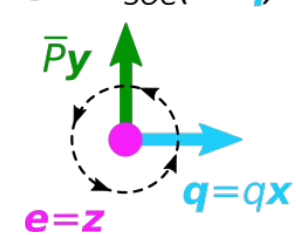
# Multiferroicity in $NiI_2$



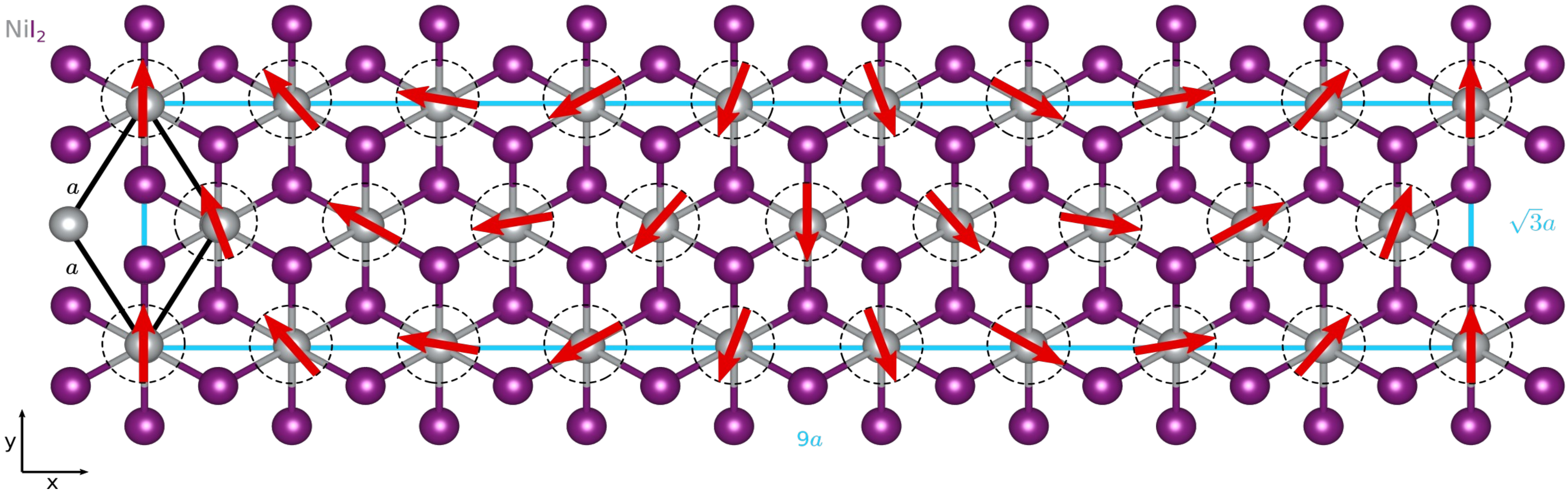

Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006)

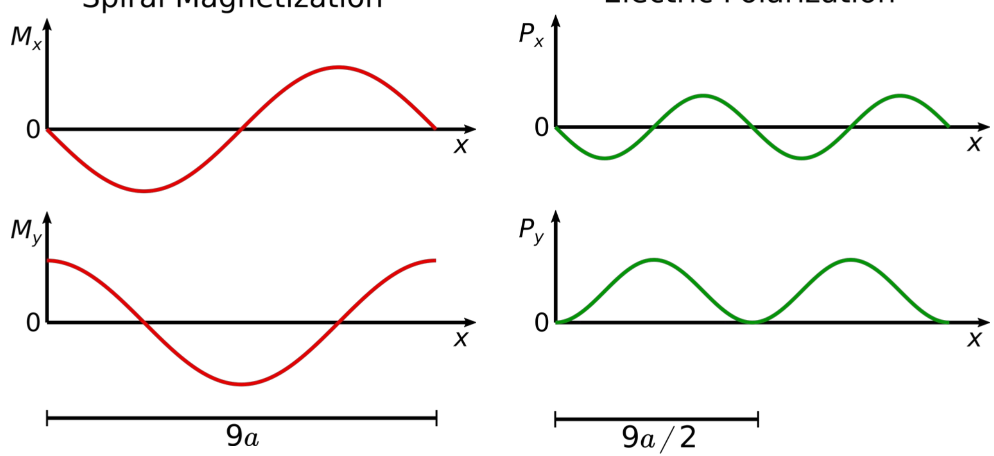
$\bar{\mathbf{P}} \propto \lambda_{SOC}(\mathbf{e} \times \mathbf{q})$




$$\mathbf{P} = \Lambda q(-\sin(2\mathbf{q}\cdot\mathbf{r})/2, \sin^2(\mathbf{q}\cdot\mathbf{r}), 0)$$

# Multiferroicity in $NiI_2$

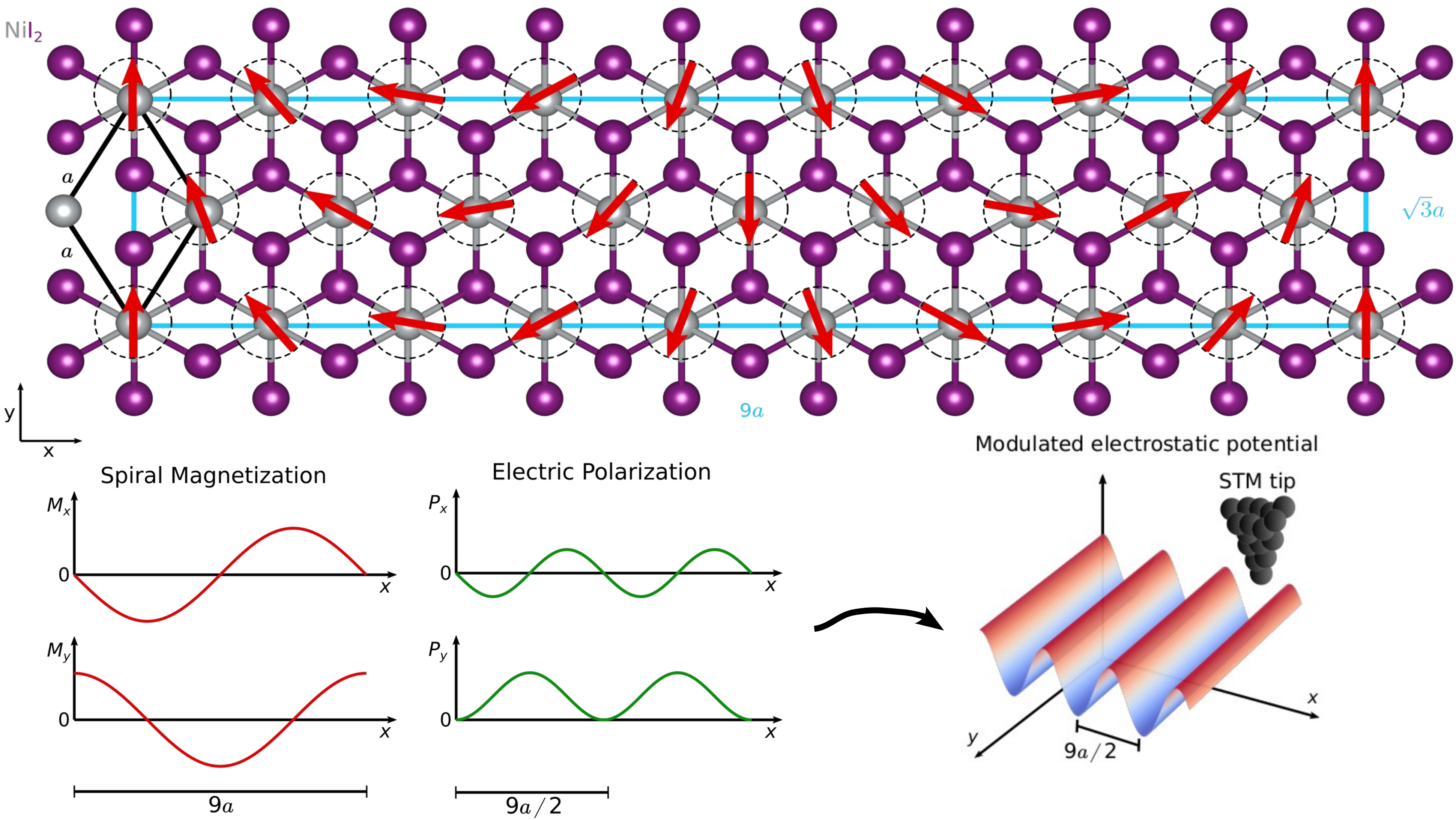


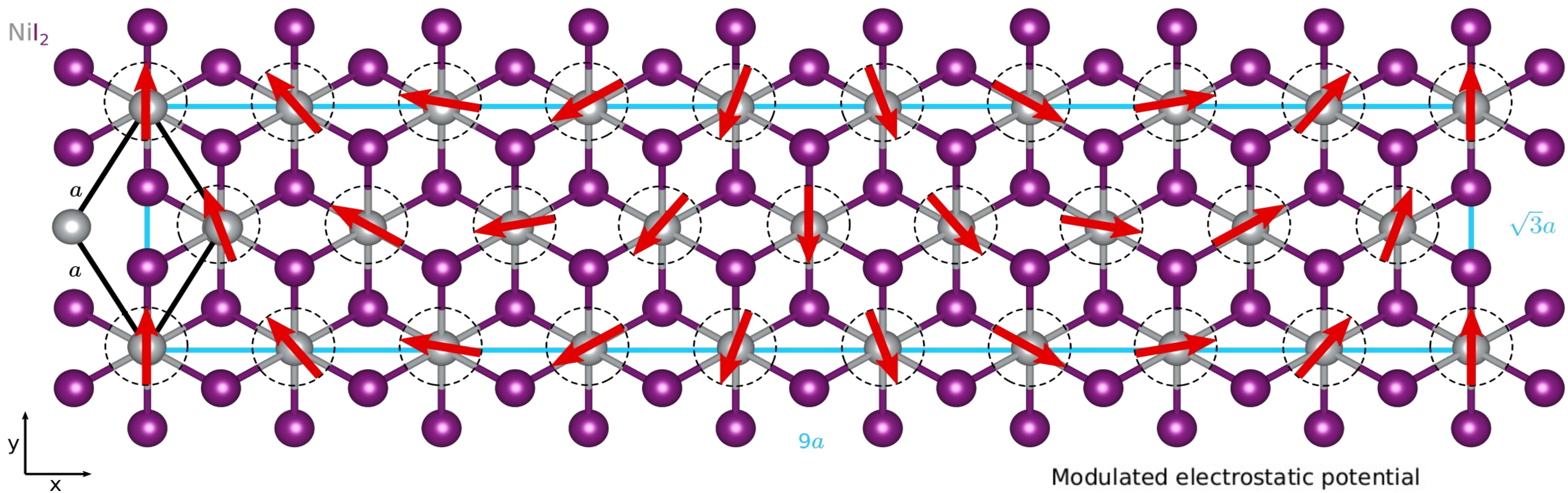

But at the atomic scale...

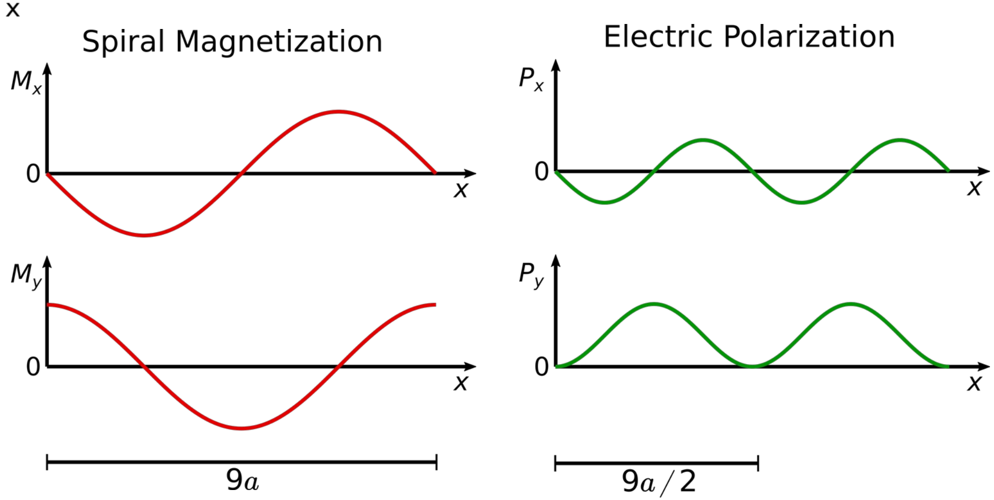
$$\mathbf{P} = \Lambda q(-\sin(2\mathbf{q}\cdot\mathbf{r})/2, \sin^2(\mathbf{q}\cdot\mathbf{r}), 0)$$

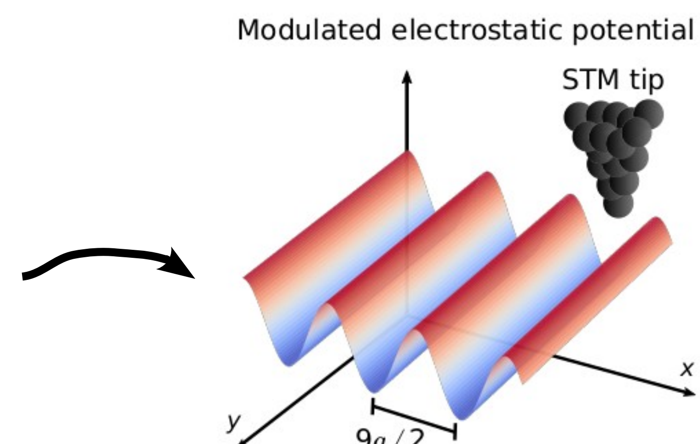
# Multiferroicity in $NiI_2$



# Multiferroicity in $NiI_2$

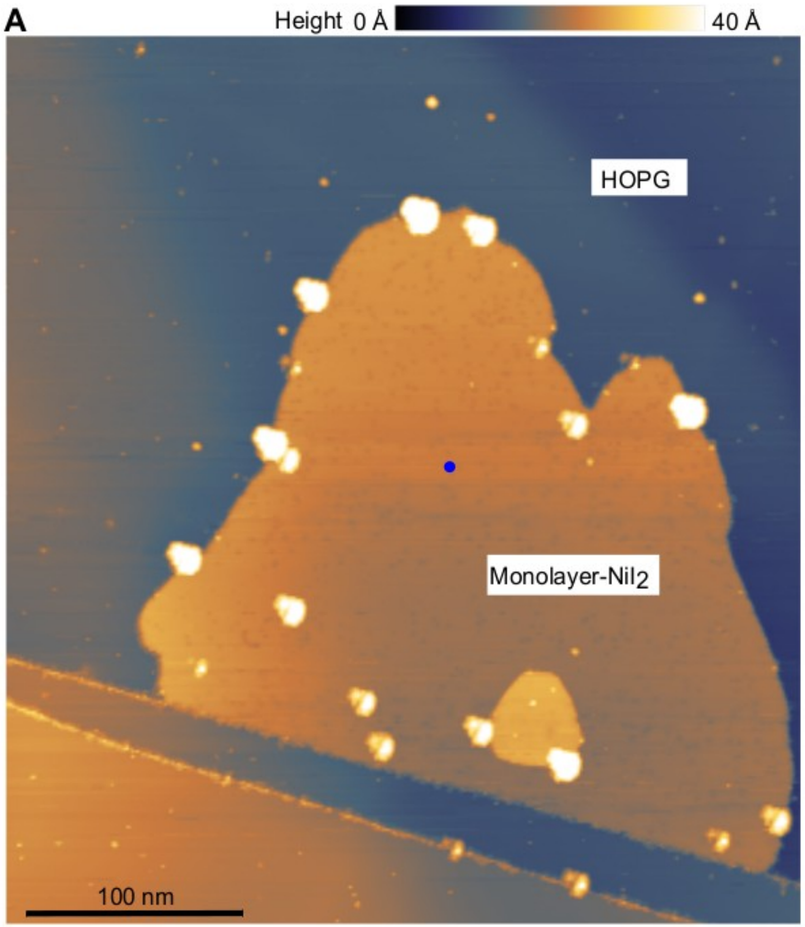


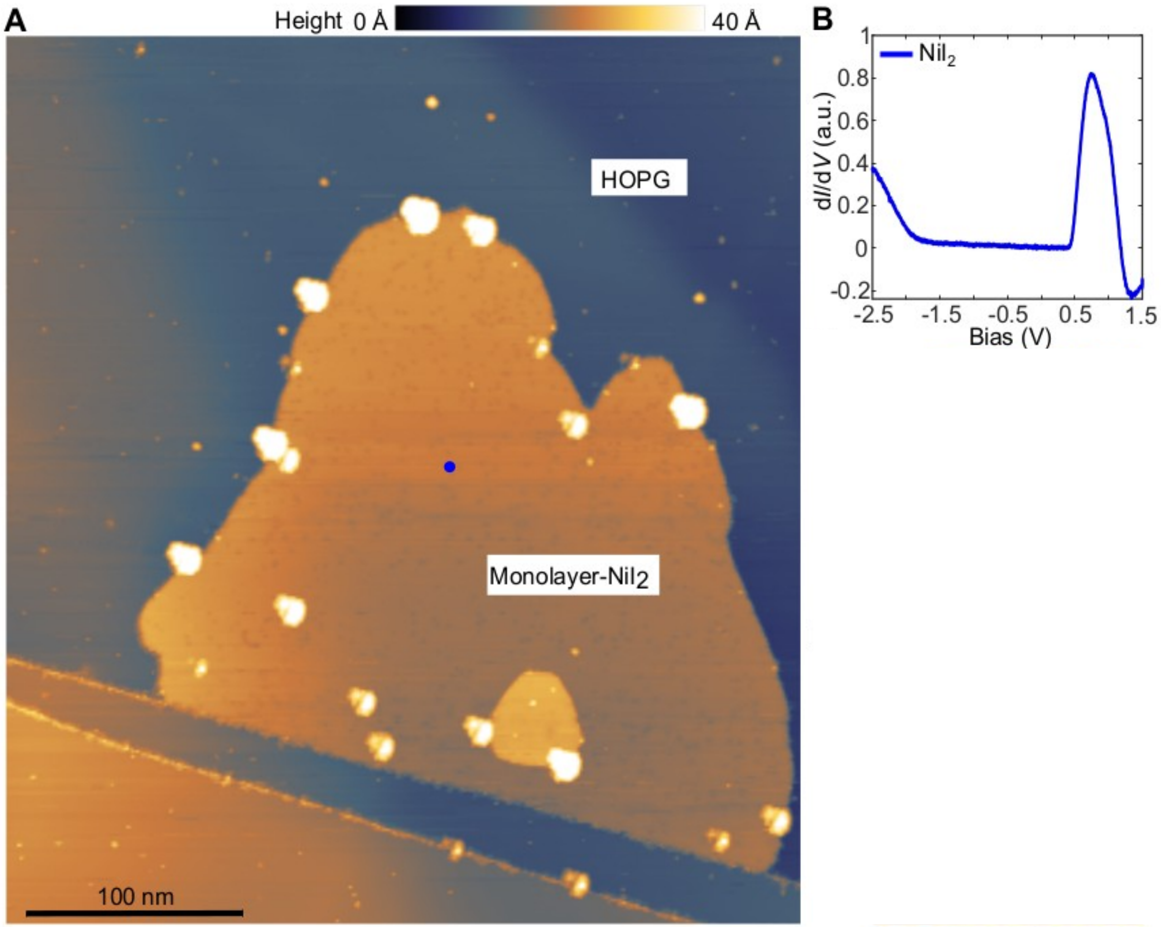

No need of spin-polarized techniques!

