Origin and Microscopic Mechanisms of Magnetoelectric Coupling in Multiferroic Manganites

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Origins of Ferroelectricity

spontaneous electric polarization $\mathbf{P} = \langle \Psi | \hat{\mathbf{r}} | \Psi \rangle$

inversion symmetry needs to be broken

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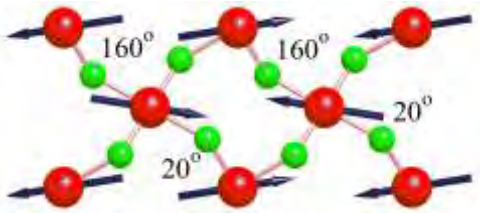

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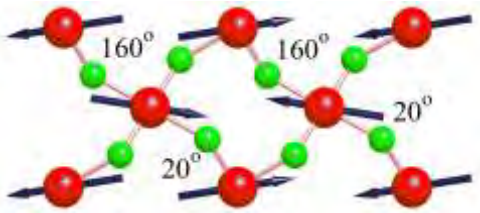

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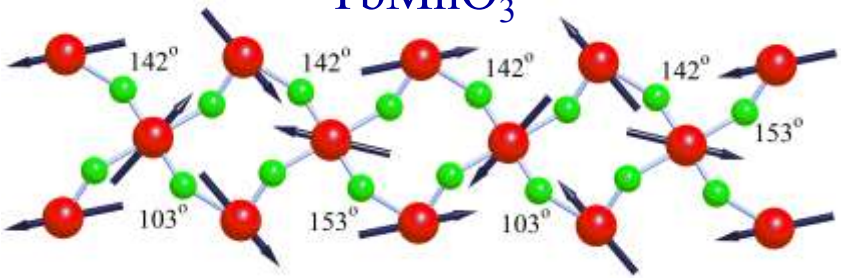

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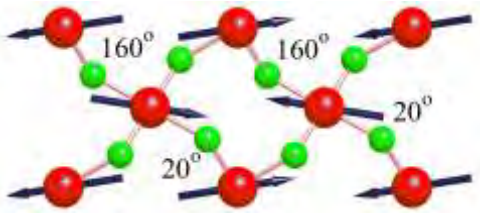

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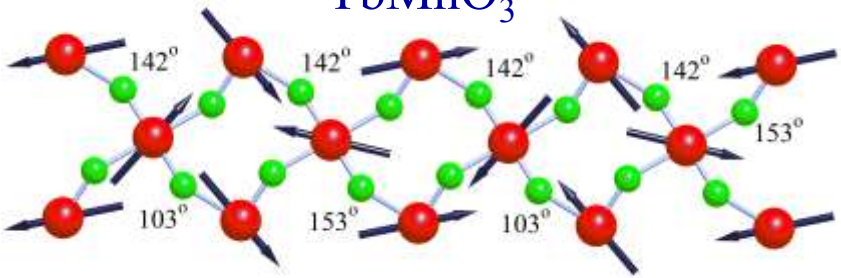

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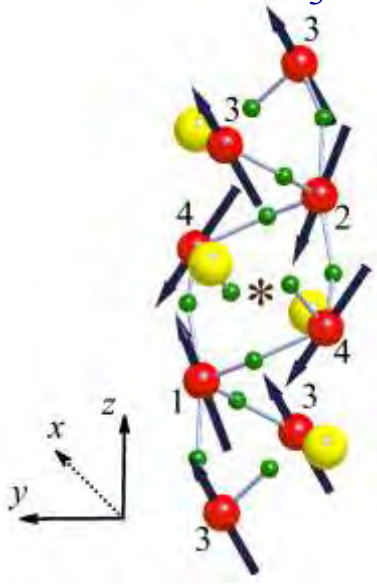

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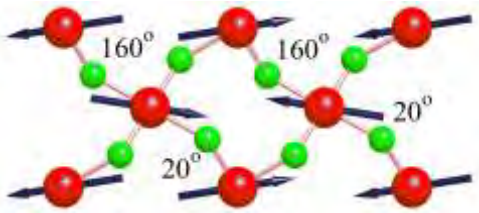
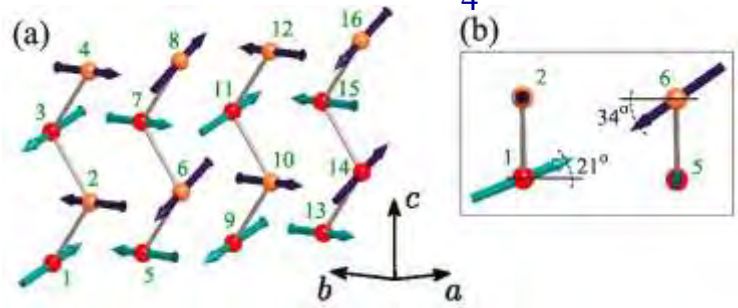


$MnWO_4$



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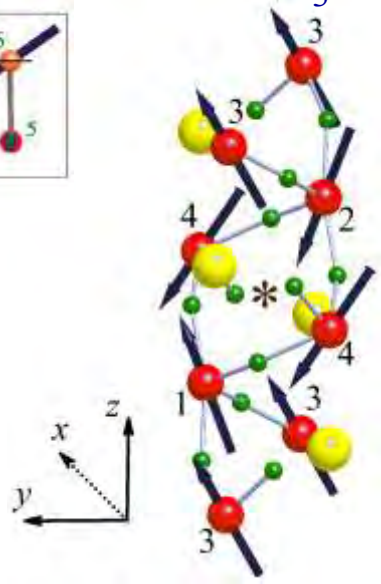

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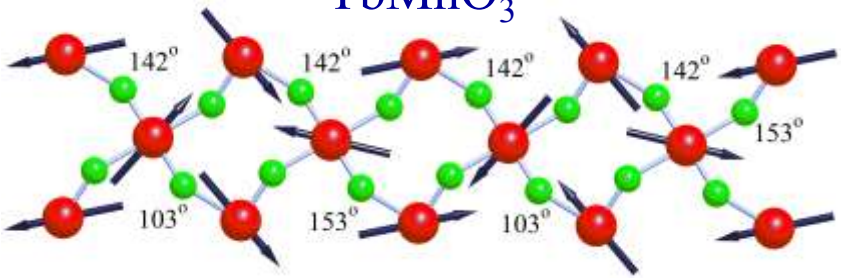


Improper Multiferroics

strong coupling

$$\mathbf{M} = \langle \Psi | \hat{\mathbf{S}} | \Psi \rangle \quad \Leftrightarrow \quad \mathbf{P} = \langle \Psi | \hat{\mathbf{r}} | \Psi \rangle$$

Magnetic structure — Electric polarization

P is driven by **M**

Contents

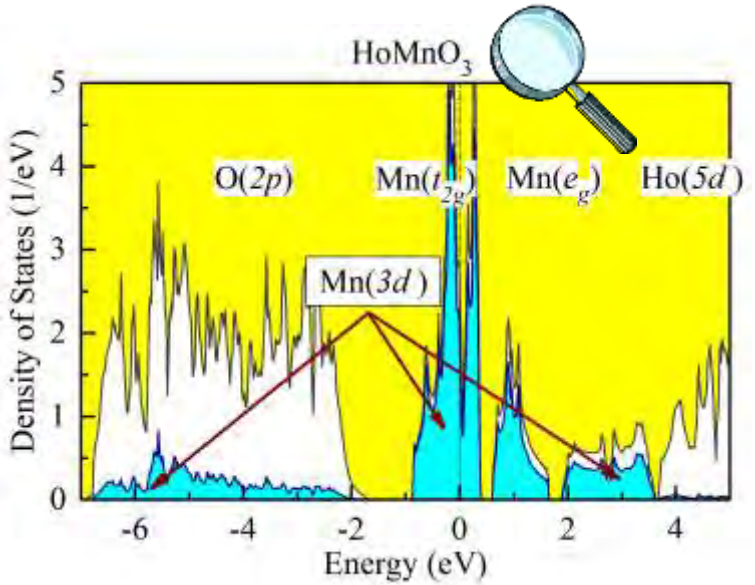
1. complex spin structures: the origin
2. spin spirality and spontaneous polarization
3. Hund's rule physics and inversion symmetry breaking
4. microscopic model
5. ferroelectricity and ferromagnetism