# STM characterization of monolayer $NiI_2$



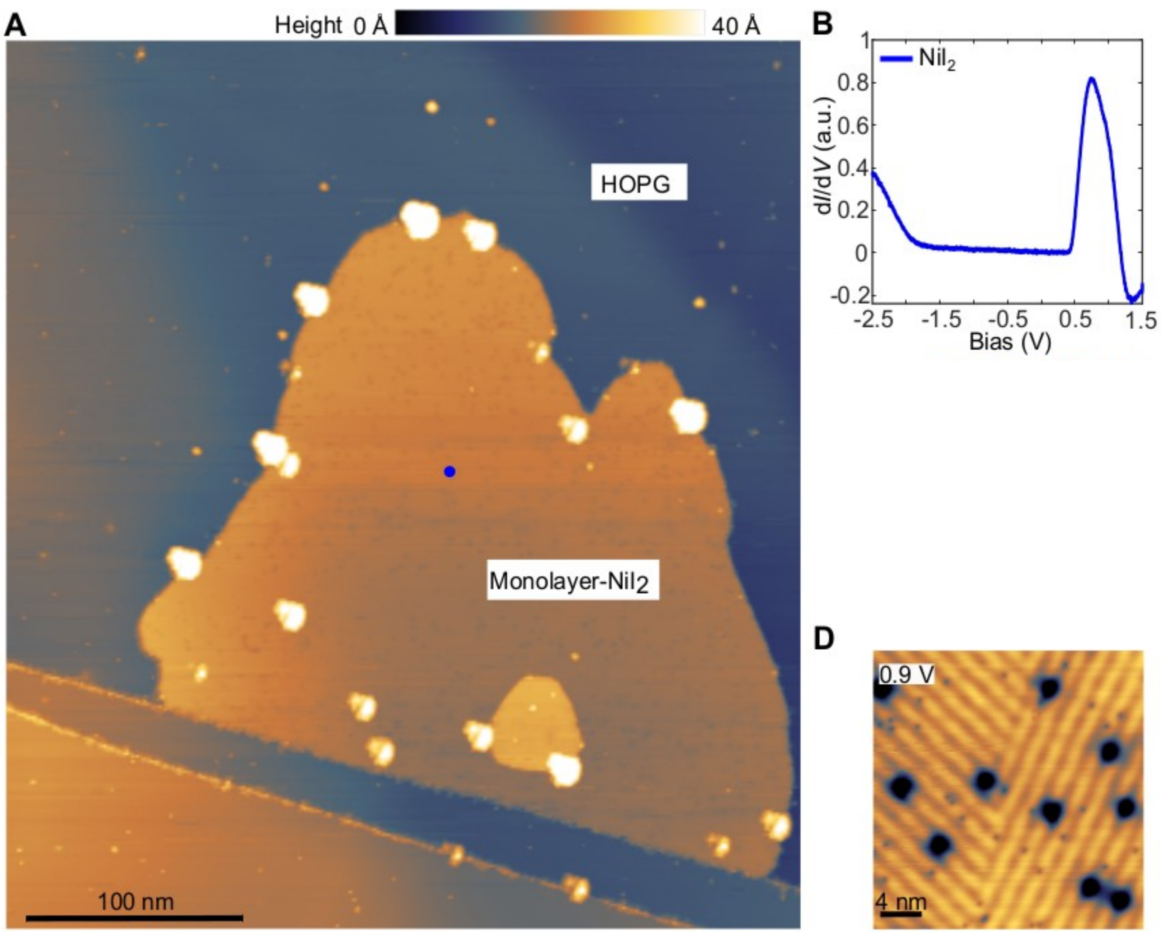

Monolayer $NiI_2$ on top of Highly-oriented pyrolytic Graphite (HOPG)

# STM characterization of monolayer $NiI_2$




Monolayer $NiI_2$ is an insulator with a gap of 2.3 eV (from -1.9 to 0.4 V)

# STM characterization of monolayer $NiI_2$




Monolayer $NiI_2$ is an insulator with a gap of 2.3 eV (from -1.9 to 0.4 V)

Scan within the conduction band of $NiI_2$

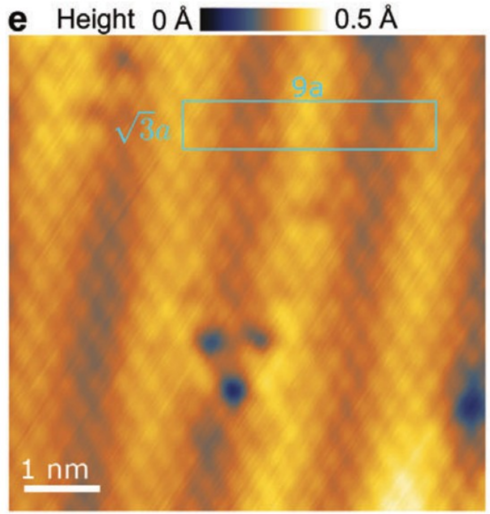
→

Stripy modulation

Demonstration of multiferroicity!

# STM characterization of monolayer $NiI_2$

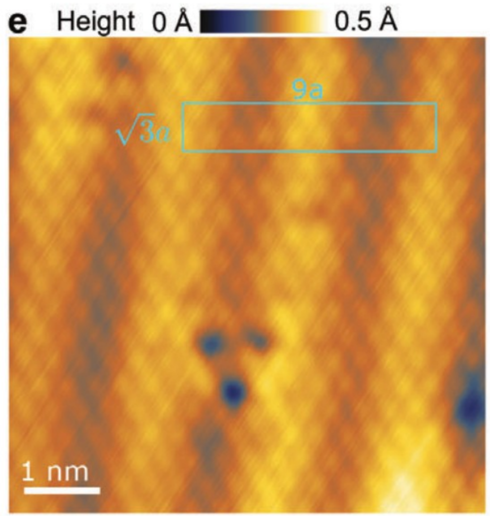
**Experiment**




Atomic resolution STM scan

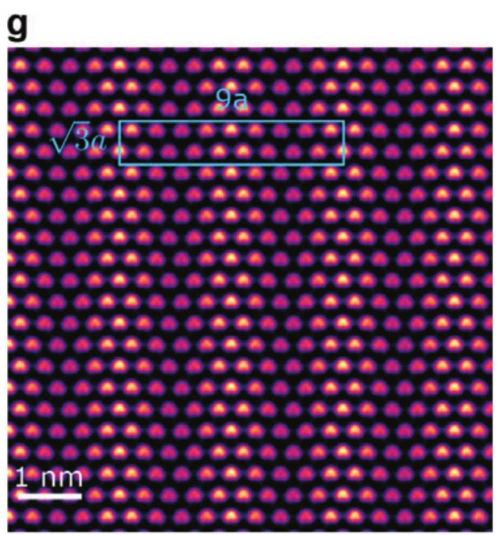
# STM characterization of monolayer $NiI_2$

Experiment

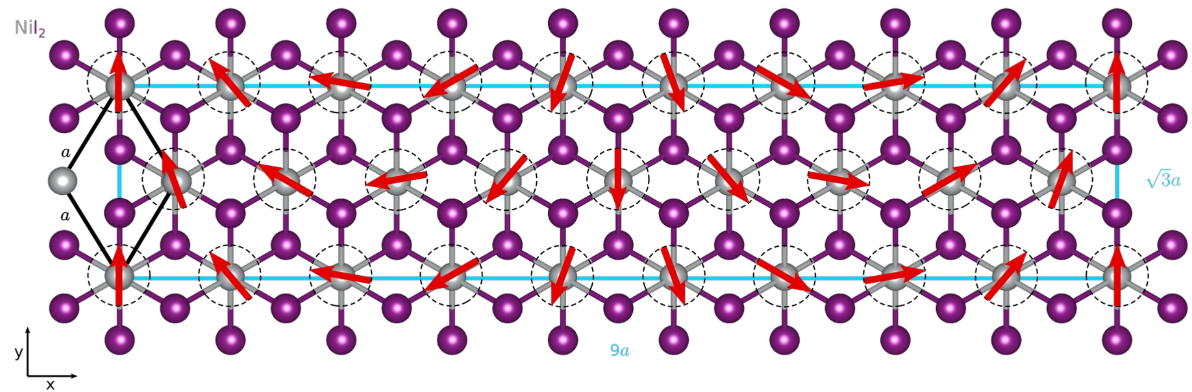



Atomic resolution STM scan

Theory



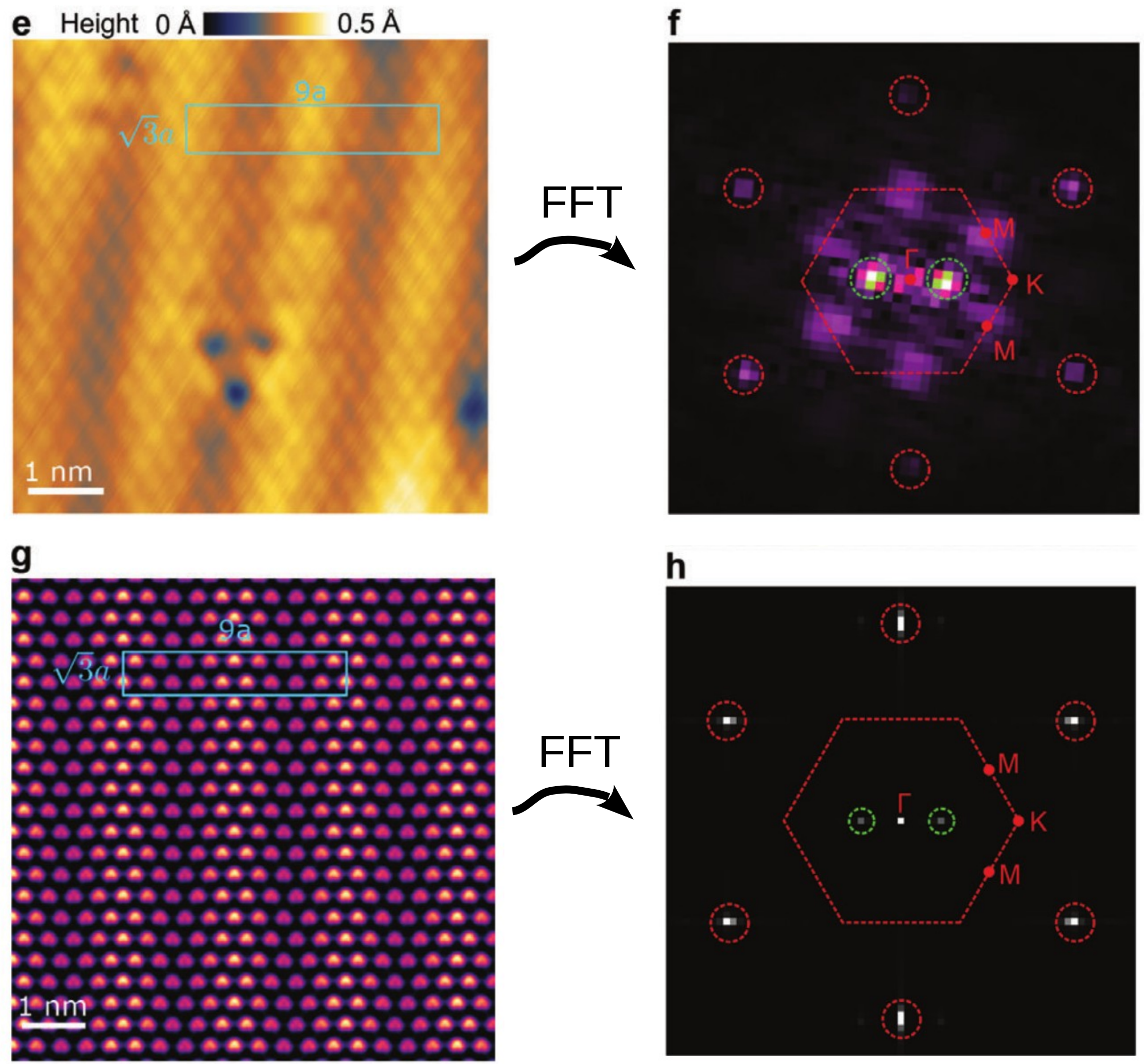

Commensurate supercell $9a \times \sqrt{3}a$



# STM characterization of monolayer $NiI_2$

Experiment

Theory

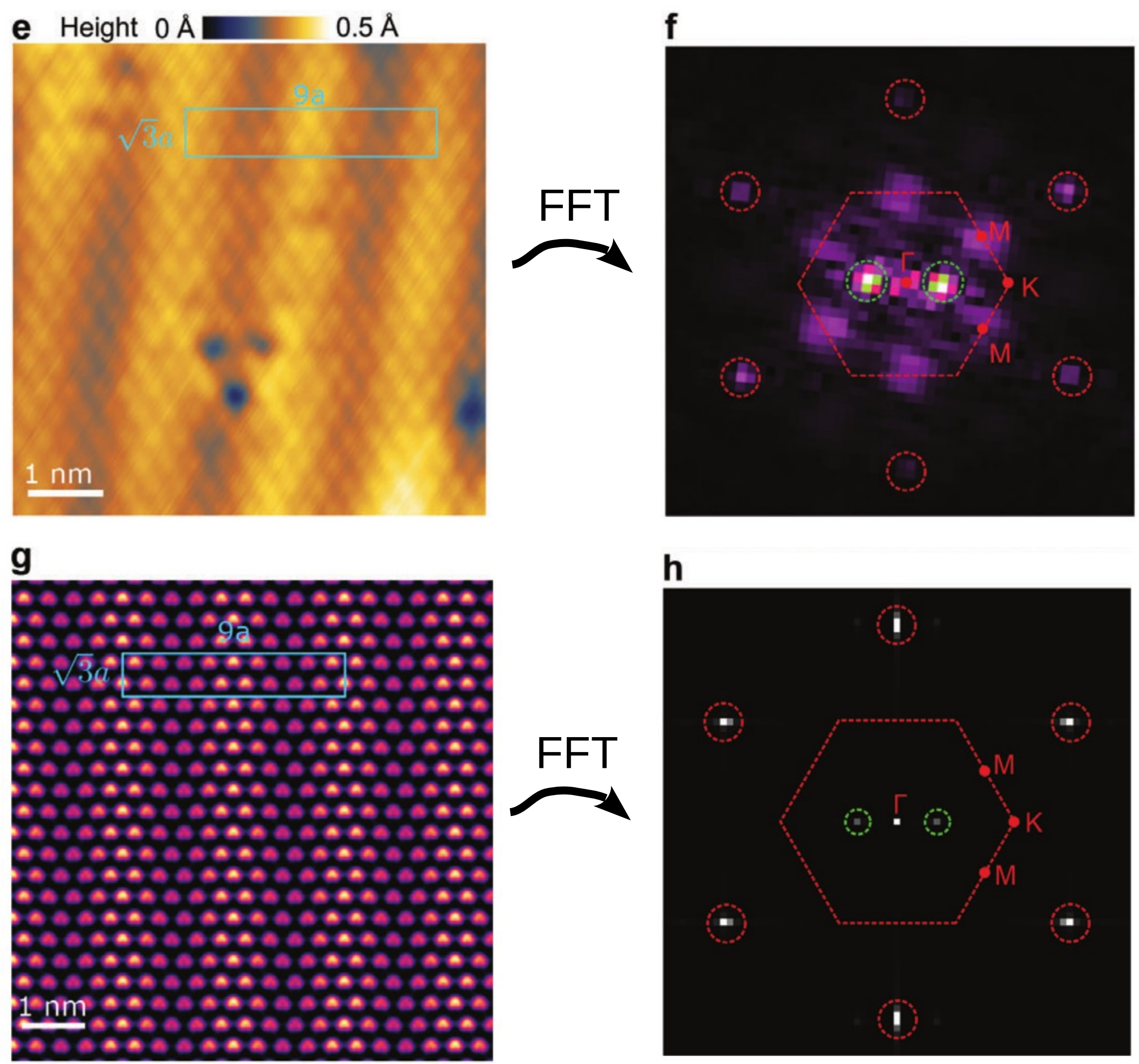



Red peaks → Atomic lattice

# STM characterization of monolayer $NiI_2$

Experiment

Theory




Red peaks → Atomic lattice

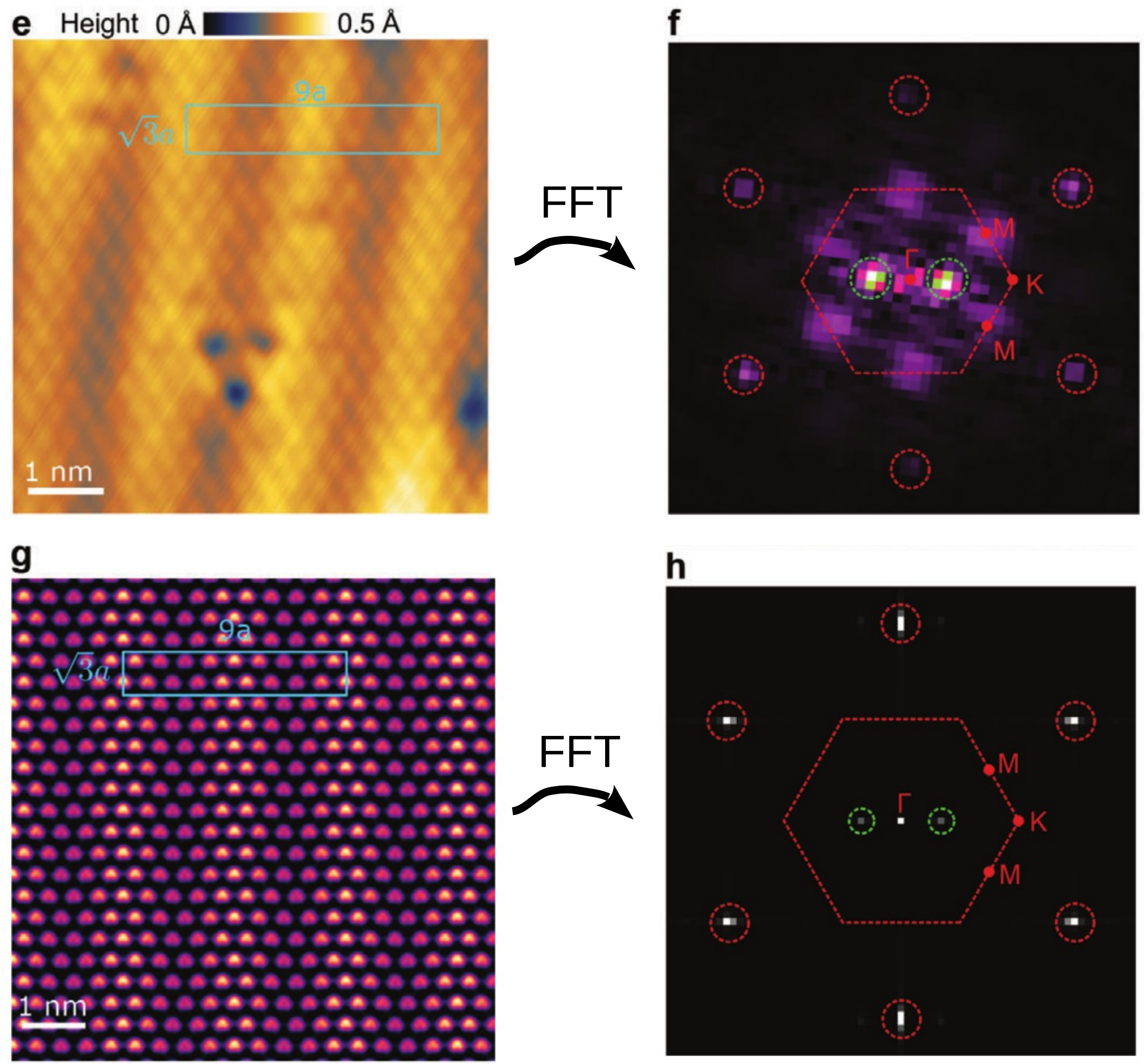
Green peaks → Half of the spin spiral periodicity