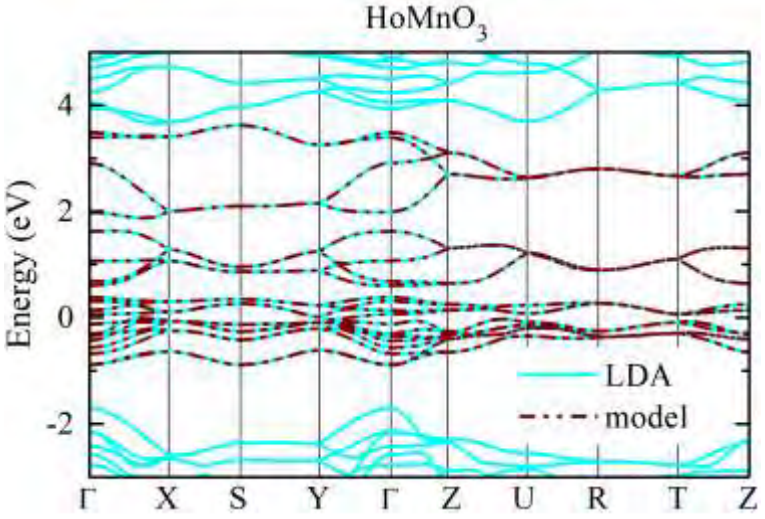
Collaboration

Sergey Nikolaev (poster….)
Vladimir Mazurenko
Mariya Valentyuk

RSF Project No. 14-12-00306

"Realistic Modeling"





- effective Hamiltonian for magnetic *3d* bands:

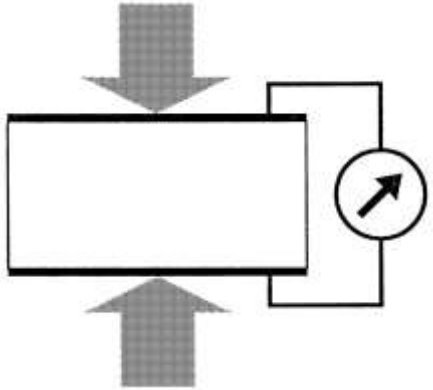
$$\hat{\mathcal{H}}_e = \sum_{ij}\sum_{\alpha\beta} t_{ij}^{\alpha\beta}\hat{c}_{i\alpha}^{\dagger}\hat{c}_{j\beta} + \frac{1}{2}\sum_{i}\sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta}\hat{c}_{i\alpha}^{\dagger}\hat{c}_{i\gamma}^{\dagger}\hat{c}_{i\beta}\hat{c}_{i\delta}$$

Downfolding and /or
Wannier functions technique

RPA (GW) and /or
constrained DFT

- solution: unrestricted Hartree-Fock
- details: J. Phys.: Condens. Matter **20**, 293201 (2008)

Berry-phase theory of Polarization



in periodic systems, P is related to the current flowing through the sample

$$\Delta\mathbf{P} = \mathbf{P}(\Delta t) - \mathbf{P}(0) = \int_0^{\Delta t} \mathrm{d}t\, \mathbf{j}(t)$$

- depends on the phase of the wavefunction (Berry phase)
- only difference is measurable

$$\mathbf{P} = -\frac{ie}{(2\pi)^3} \sum_{n=1}^{M} \int_{\mathrm{BZ}} \langle n\mathbf{k}|\nabla_{\mathbf{k}}|n\mathbf{k}\rangle d\mathbf{k}$$

in **k**-space
(via Berry connection)