$$\mathbf{q} = (0.057, 0.057, 0)$$

# STM characterization of monolayer $NiI_2$

Experiment

Theory




Red peaks → Atomic lattice

Green peaks → Half of the spin spiral periodicity

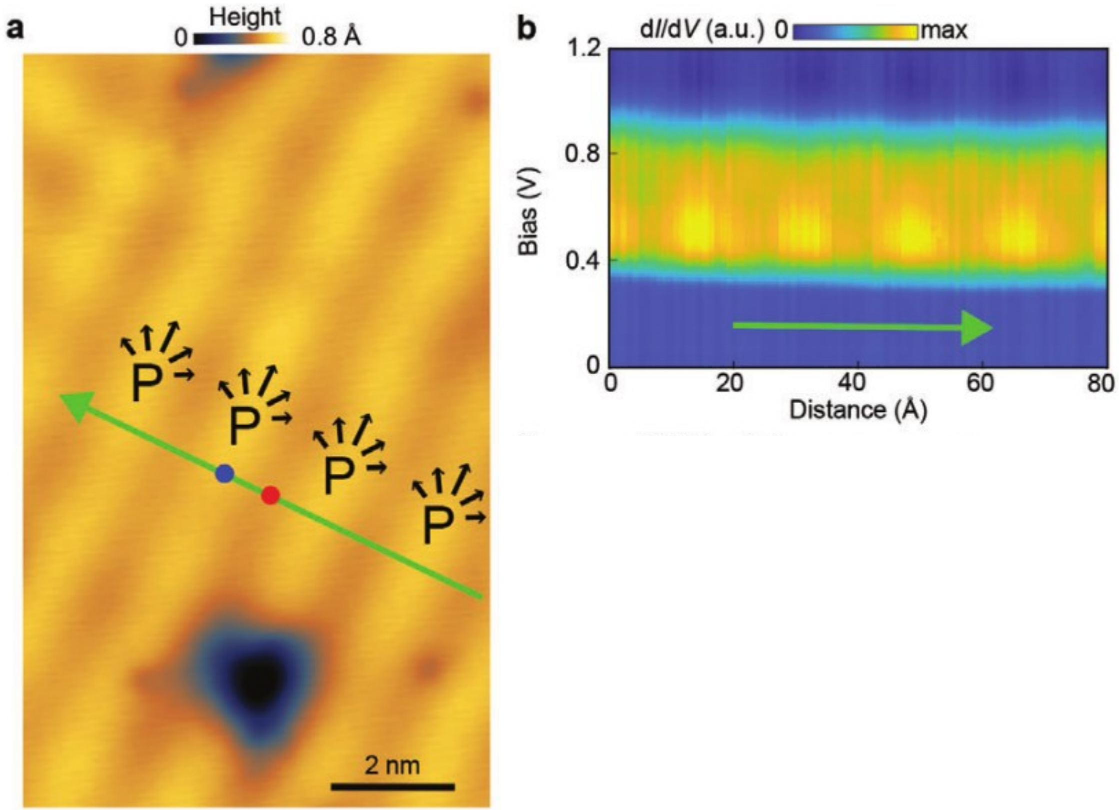
$$\mathbf{q} = (0.057, 0.057, 0)$$

$$J_3/J_1 = -0.263$$

Characterization of the spin spiral magnetic order!

# STM characterization of monolayer $NiI_2$

Inhomogeneous Polarization → Band bending of the conduction band

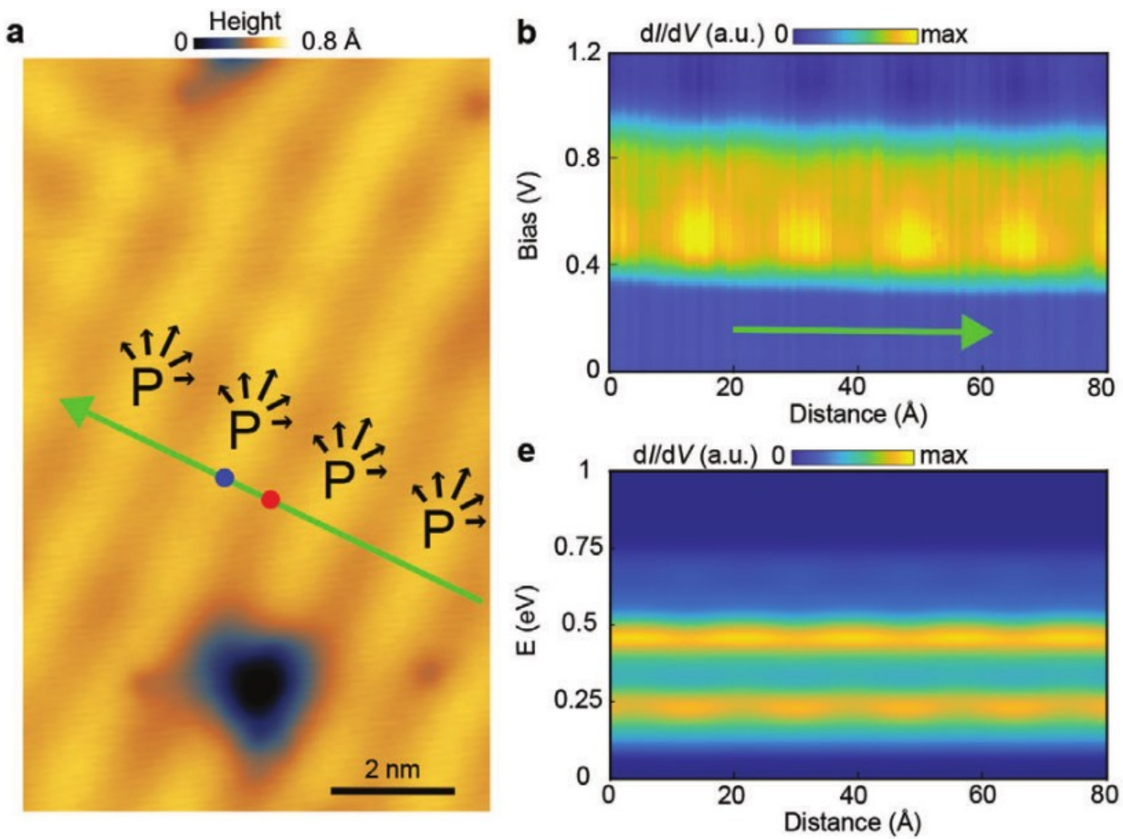



## Experiment

Line spectra showing the conduction band

# STM characterization of monolayer $NiI_2$

Inhomogeneous Polarization → Band bending of the conduction band

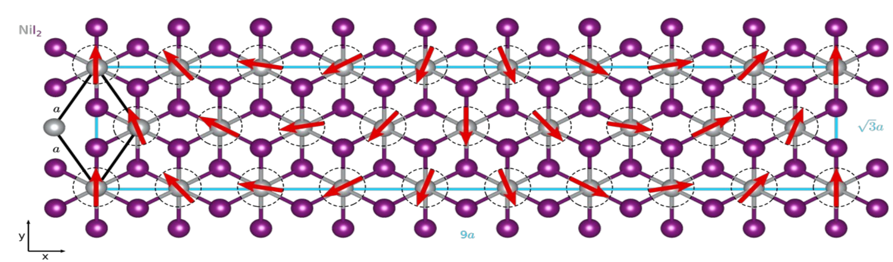



## Experiment

Line spectra showing the conduction band

## Theory

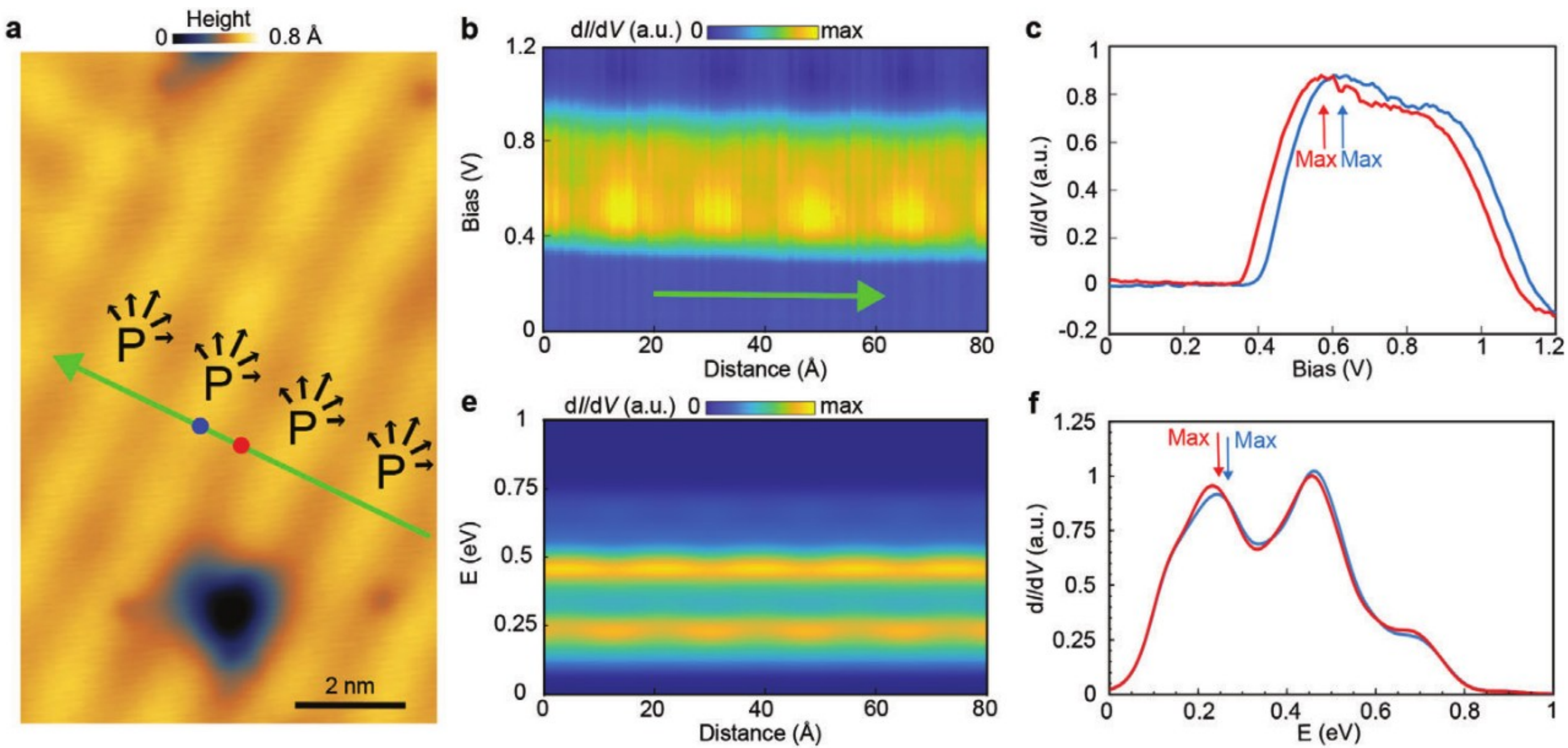
Commensurate supercell $9a \times \sqrt{3a}$




Underestimation of the band gap in DFT,
but the ferroelectric modulation is well captured!

# STM characterization of monolayer $NiI_2$

Inhomogeneous Polarization → Band bending of the conduction band



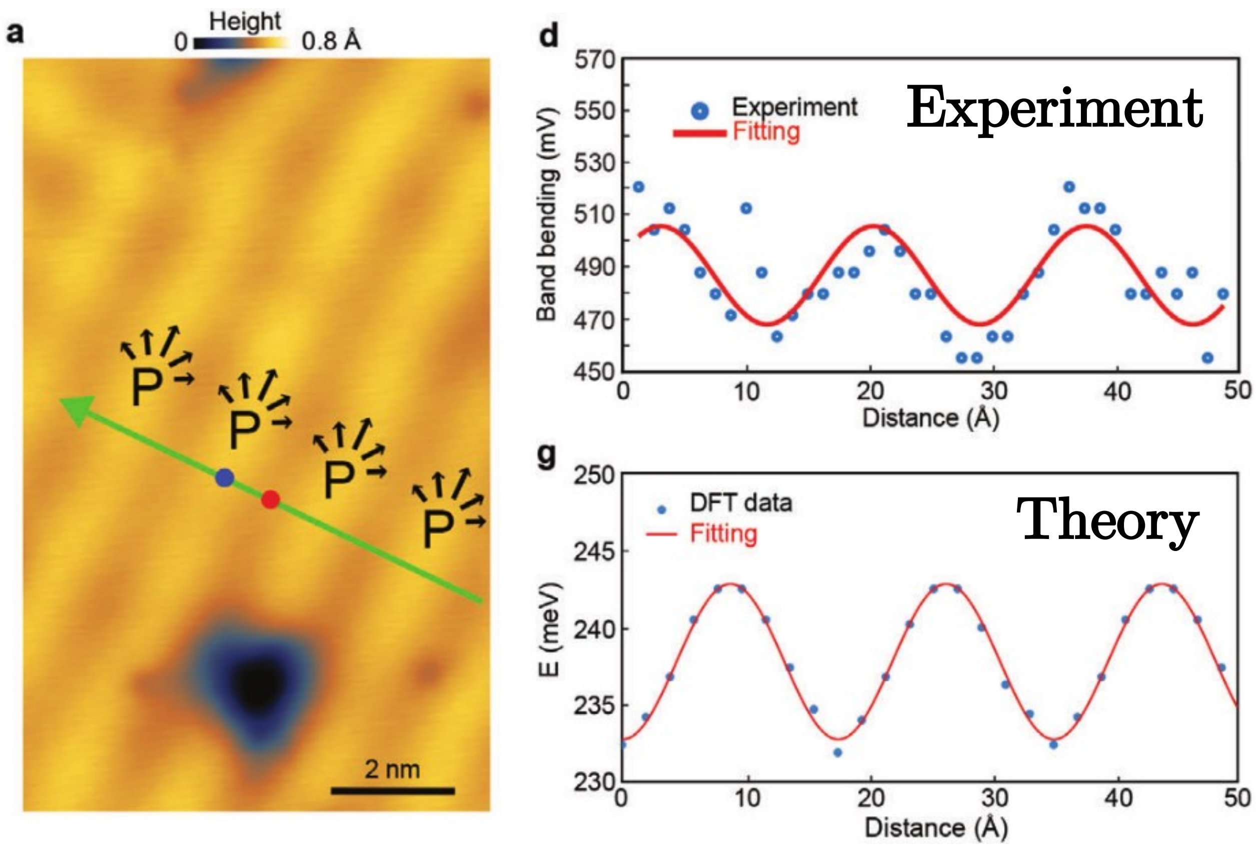

Experiment

Theory

→ Shift in energy of the conduction band

# STM characterization of monolayer $NiI_2$

Inhomogeneous Polarization → Band bending of the conduction band



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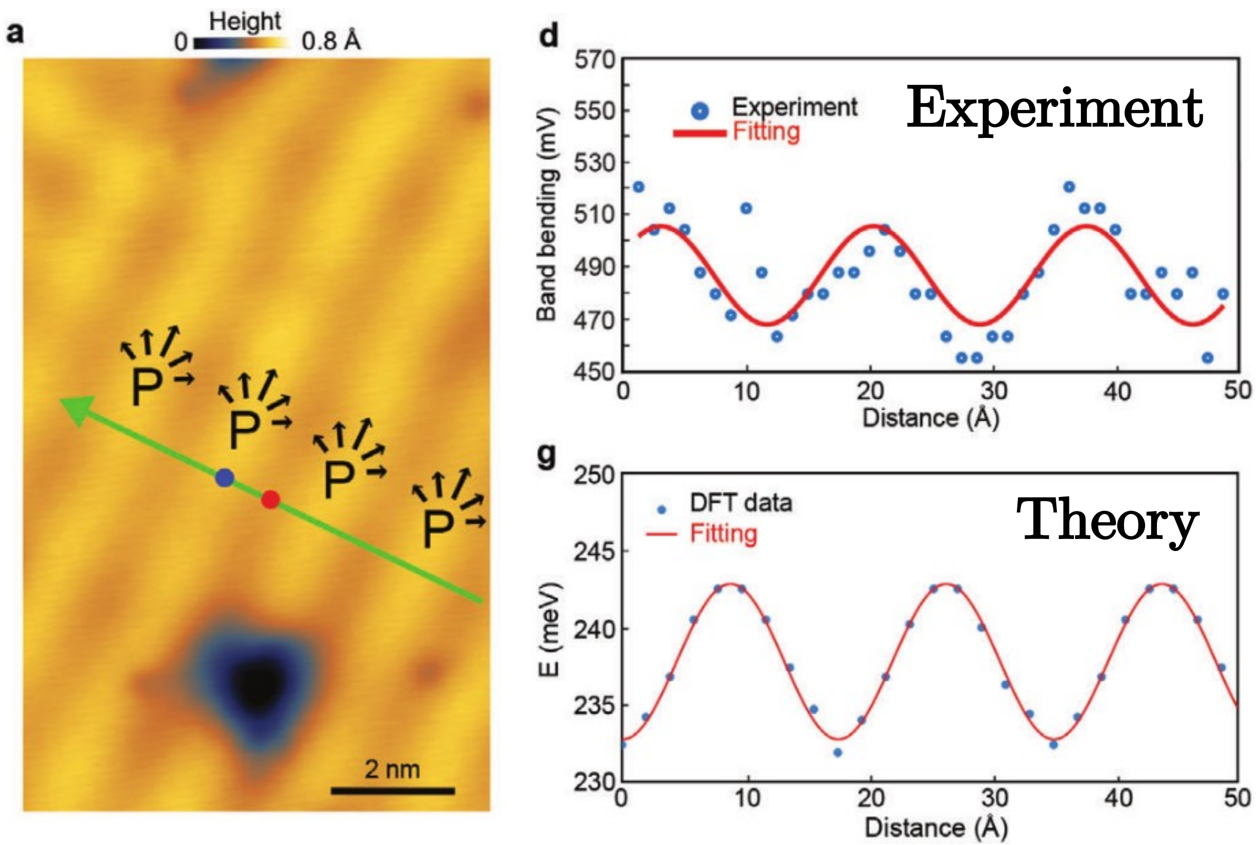


→ Fitting

$$E = E_0 + E_P \sin(2\pi x / L_S + \phi)$$

$$E_P = 16.8 \text{ mV}$$

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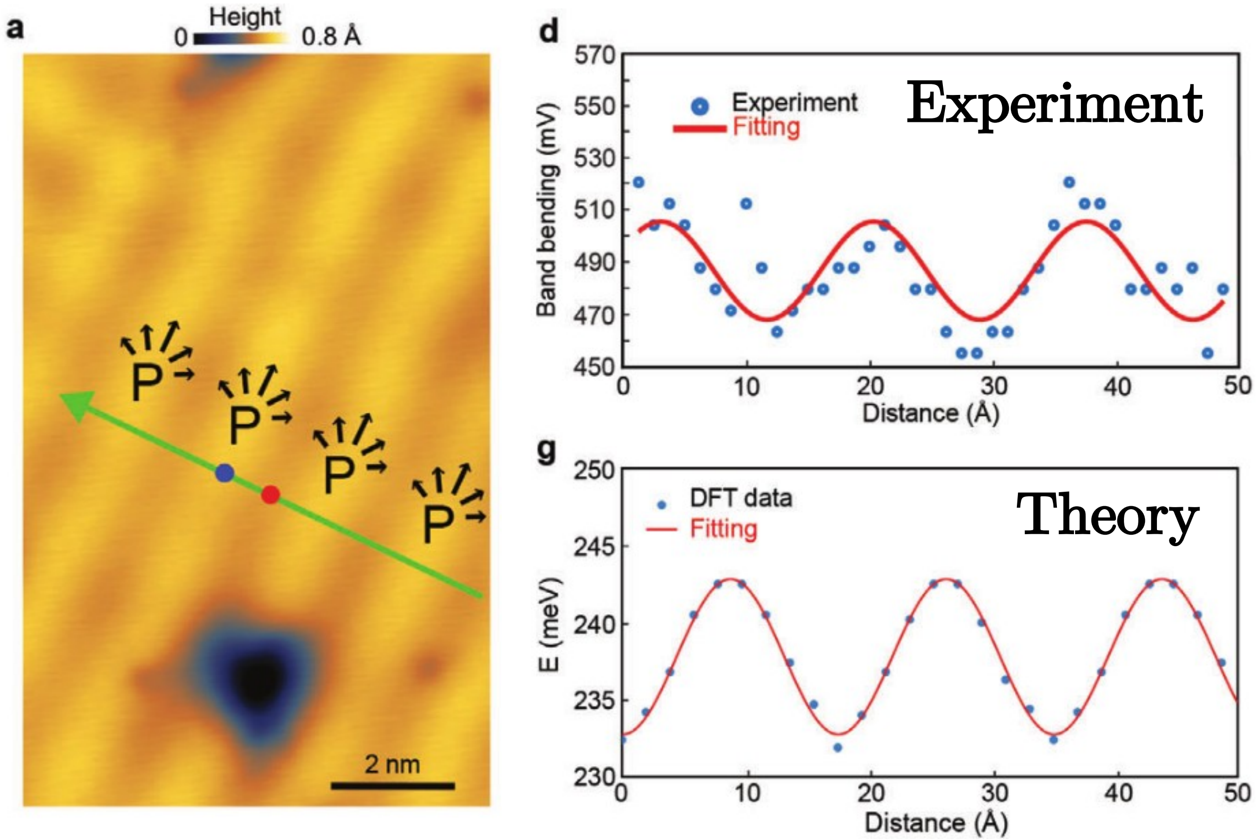


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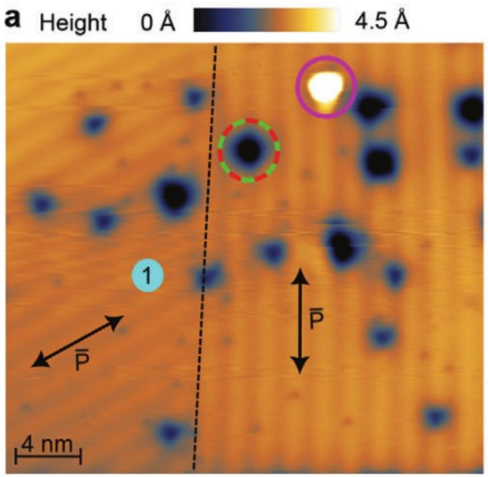
$$E_P = 16.8 \text{ mV}$$

$$P \sim 10^{-12} \text{ C/m}$$

Characterization of the ferroelectric order!