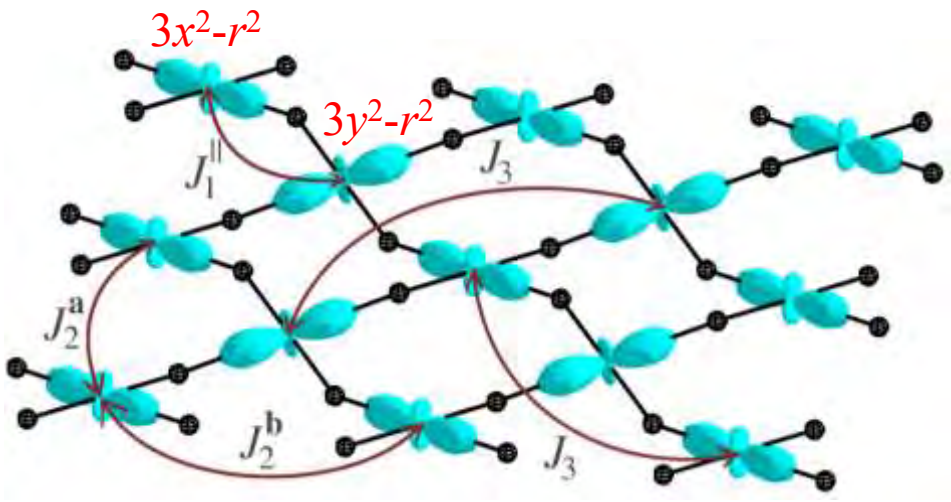
$$\mathbf{P} = -\frac{e}{V} \sum_{n=1}^{M} \int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$

in **r**-space
(via Wannier functions)

D. Vanderbilt and R. D. King-Smith, Phys. Rev. B **48**, 4442 (1993);
R. Resta, Rev. Mod. Phys. **66**, 899 (1994); J. Phys.: Condens. Matter **22**, 123201 (2010).

Orbital Ordering
and
Competing Exchange Interactions

Example: $TbMnO_3$ (*Pbnm* symmetry)



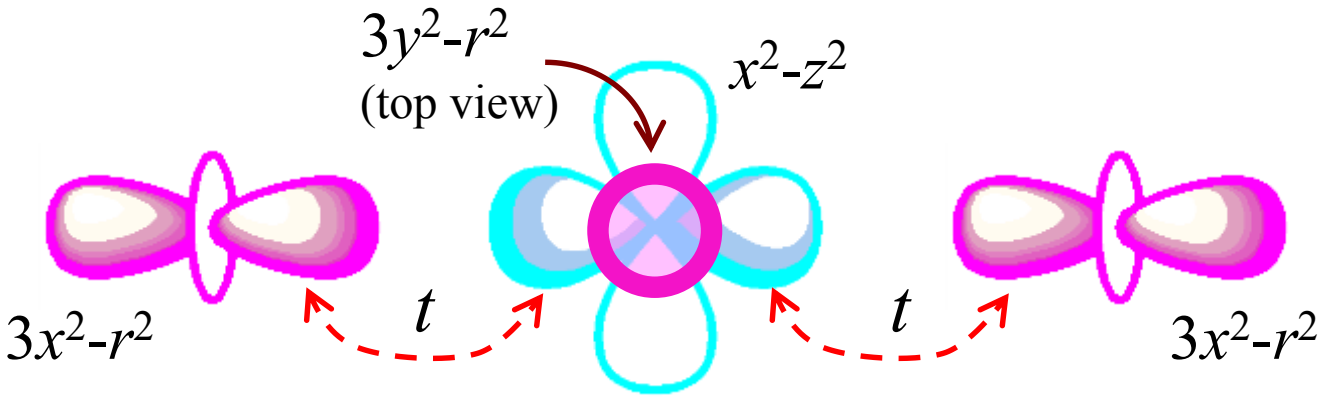
$$J_1^{\parallel} = -3.7 \quad J_3 = -2.3$$
$$J_2^{\mathbf{a}} = -0.2 \quad J_2^{\mathbf{b}} = -1.2$$

(in meV)