# Manipulation of multiferroic domains in monolayer $NiI_2$



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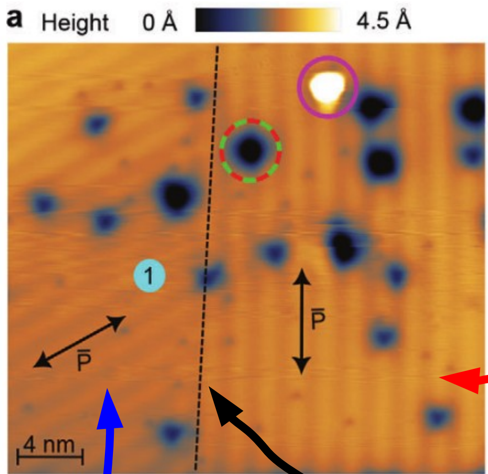
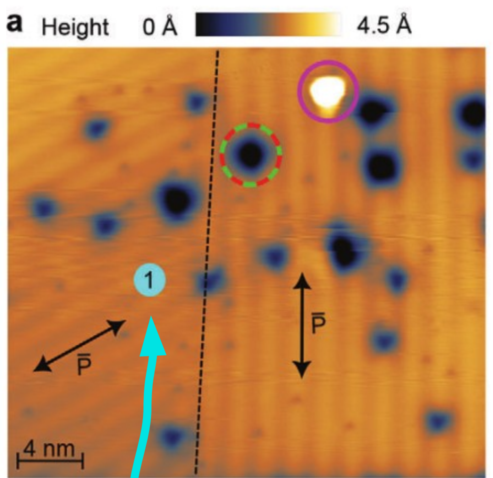


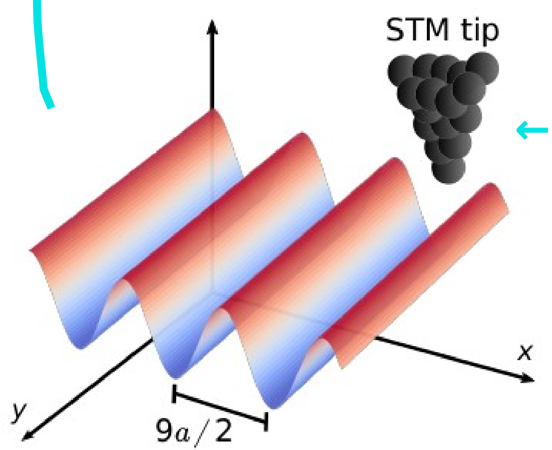

Right
Multiferroic Domain

Multiferroic Domain
Boundary

Left
Multiferroic Domain

# Manipulation of multiferroic domains in monolayer $NiI_2$




← Voltage pulses

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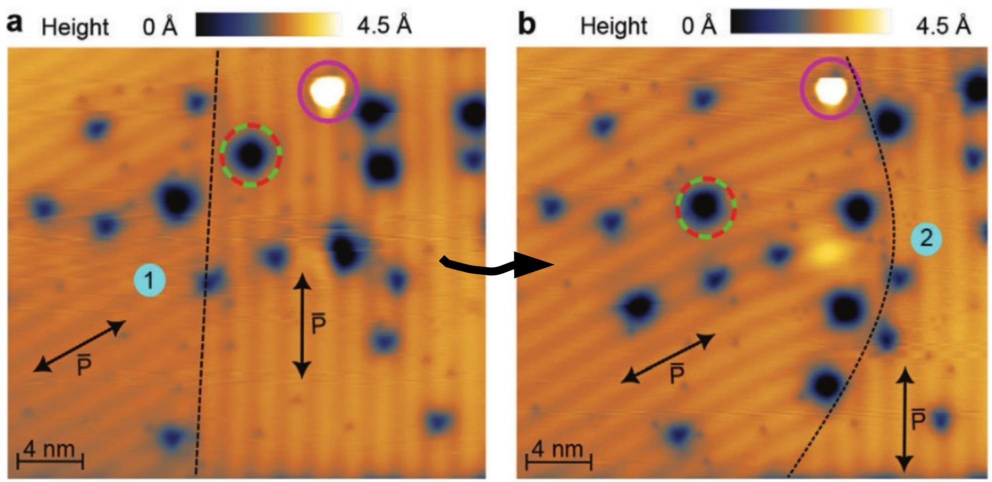

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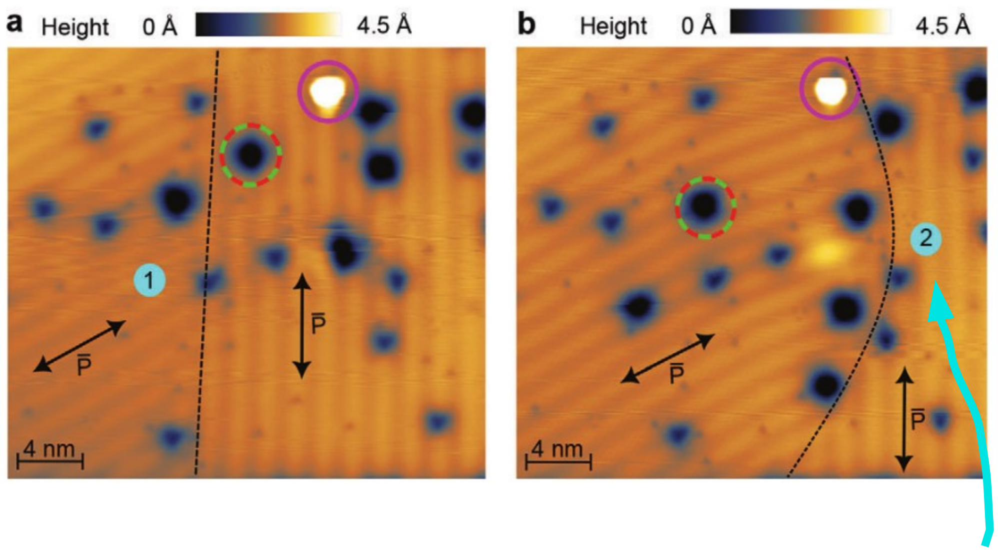


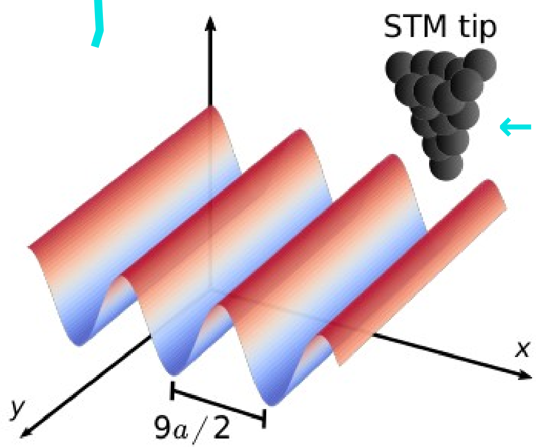


Voltage pulses

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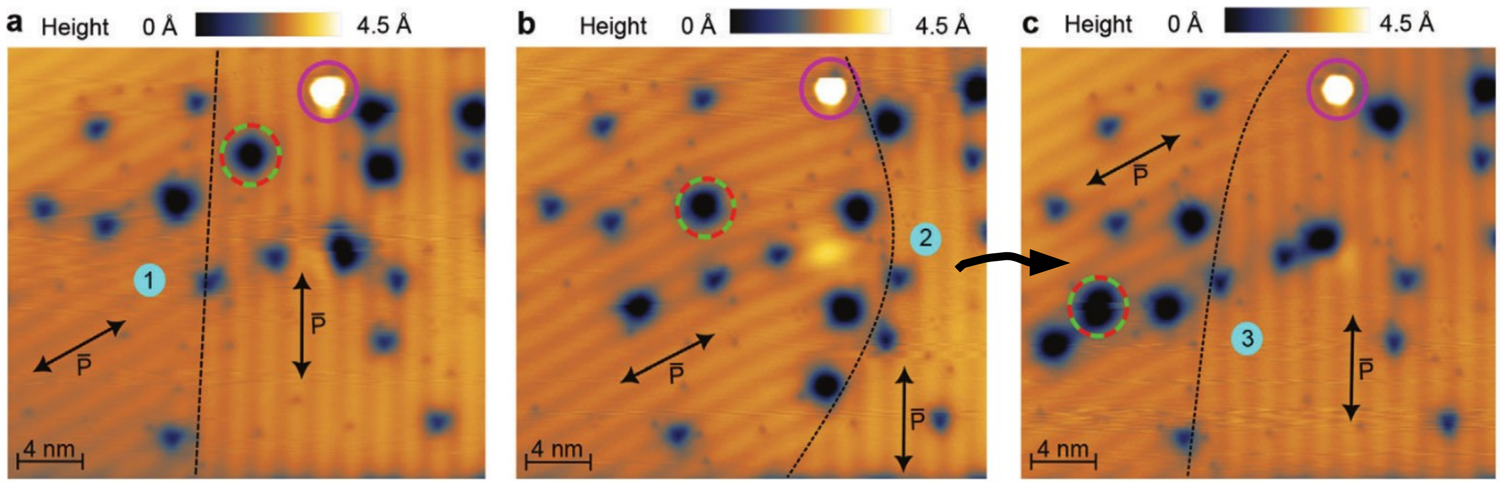

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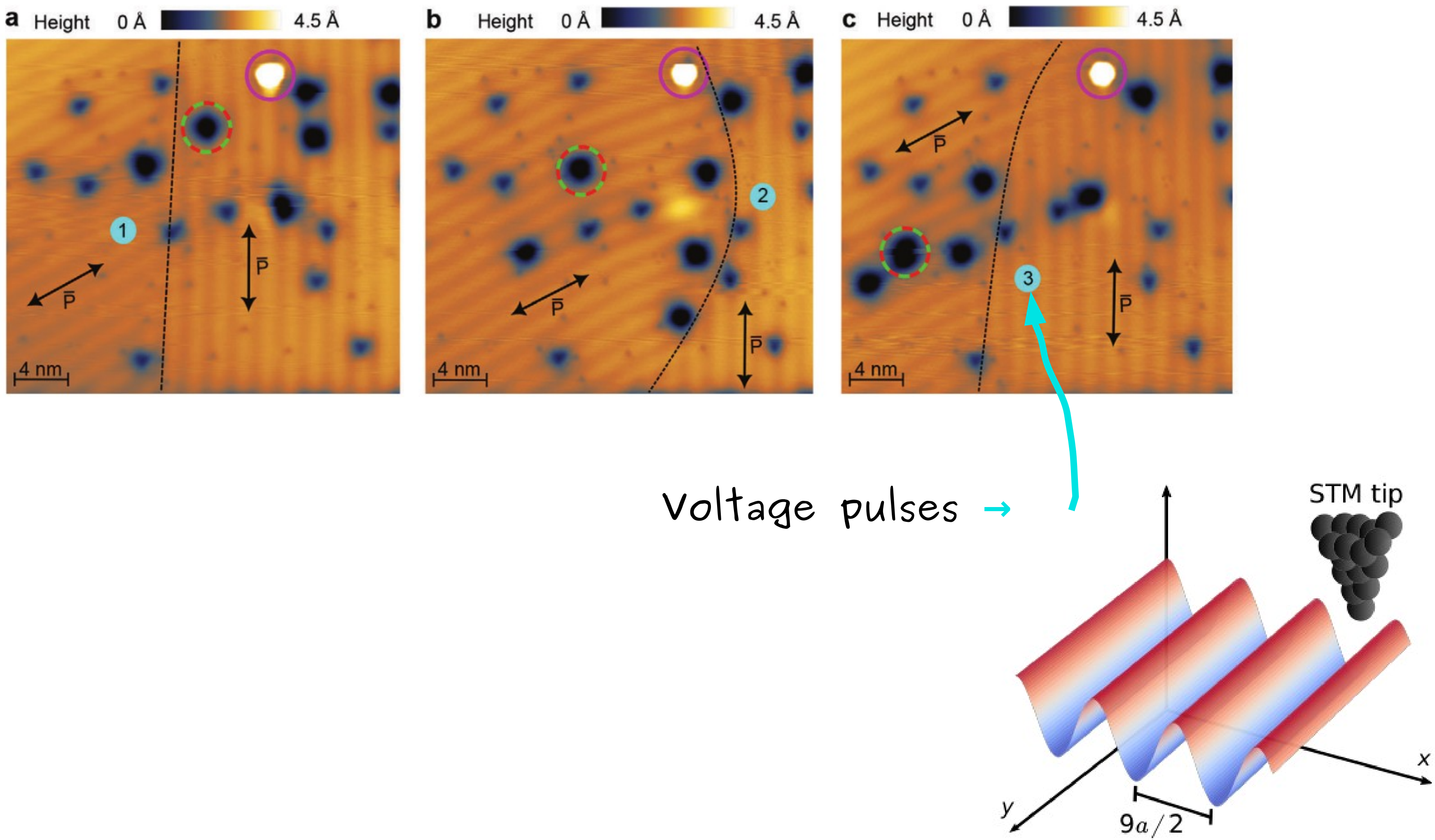

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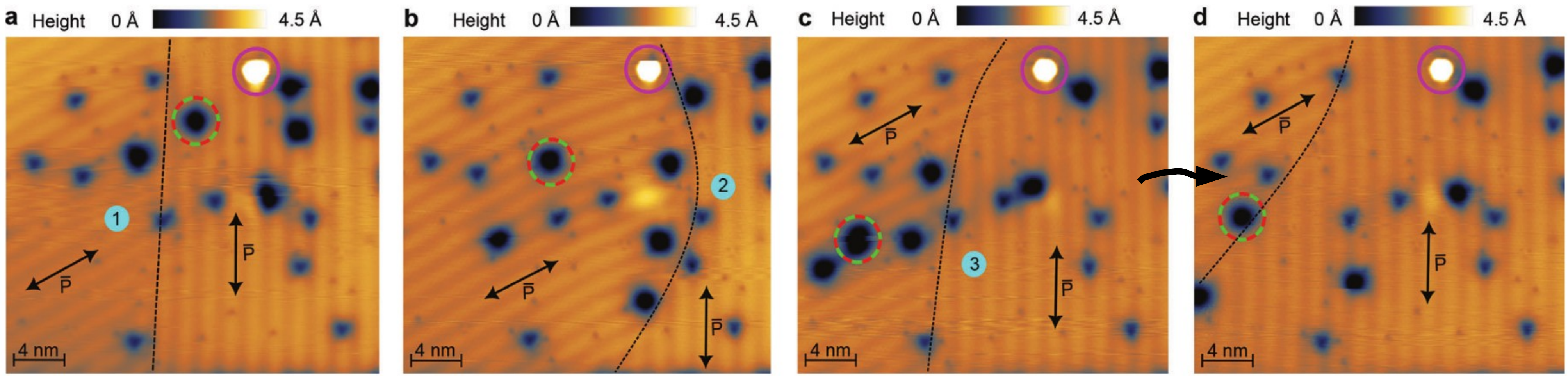



Manipulation of multiferroic domains!

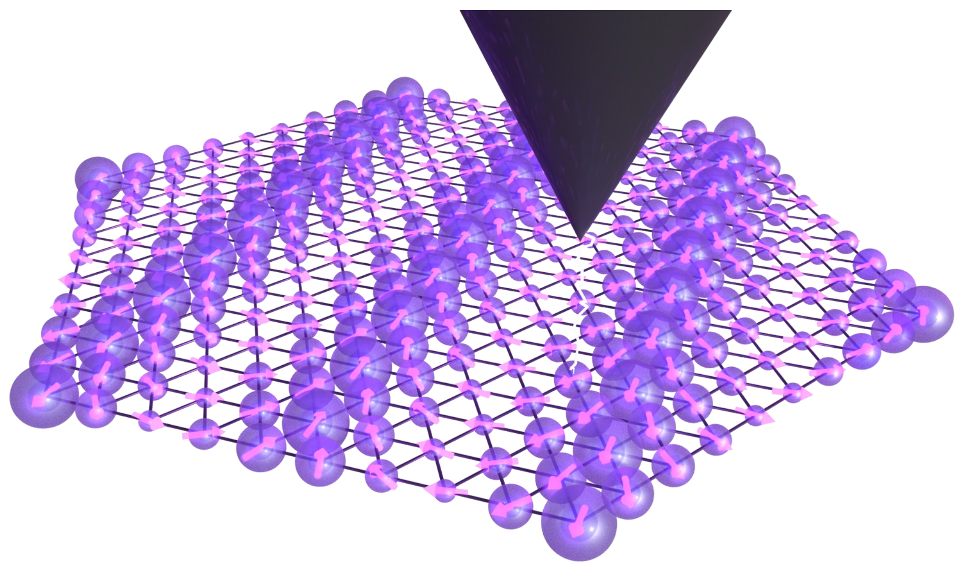
# Take home messages

→ The multiferroic order of $NiI_2$ can stems from the combination of a spin-spiral order + a strong spin-orbit coupling from I atoms

**Adolfo O. Fumega** and Jose L. Lado 2D Materials 9, 025010 (2022)

→ The multiferroic order of $NiI_2$ can be demonstrated, characterized and manipulated with an STM

Mohammad Amini,* **Adolfo O Fumega**,*
Héctor González-Herrero,
Viliam Vaňo, Shawulienu Kezilebieke,
Jose L Lado[+], Peter Liljeroth[+]
*Advanced Materials 2311342* (2024)



# Motivation

## Layered van der Waals

Monolayer

| Semimetal | Insulator | Superconductor | Ferromagnet | Ferroelectric | Multiferroic | ... |
|---|---|---|---|---|---|---|
| Graphene | BN | $NbSe_2$ | $CrI_3$ | $MoTe_2$ | $NiI_2$ | |

**Ingredients for Multiferroicity**

**1) Non-collinear Magnetism**

**+**

**2) Spin Orbit Coupling**

Inverse Dzyaloshinskii–Moriya interaction

$$\mathbf{P}_{ij} = \alpha\lambda_{SOC}\left(\mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)\right)$$

# Motivation

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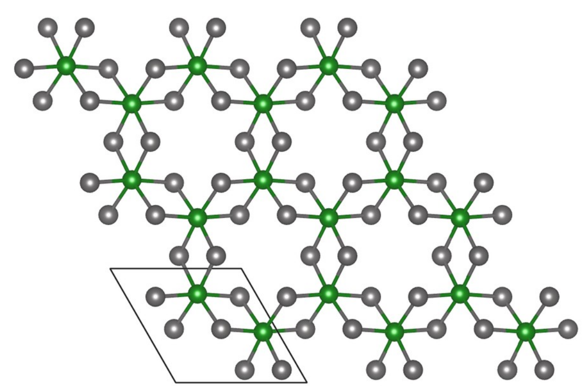
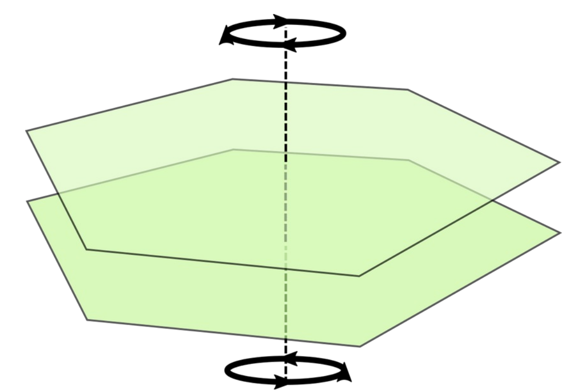
**Moiré–driven multiferroic order**

$CrX_3$



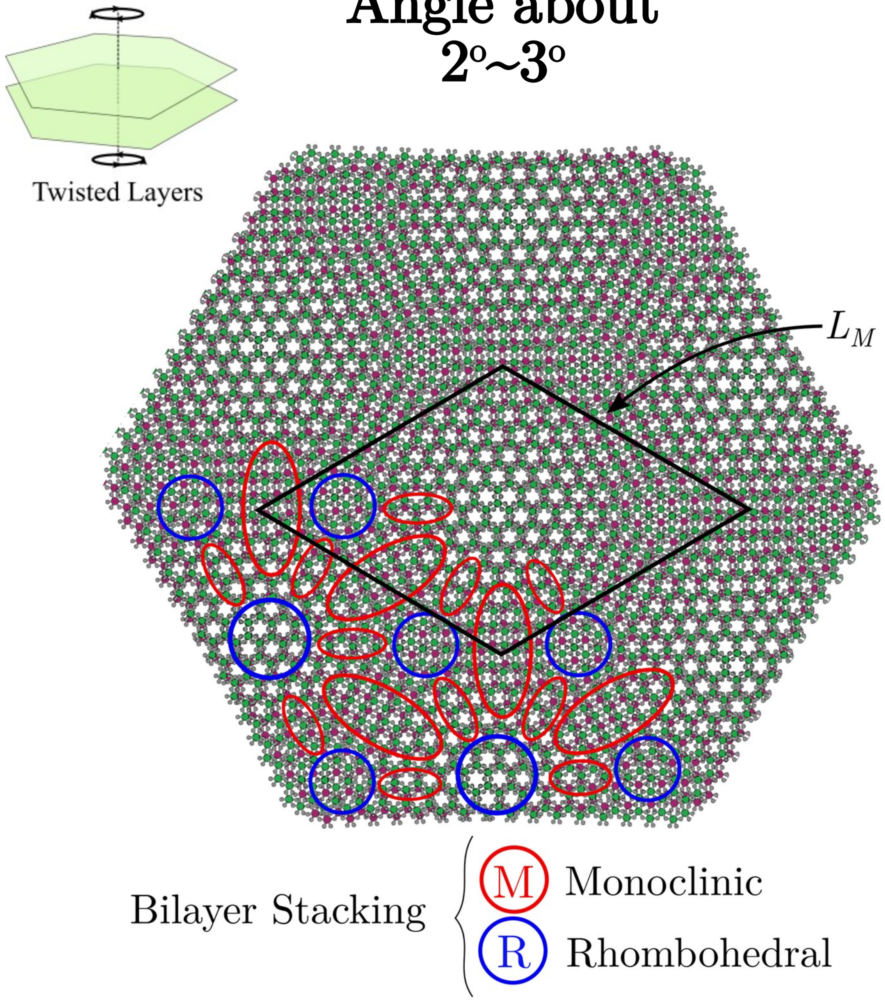
+

Twisted layers



# Twisted $CrCl_3$, $CrBr_3$ and $CrI_3$ bilayers

**Angle about $2^o \sim 3^o$**



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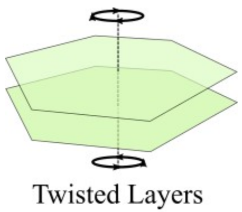


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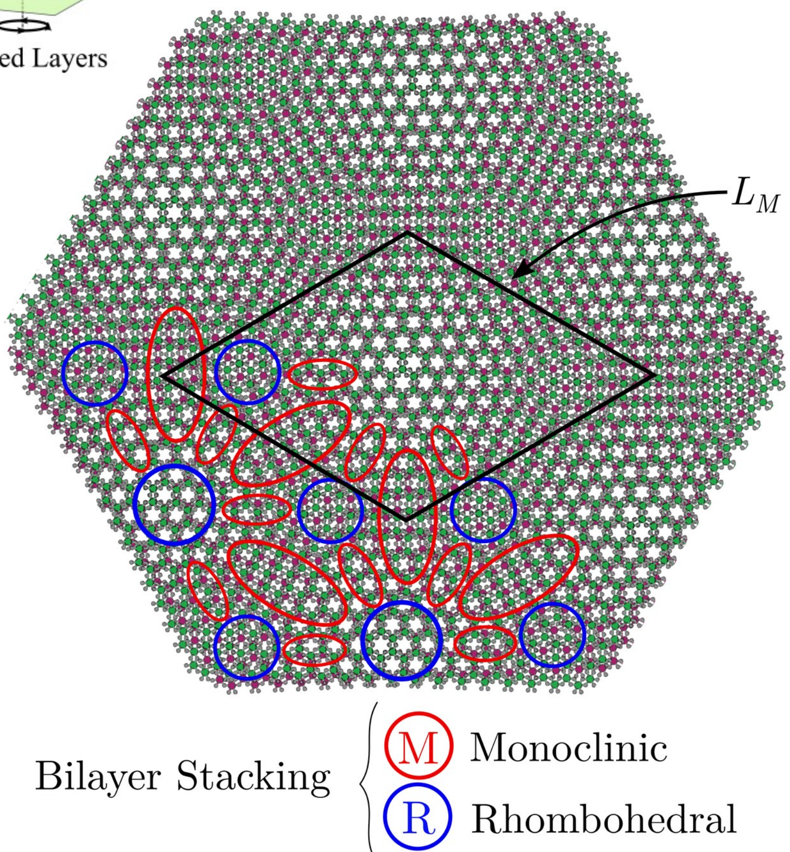
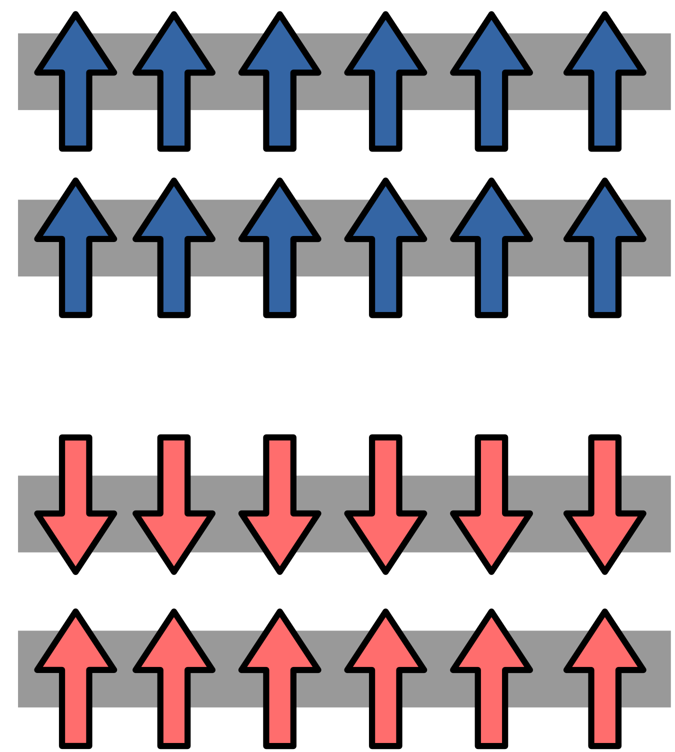



## Stacking-dependent Interlayer Magnetic Exchange



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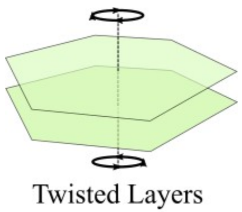


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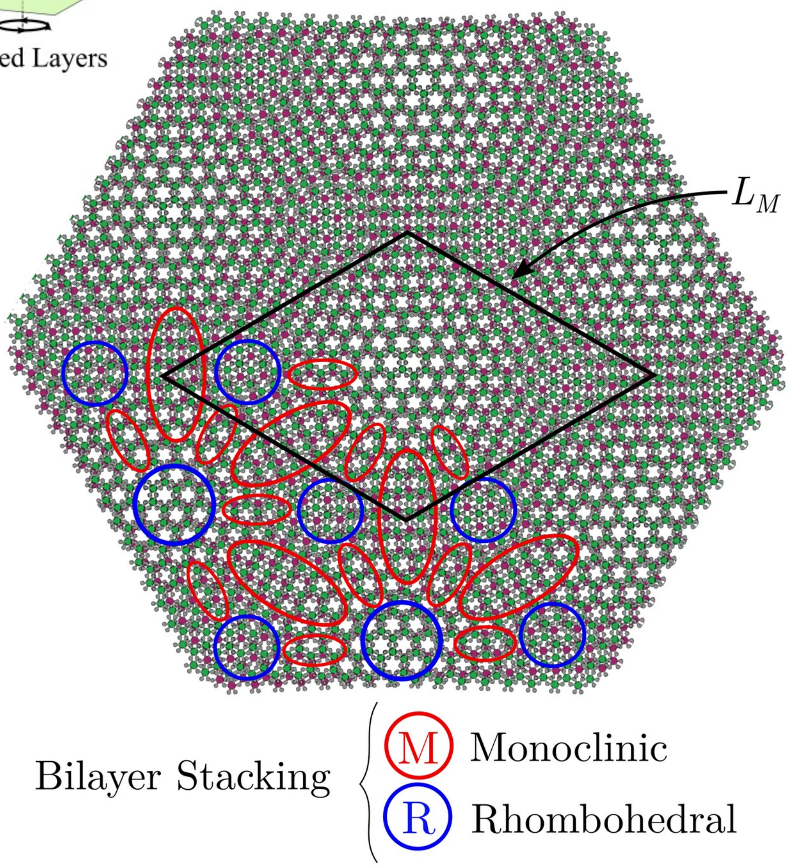
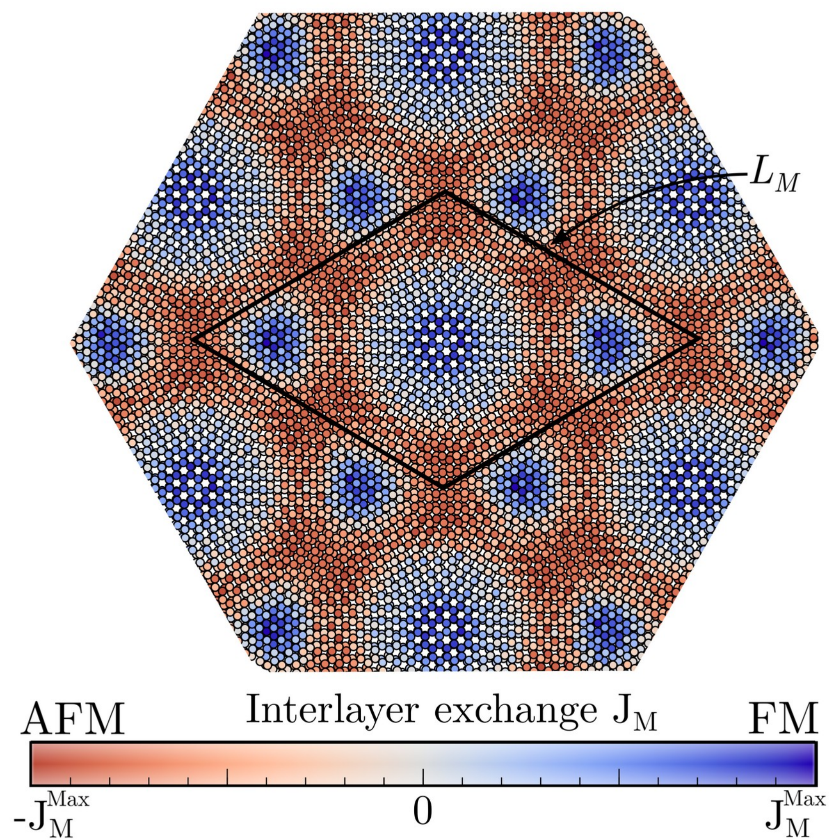


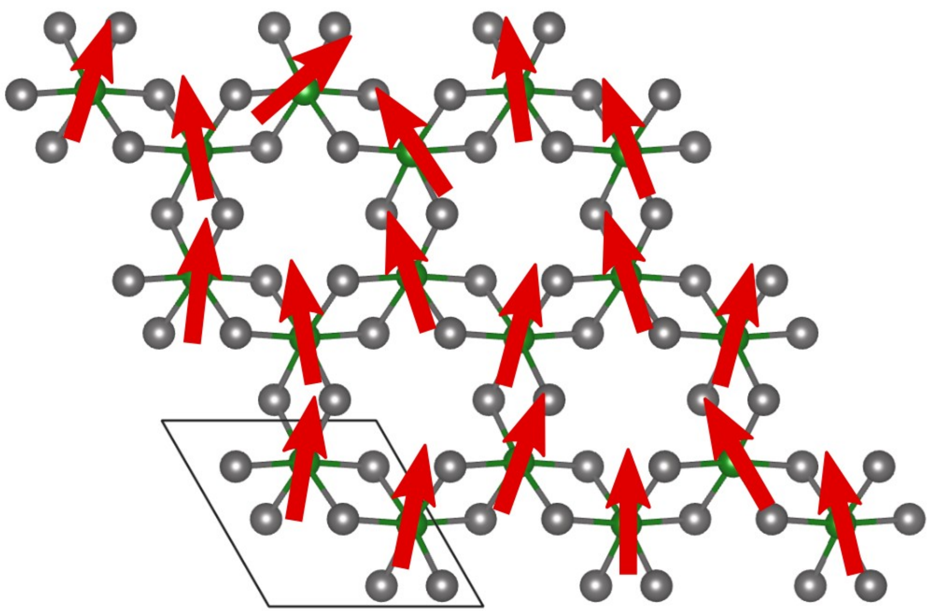

## Stacking-dependent Interlayer Magnetic Exchange



# Spin Hamiltonian

## Intralayer terms

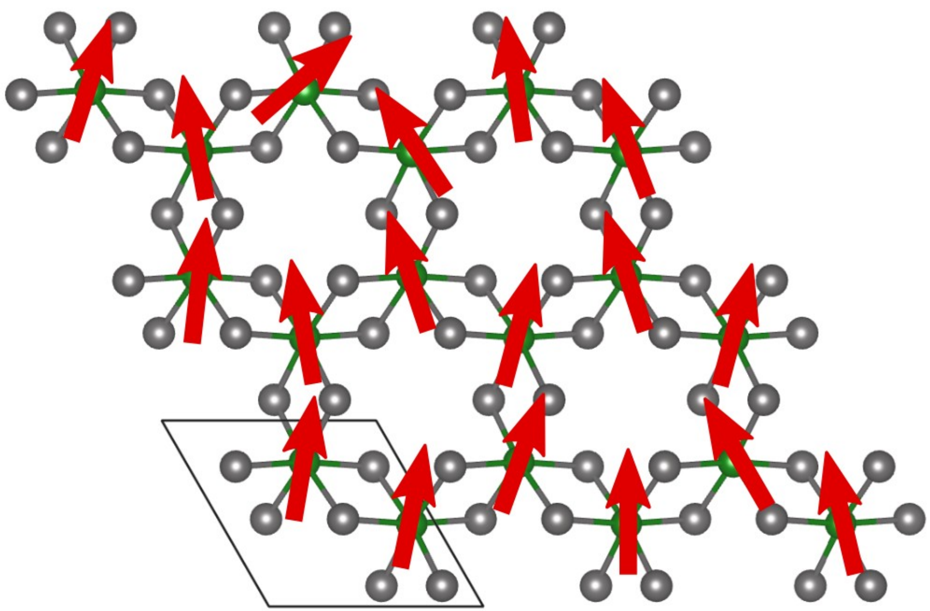
$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j - \frac{A_v}{2}\sum_{\langle i,j\rangle}S_i^z S_j^z - A_u\sum_i (S_i^z)^2$$



# Spin Hamiltonian

## Intralayer terms

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j - \frac{A_v}{2}\sum_{\langle i,j\rangle}S_i^z S_j^z - A_u\sum_i (S_i^z)^2$$



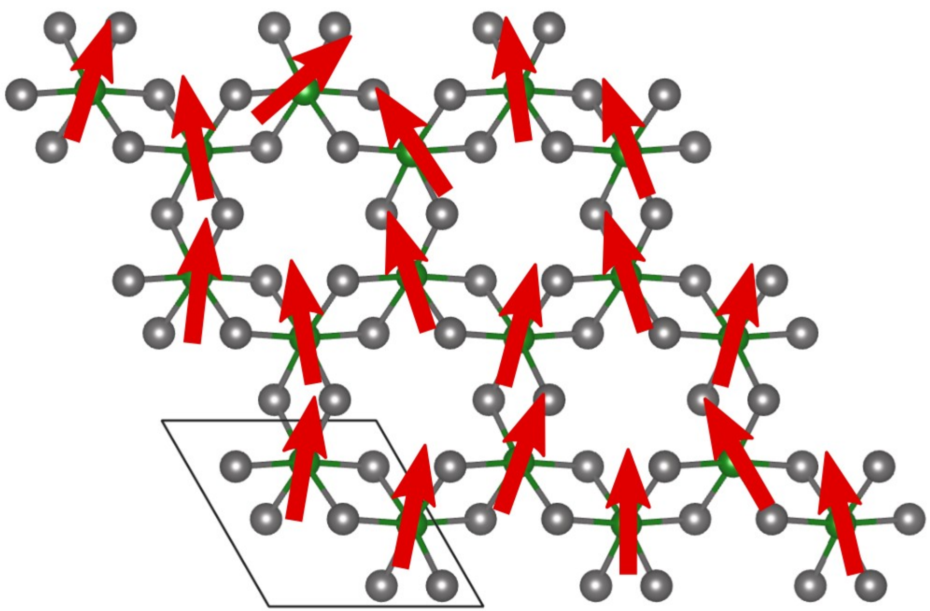
First Neighbor

Ferromagnetic Exchange

# Spin Hamiltonian

## Intralayer terms

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j - \frac{A_v}{2}\sum_{\langle i,j\rangle}S_i^z S_j^z - A_u\sum_i (S_i^z)^2$$