Key players: $J_1{}^{\parallel}$, $J_2{}^{\mathbf{b}}$, and J_3

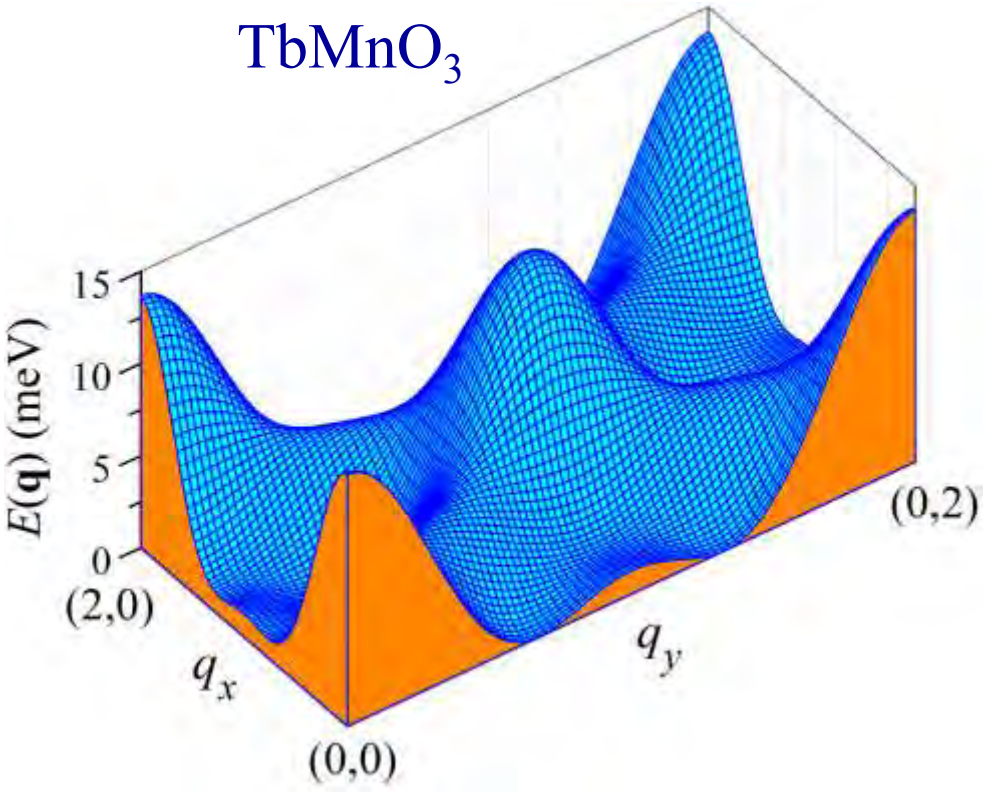
J. Phys. Soc. Jpn. **78**, 054710 (2009).

origin of long-range interactions:

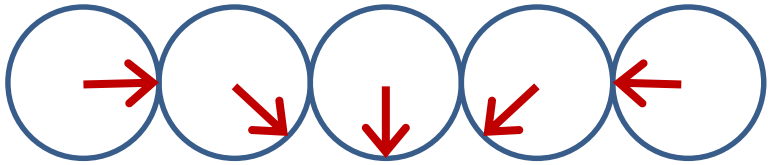


"super-super-exchange" ~ $1/U^3$ ➔ U should not be large

Magnetic ground state without spin-orbit coupling



homogeneous spin-spiral



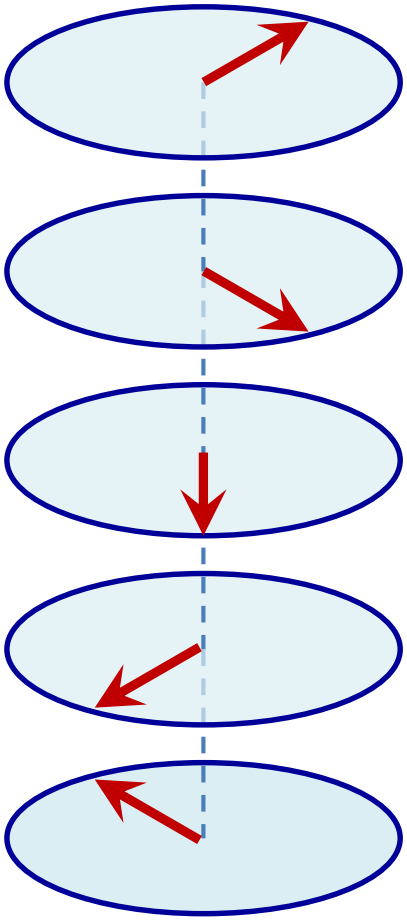
Theoretical minimum: $q_y \approx 0.675$
(units of reciprocal translations)