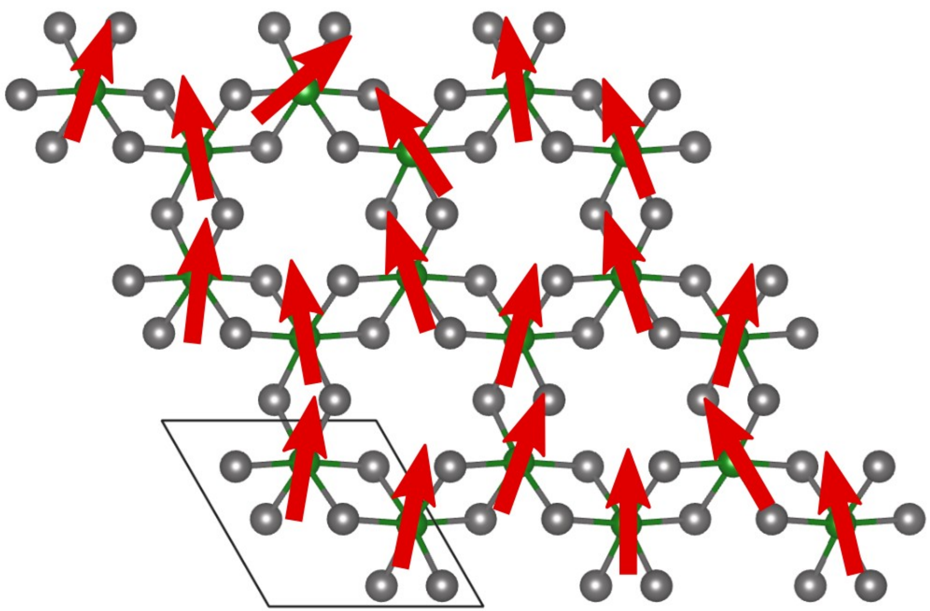


Anisotropic Magnetic Exchange

# Spin Hamiltonian

## Intralayer terms

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j - \frac{A_v}{2}\sum_{\langle i,j\rangle}S_i^zS_j^z - A_u\sum_i (S_i^z)^2$$

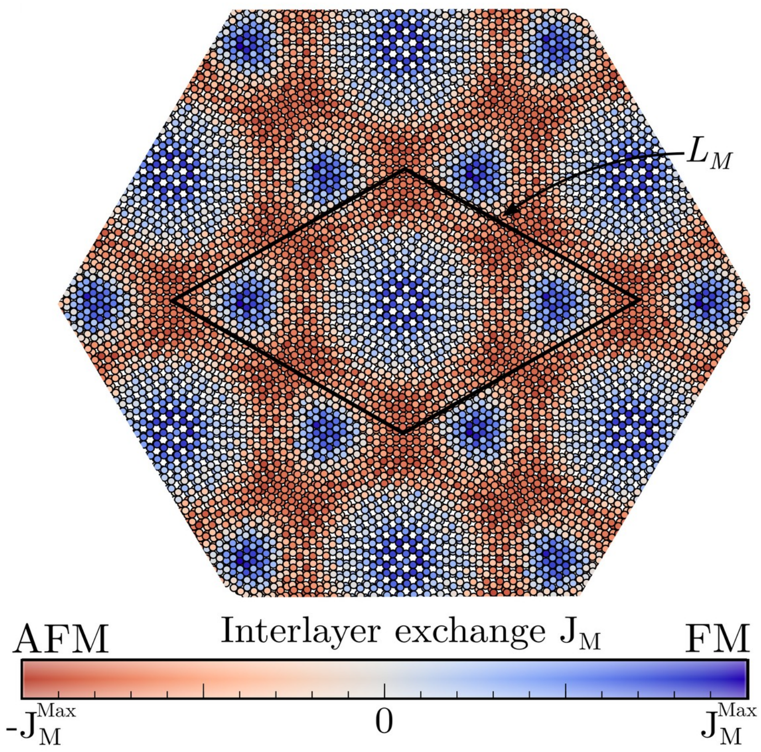


Single Ion Anisotropy

# Spin Hamiltonian

## Interlayer term

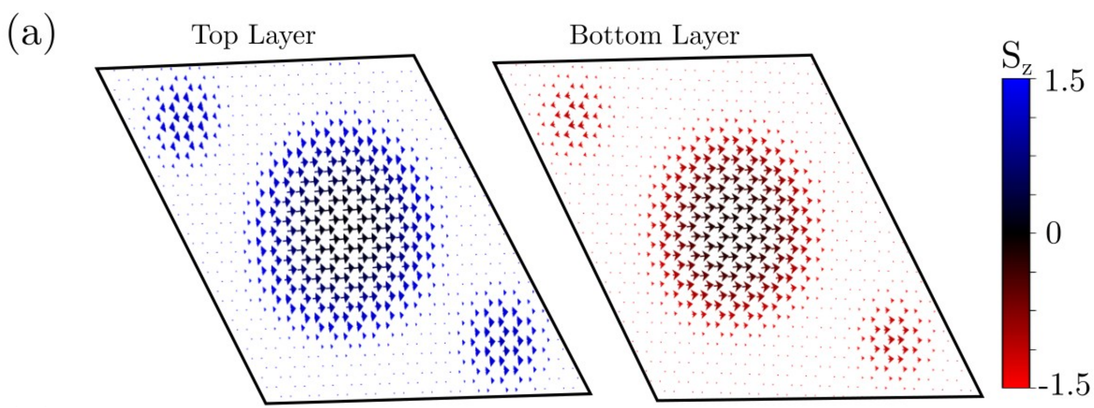
$$\mathcal{H}_{Inter} = -\frac{1}{2}\sum_{i,j} J_M(\mathbf{r}_i,\mathbf{r}_j)\mathbf{S}_i \cdot \mathbf{S}_j$$




Interpolation between AFM and FM regions using harmonic functions

# Spin Hamiltonian

Solve the Spin Hamiltonian → Ground State




Spin Texture

# Spin Hamiltonian

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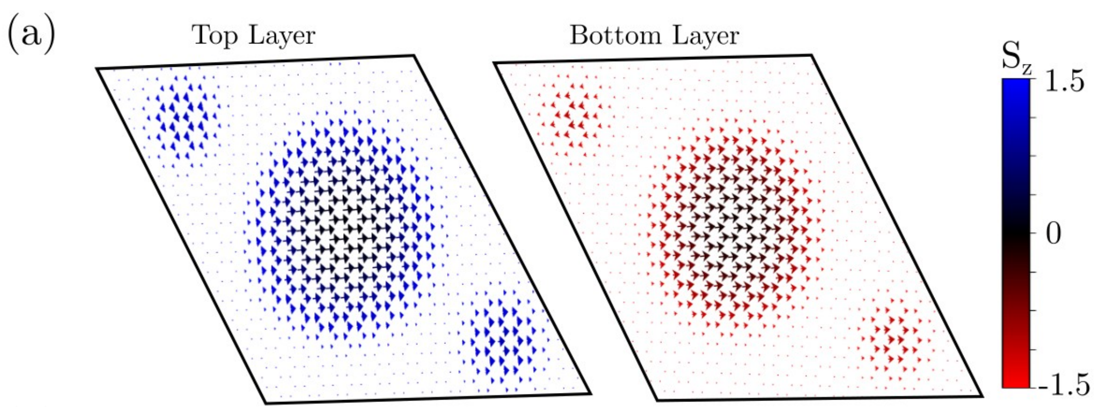



Spin Texture

↓

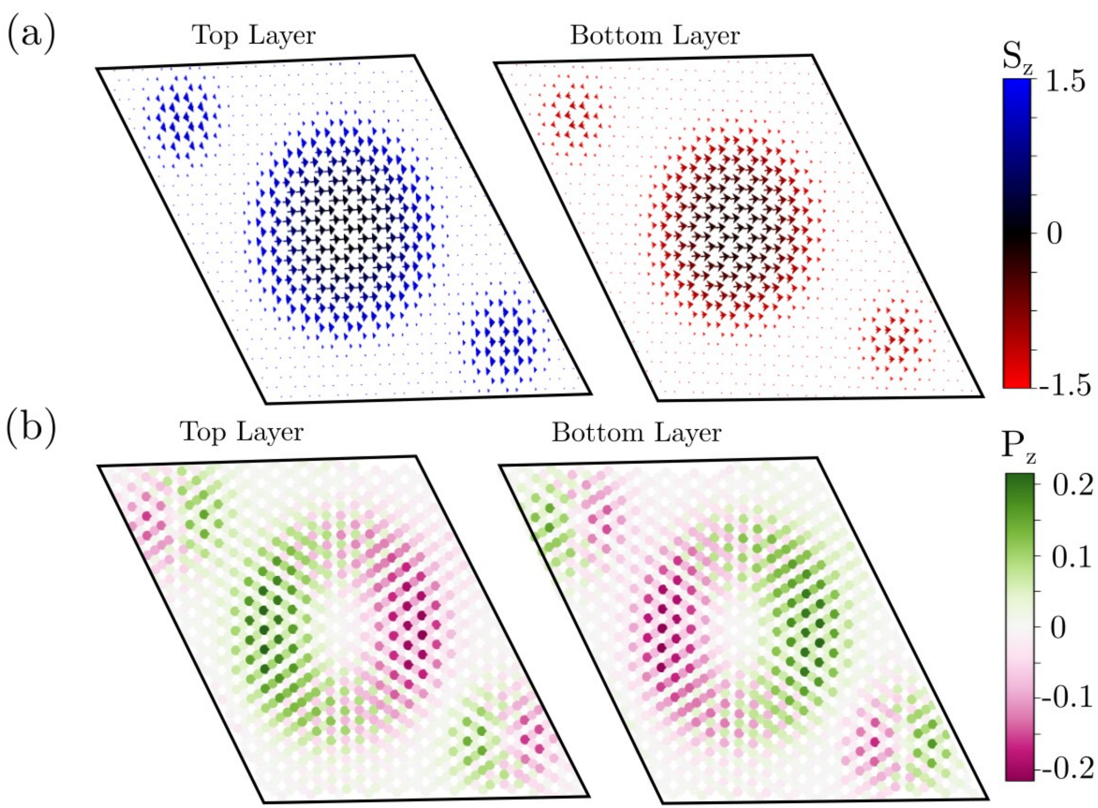
Electric Polarization

$$\mathbf{P}_{ij} = \alpha\lambda_{SOC}\left(\mathbf{r}_{ij} \times \left(\mathbf{S}_i \times \mathbf{S}_j\right)\right)$$

Inverse Dzyaloshinskii–Moriya interaction

# Spin Hamiltonian

Solve the Spin Hamiltonian → Ground State




Spin Texture

↓

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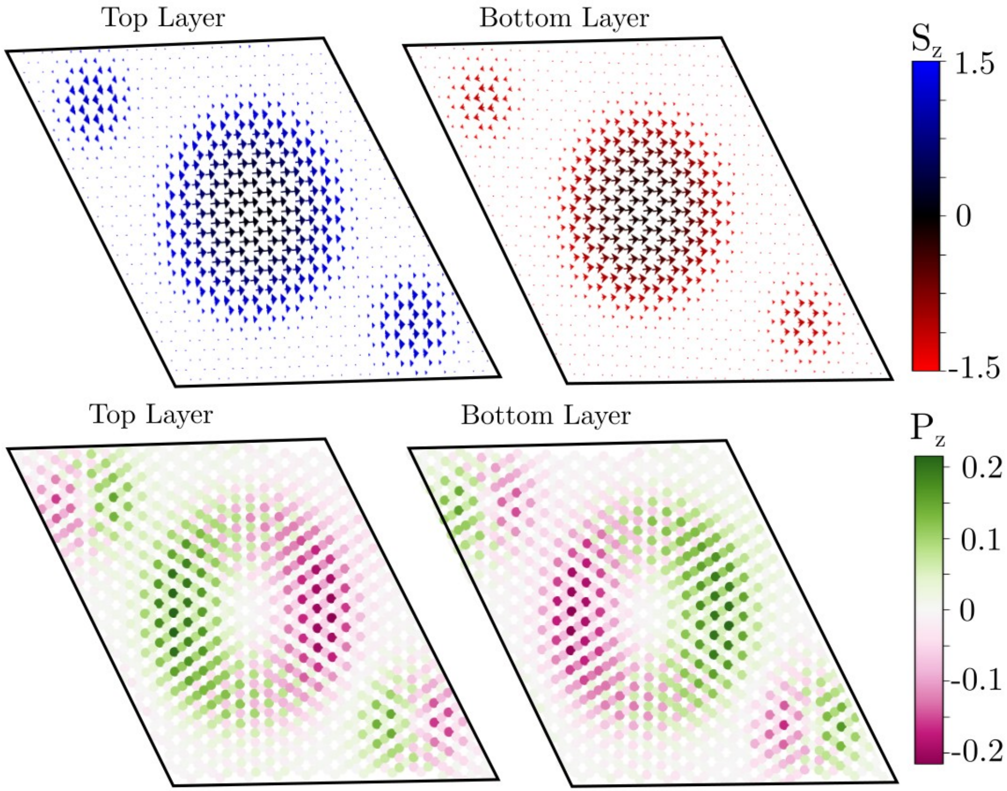
Inverse Dzyaloshinskii–Moriya interaction

# Spin Hamiltonian

Considering the different parameters: $\lambda_{soc}$ and $A_v$

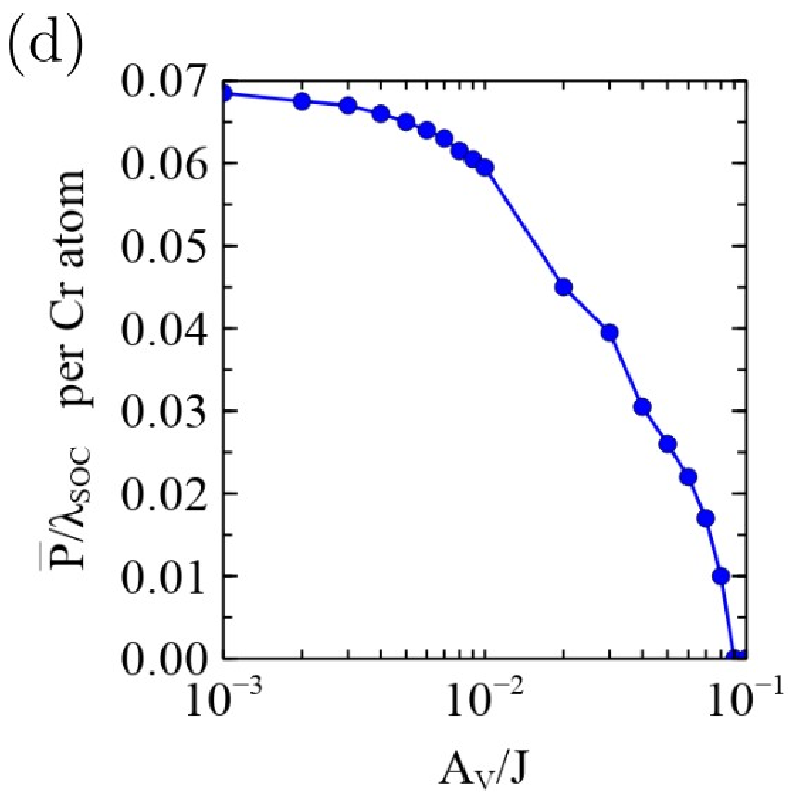



Which $CrX_3$ displays the strongest multiferroic order?

# Spin Hamiltonian

## Parameters dependence

Anisotropic Exchange




Electric Polarization

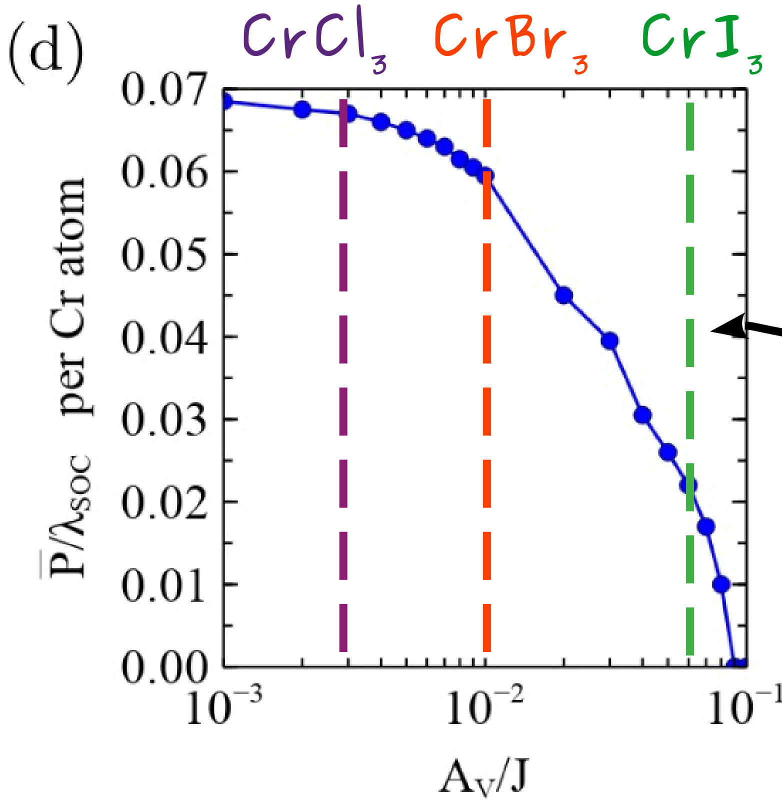
$$\mathbf{P}_{ij} = \alpha\lambda_{SOC}\left(\mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)\right)$$

$A_V$ → Collinearity → Decrease P

# Spin Hamiltonian

## Parameters dependence

Anisotropic Exchange




Electric Polarization

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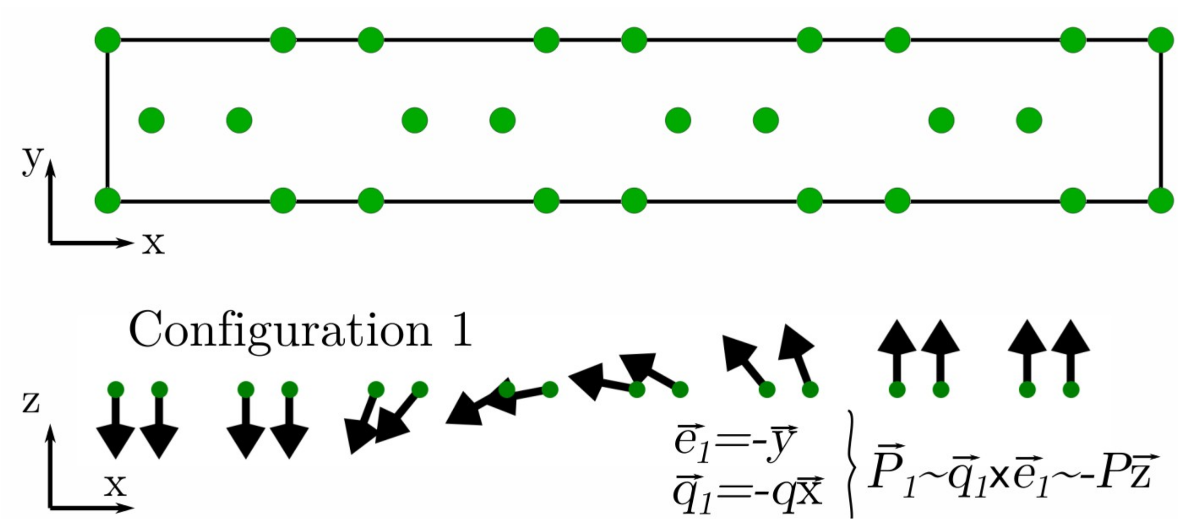
$A_V$ → Collinearity → Decrease P