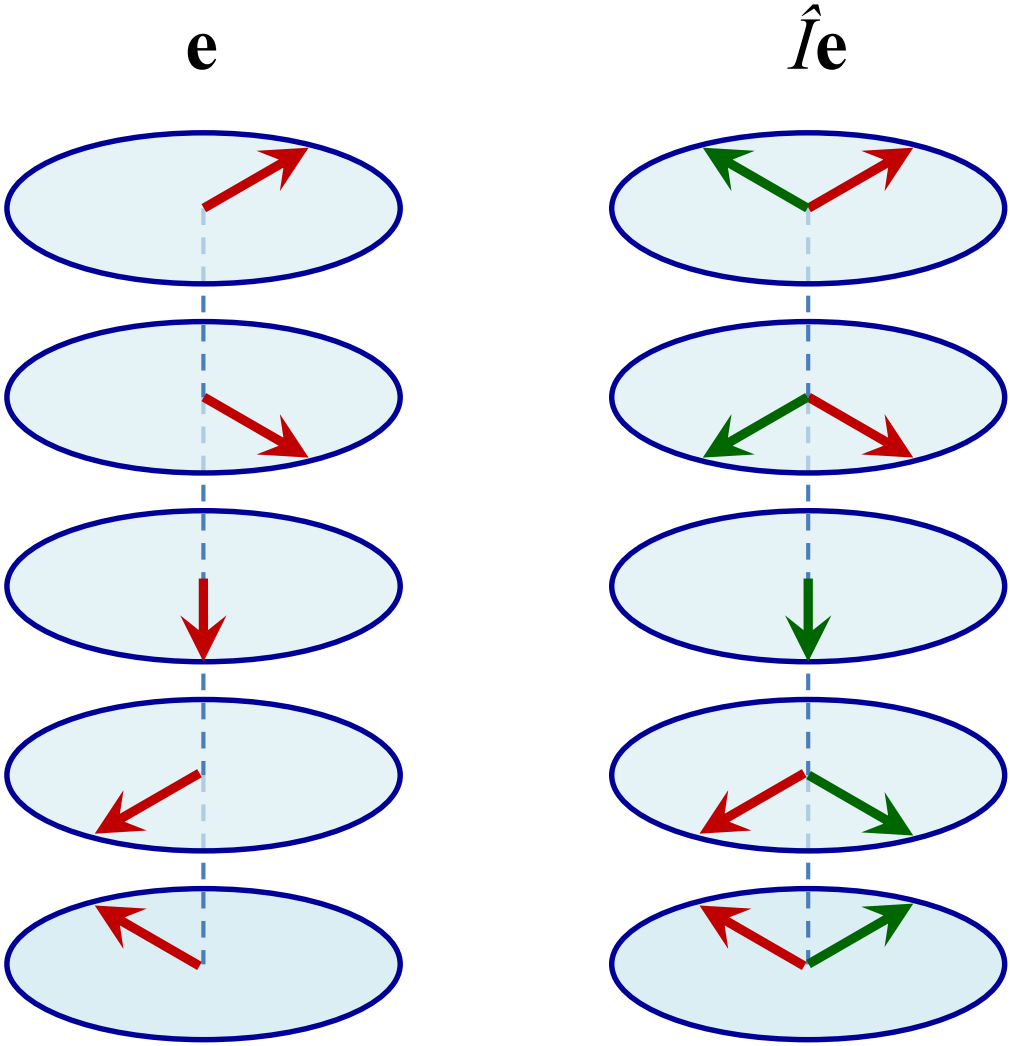
nearly fourfold periodic
magnetic structure
(experimental situation in $TbMnO_3$)