$CrI_3$ in the verge of displaying a multiferroic behavior due to the strong anisotropy

# Ab initio calculations

## Electric polarization in a spin texture of $CrX_3$

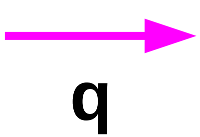



$$\mathbf{P}_{ij} = \alpha \lambda_{SOC} \left( \mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j) \right)$$

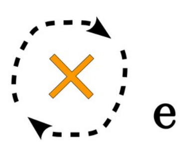
Electric Polarization

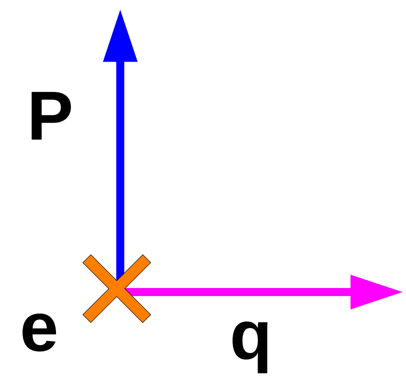
$$\mathbf{P} = \beta \lambda_{SOC} (\mathbf{q} \times \mathbf{e})$$

Propagation vector




Rotation vector



# Ab initio calculations

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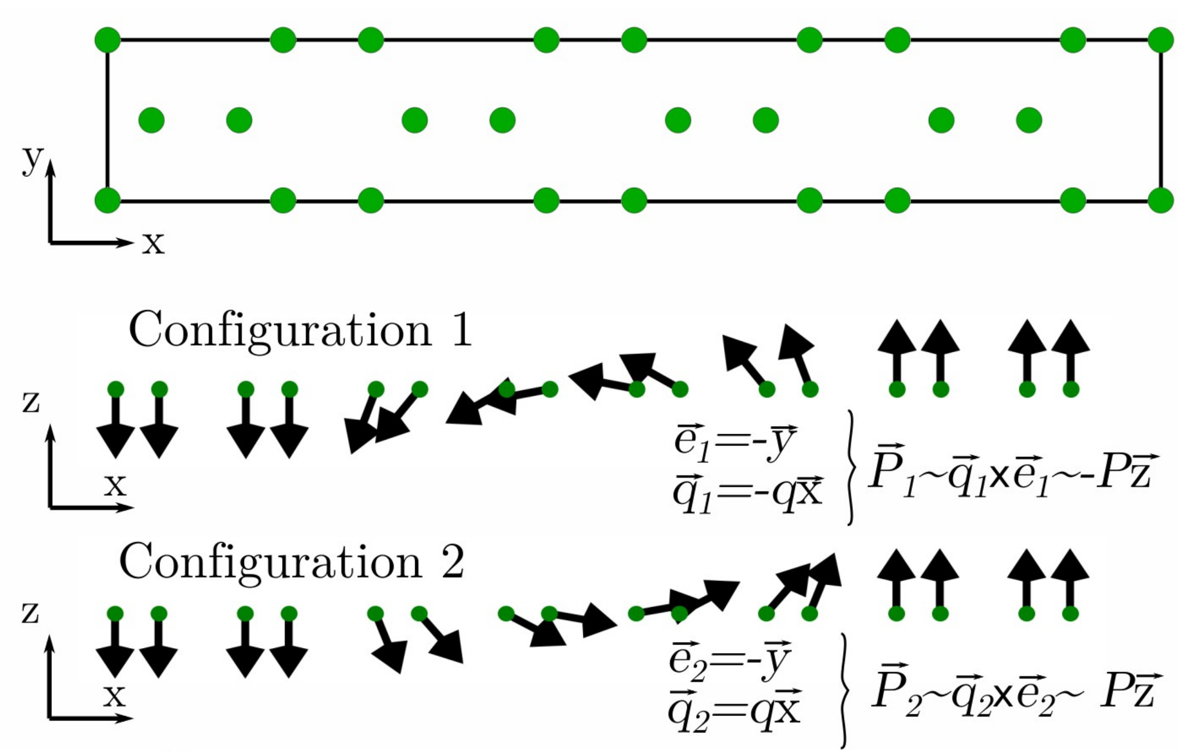
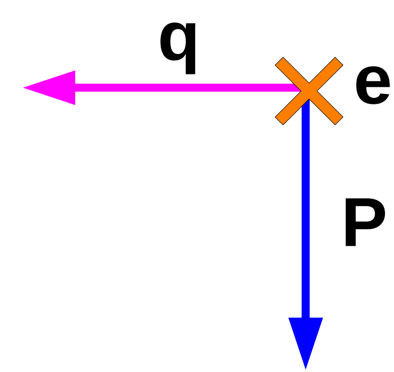
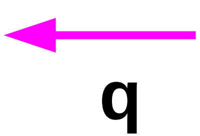



Electric Polarization

$$\mathbf{P} = \beta\lambda_{SOC}(\mathbf{q}\times\mathbf{e})$$




Propagation vector

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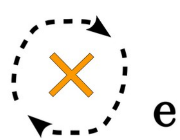

# Ab initio calculations

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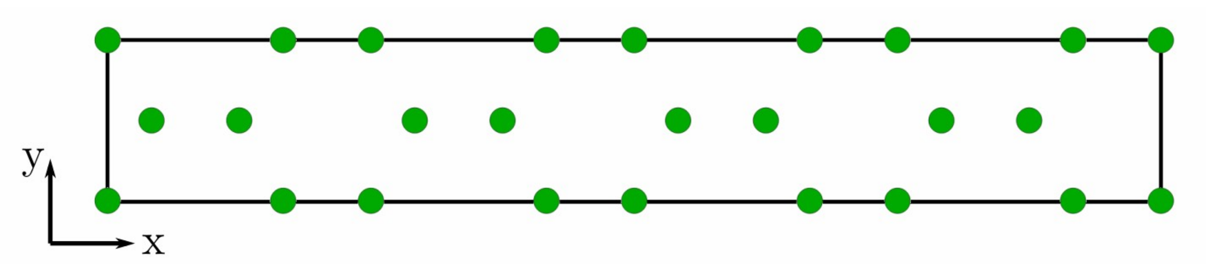


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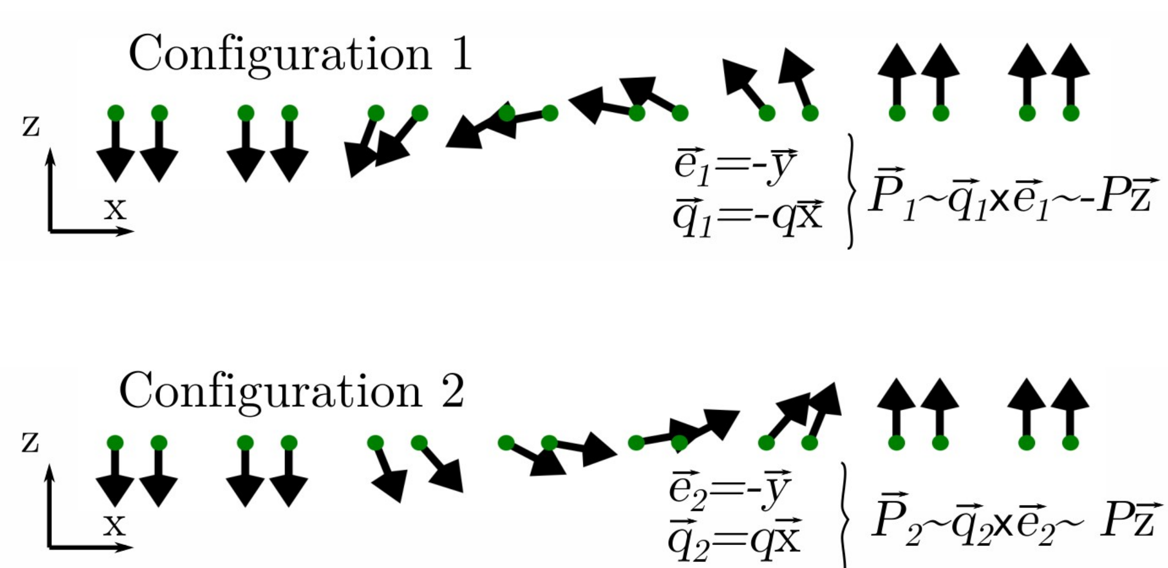
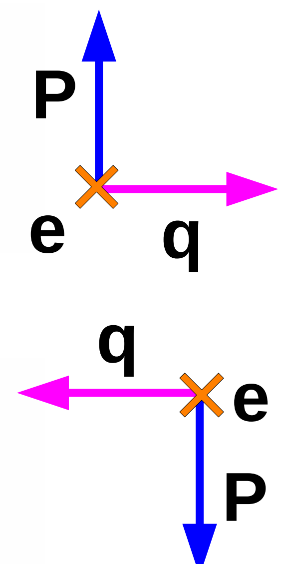


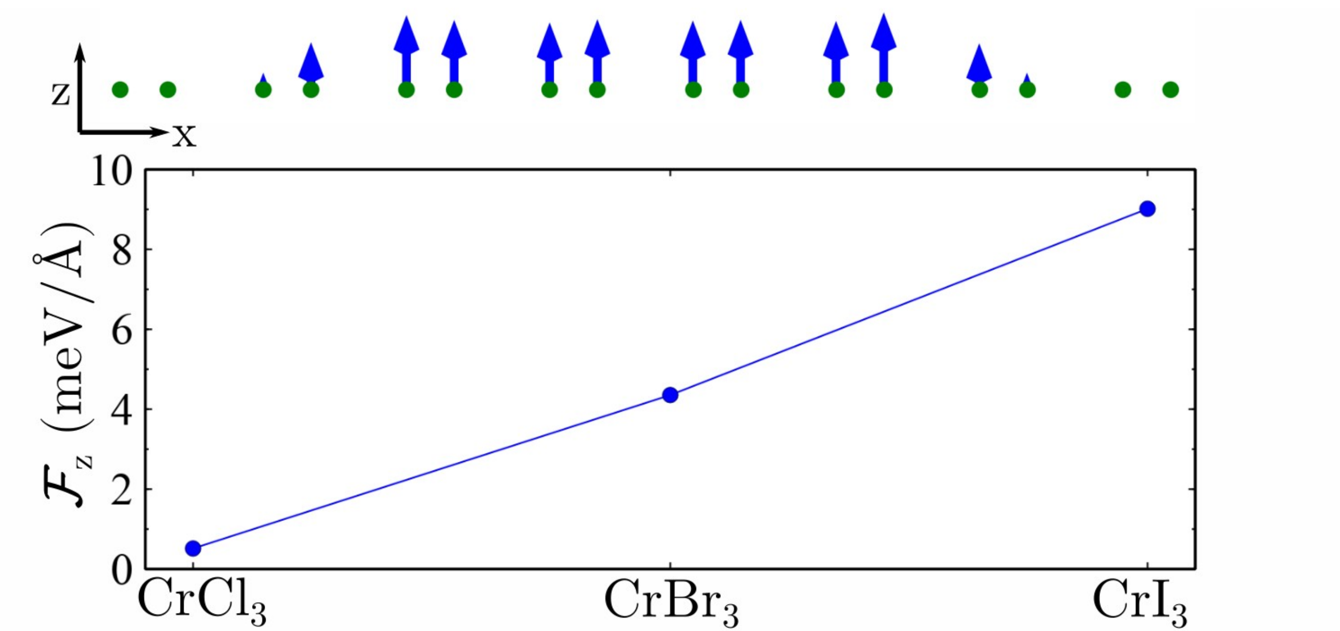




Difference between configurations
↓
Signature of Ferroelectricity

# Ab initio calculations

## Electric polarization in a spin texture of $CrX_3$

### Ferroelectric force difference




**Going down in the halide group**

↓

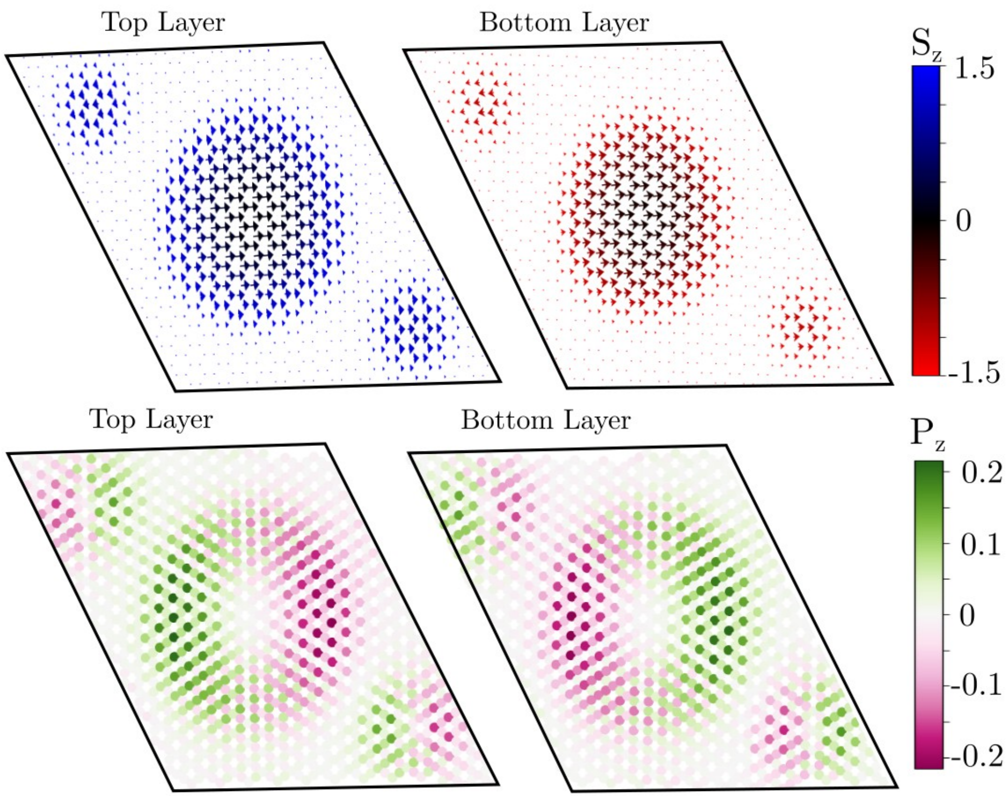
**Increase SOC**

↓

**Increase Ferroelectric force**

# Spin Hamiltonian

Considering the different parameters: $\lambda_{soc}$ and $A_v$




$CrBr_3$ displays the strongest multiferroic order

# Spin Hamiltonian

## Magnetoelectric Coupling

External Electric field

$$\mathcal{H}_E = \frac{1}{2}\sum_{ij} \mathbf{E} \cdot \mathbf{P}_{ij}$$

# Spin Hamiltonian

## Magnetoelectric Coupling

External Electric field

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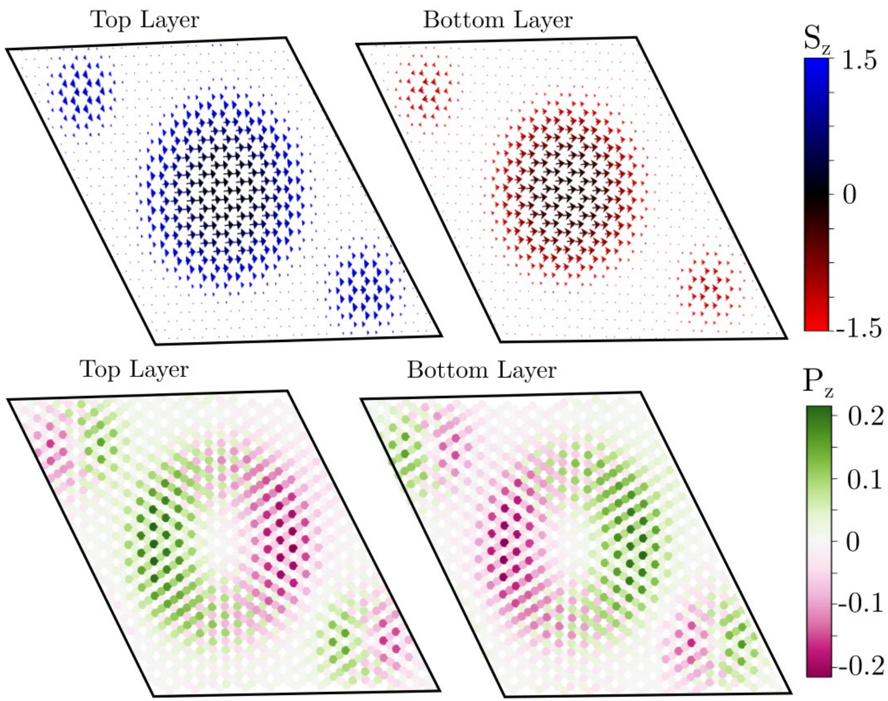
$E/J=0$