Phys. Rev. B **83**, 054404 (2011)

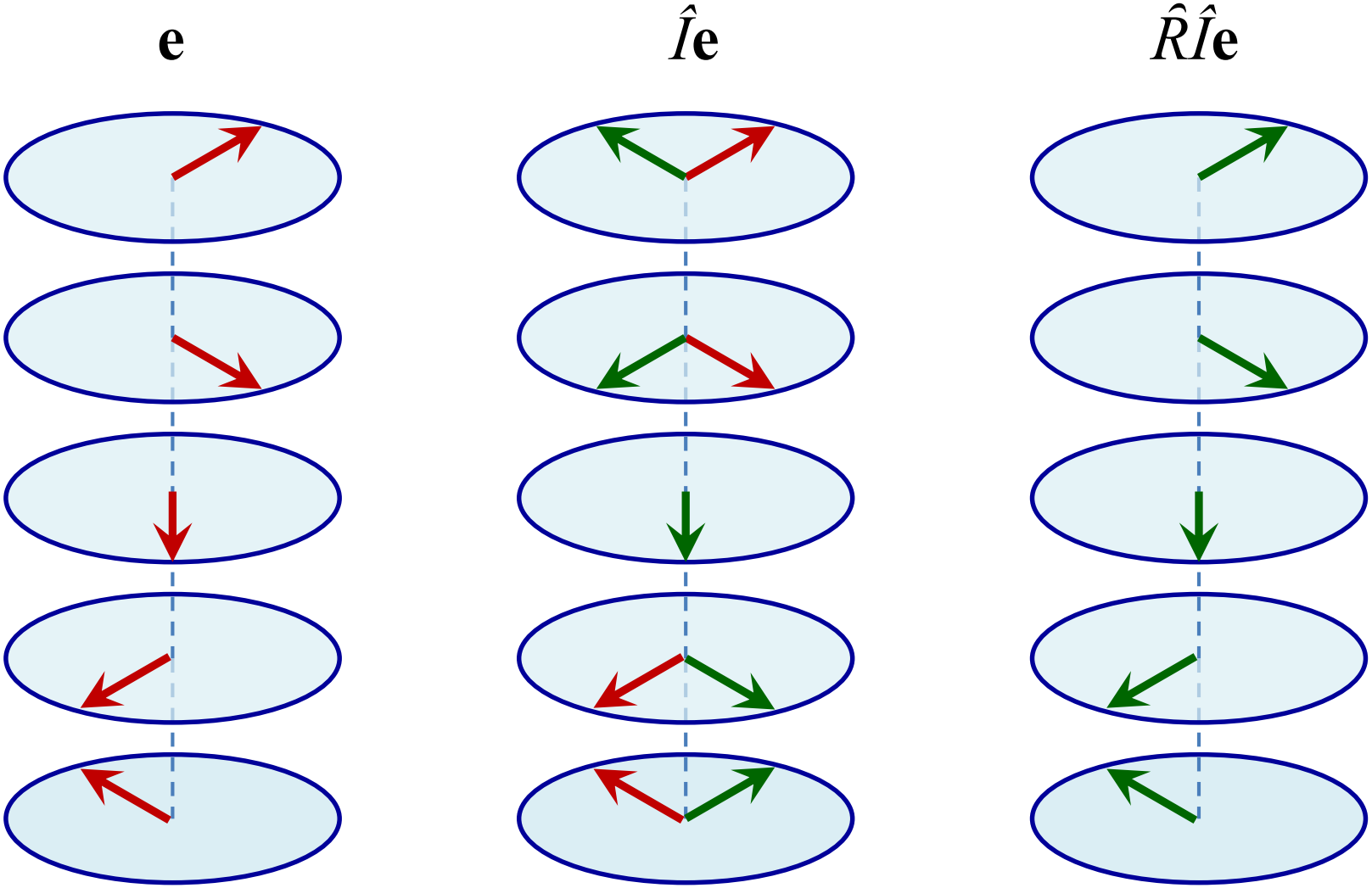
spin-spirality
and
spontaneous
electric polarization

e





formally, the inversion symmetry is broken, but….