# Spin Hamiltonian

## Magnetoelectric Coupling

External Electric field

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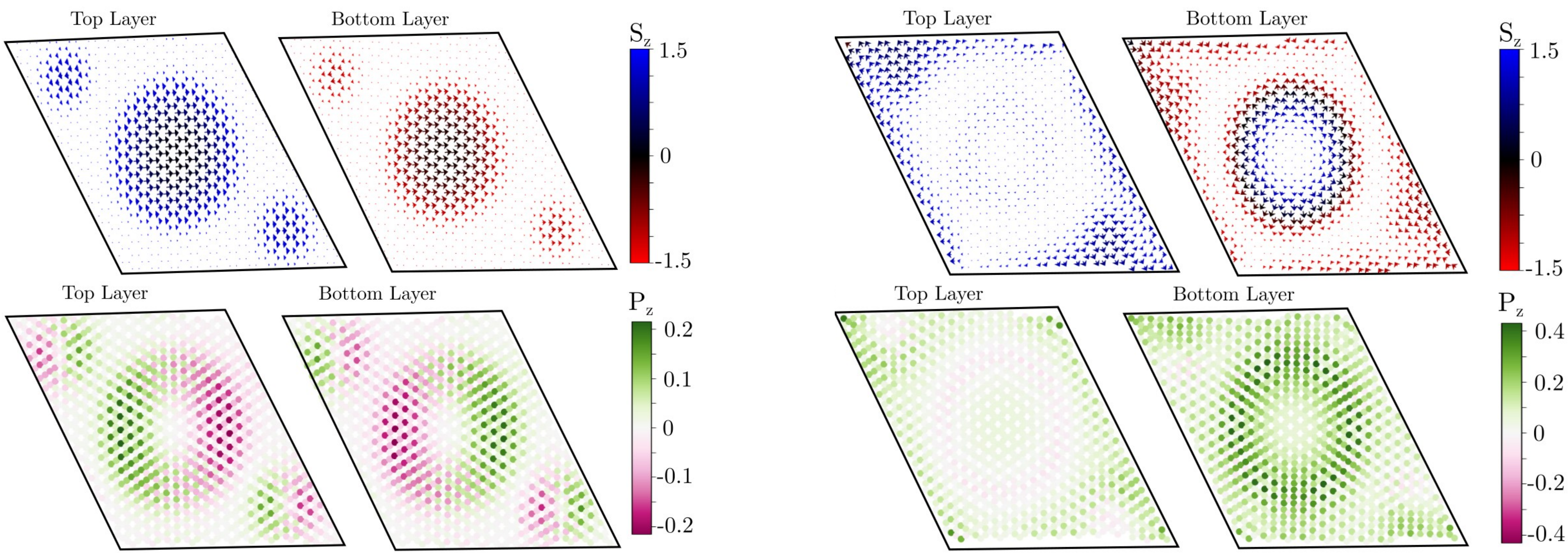
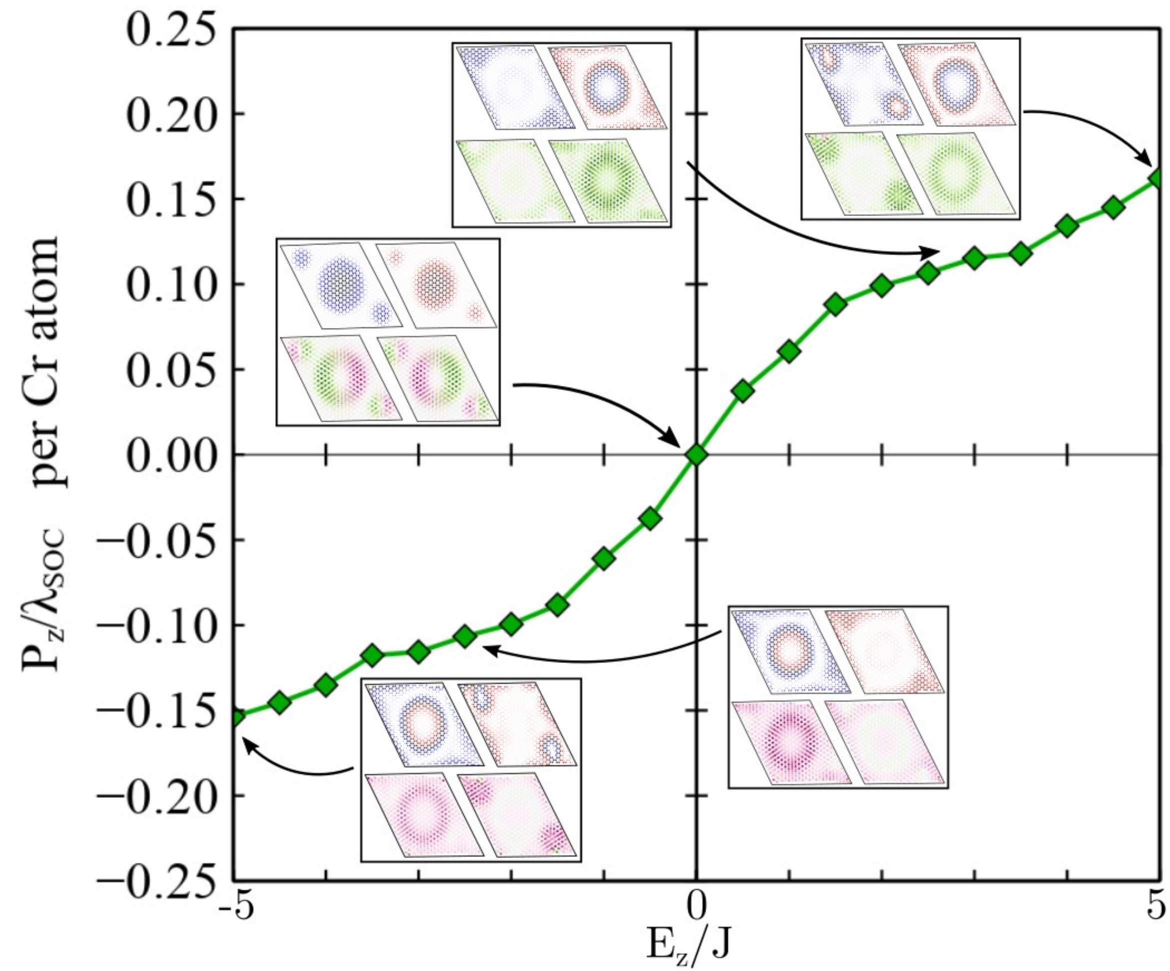
$E/J$=0 $E/J$=3



# Spin Hamiltonian

## Magnetoelectric Coupling

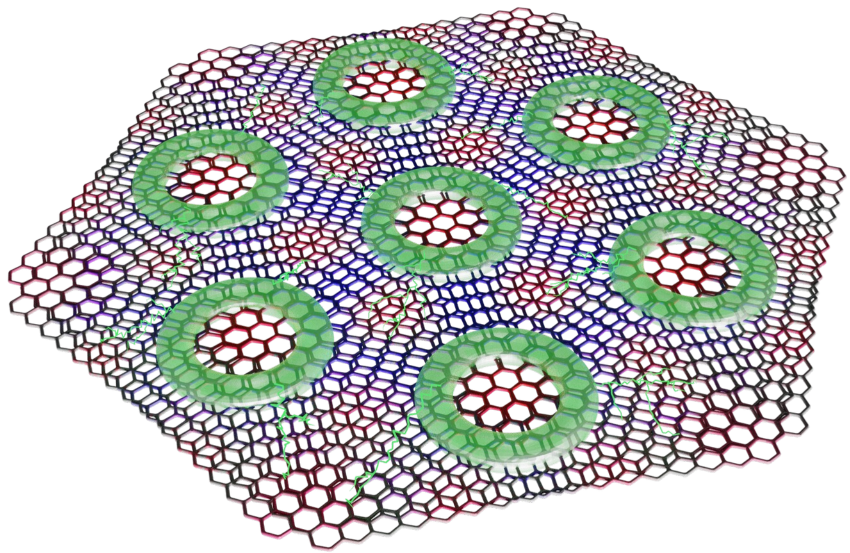
Transitions between magnetic skyrmion phases as a function of the electric field (1–10 V)



# Take home messages

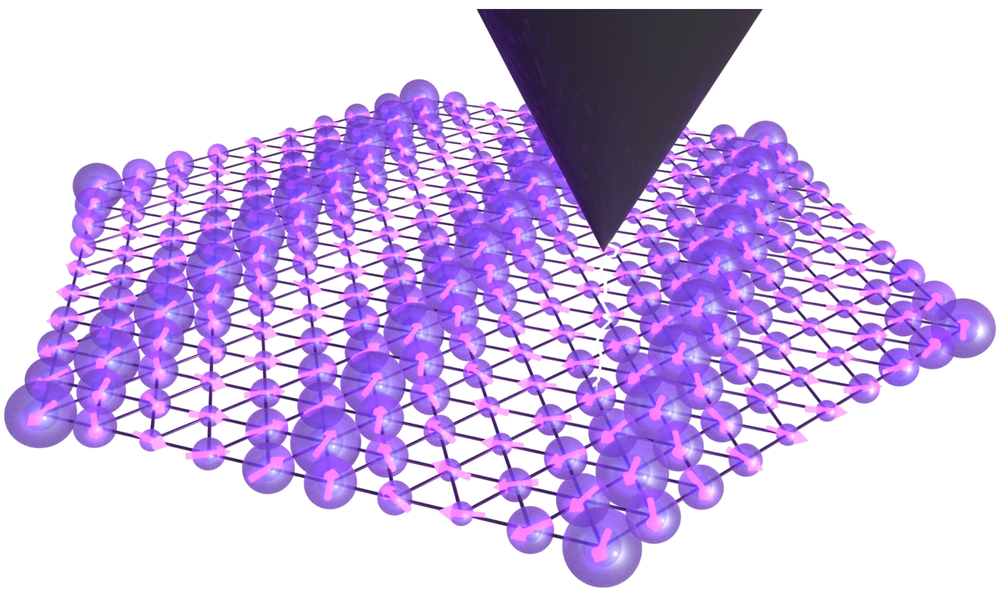
→ The strongest Artificial moiré multiferroic order is displayed by twisted $CrBr_3$ bilayers

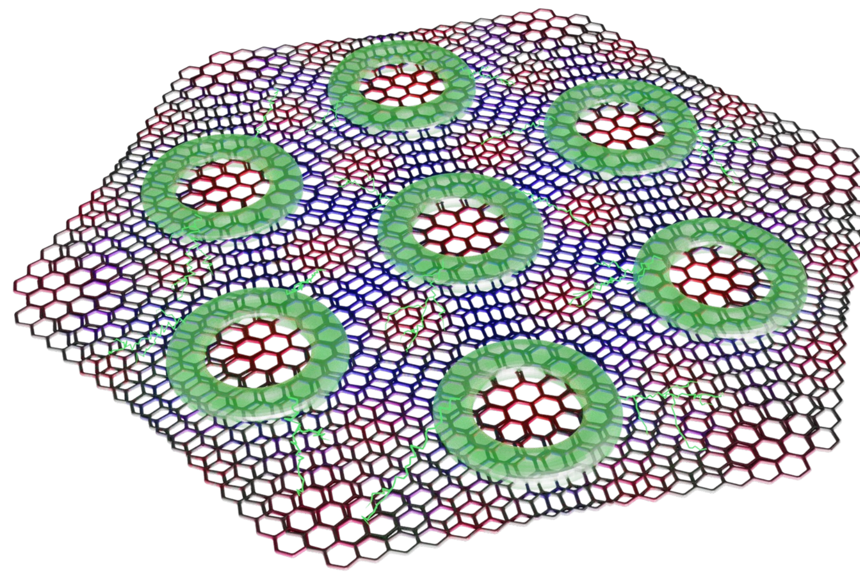
→ Accessible magnetic skyrmion phases with electric fields



Adolfo O. Fumega and Jose L. Lado, *2D Materials* 10, 025026 (2023)

# Multiferroic van der Waals Materials are promising for Novel Technological Applications





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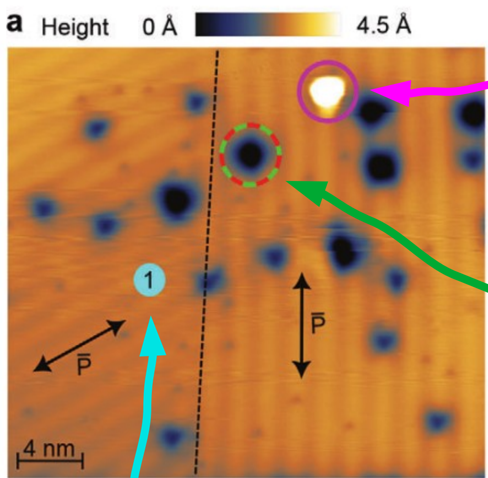
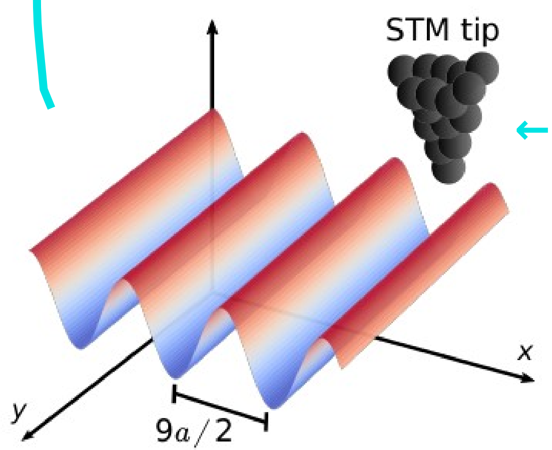
# Back-Up Slides

# Manipulation of multiferroic domains in monolayer $NiI_2$



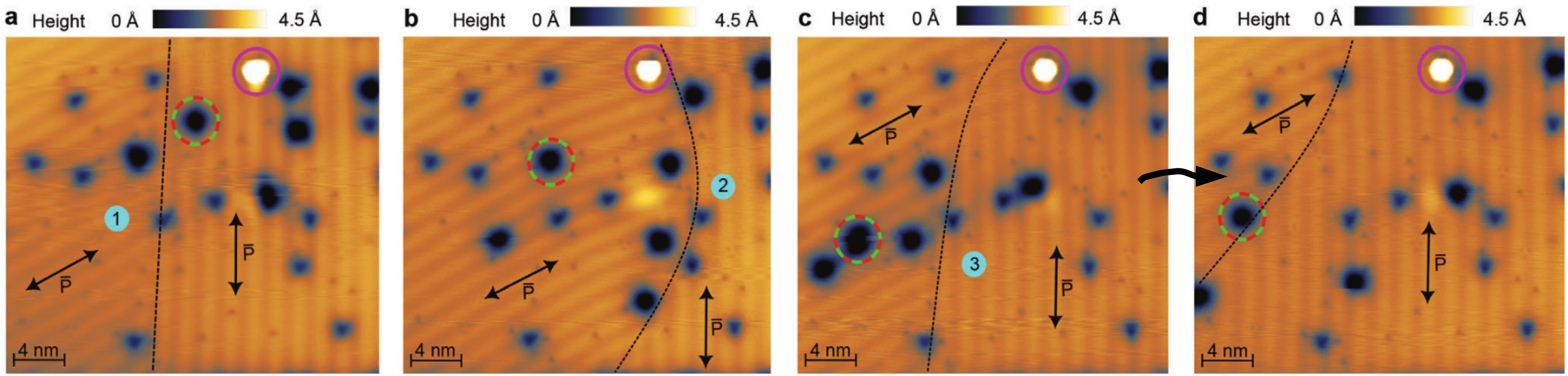

Neutral defect
(used as spatial reference)

Mobile charged defect



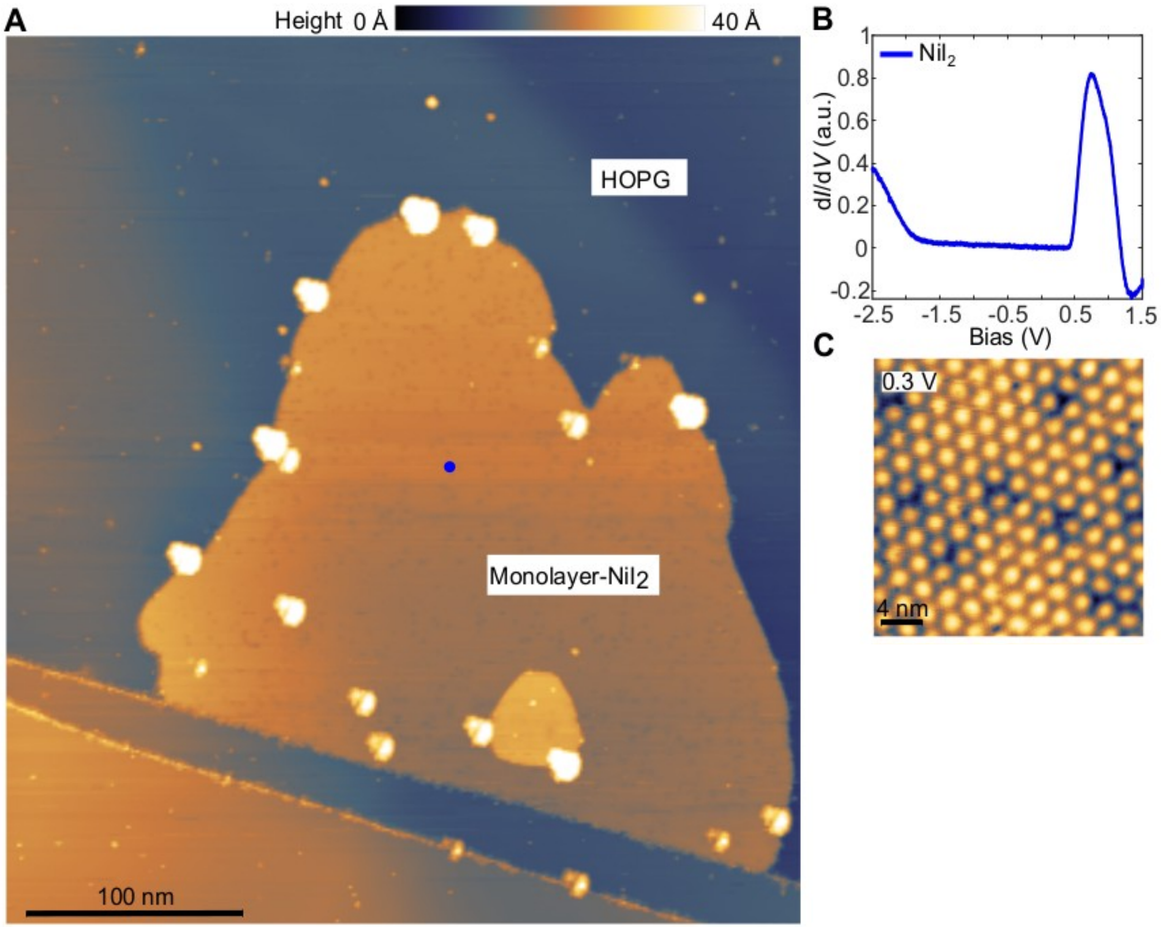

← Voltage pulses

# Manipulation of multiferroic domains in monolayer $NiI_2$




Manipulation of multiferroic domains!

# STM characterization of monolayer $NiI_2$




Monolayer $NiI_2$ is an insulator with a gap of 2.3 eV (from -1.9 to 0.4 V)

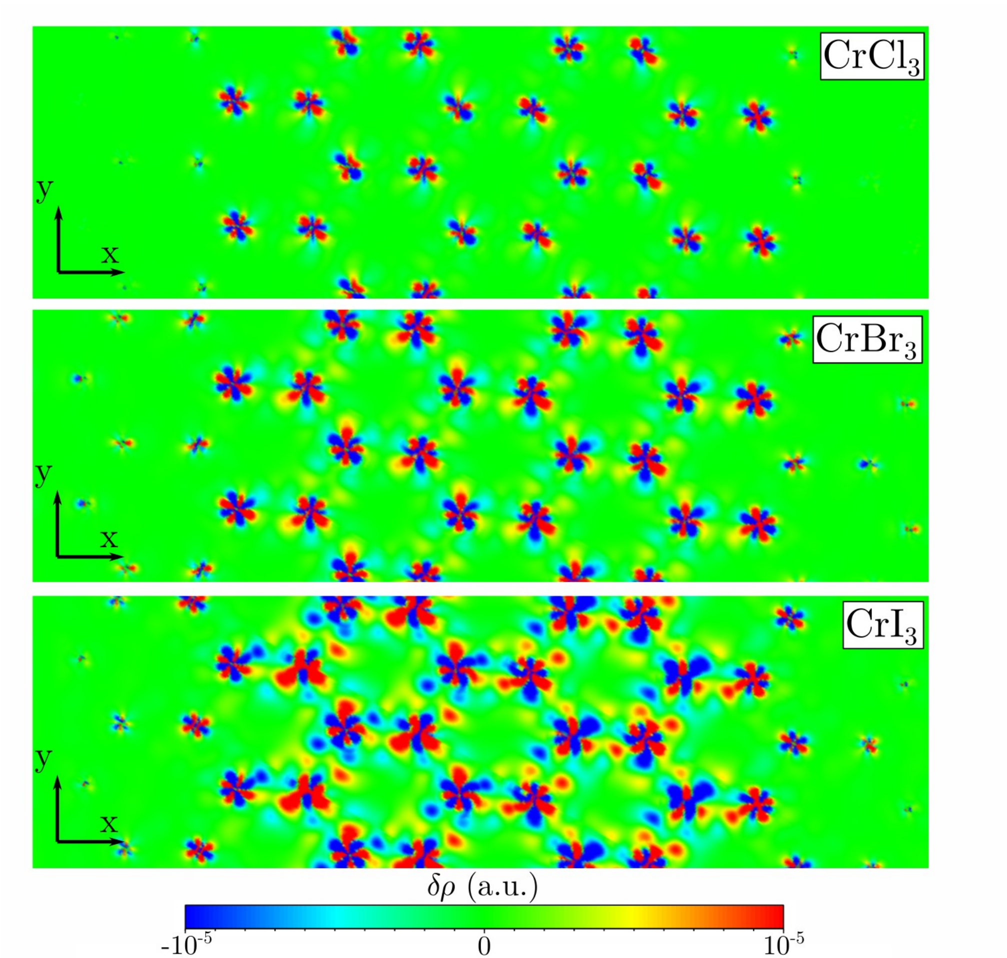
Scan within the gap (HOPG states)

→

Moiré pattern between triangular lattices of $NiI_2$ and HOPG

# Ab initio calculations

## Electric polarization in a spin texture of $CrX_3$




Electronic Density difference

**Going down in the halide group**

↓

**Increase SOC**

↓

**Increase $\delta\rho$**