the inversion can be always combined with the 180°-rotation of spins around the axis **n**||(**e**+$\hat{I}$**e**), *which is the same for all magnetic sites;*

➔ spontaneous electric polarization = 0

Very generally:

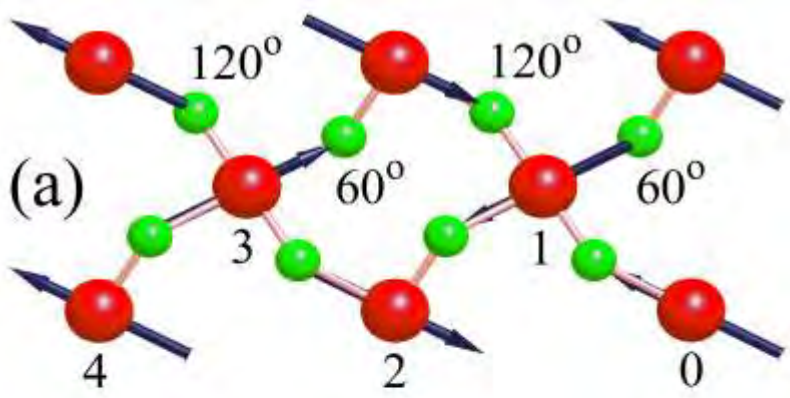
The spin-orbit interaction is needed in order to remove the spin rotation $\hat{R}$

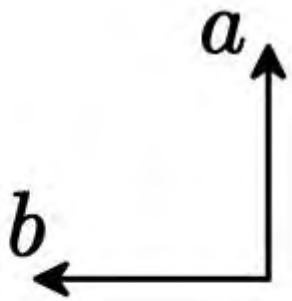
But:

The concrete scenario depend on the material (crystallographic symmetry)

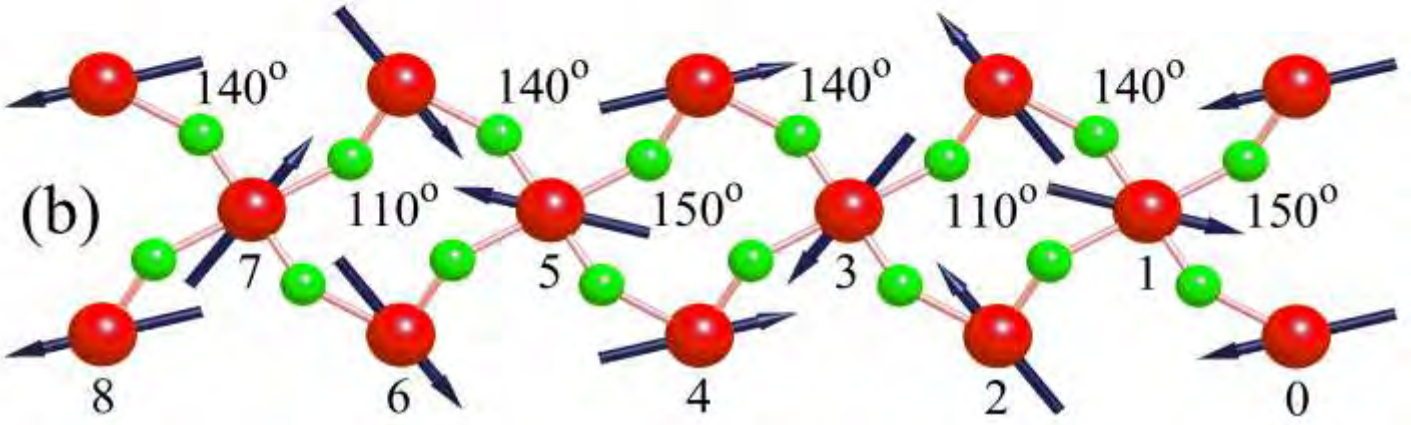
Example I: $HoMnO_3$ (*Pbnm* symmetry)

twofold



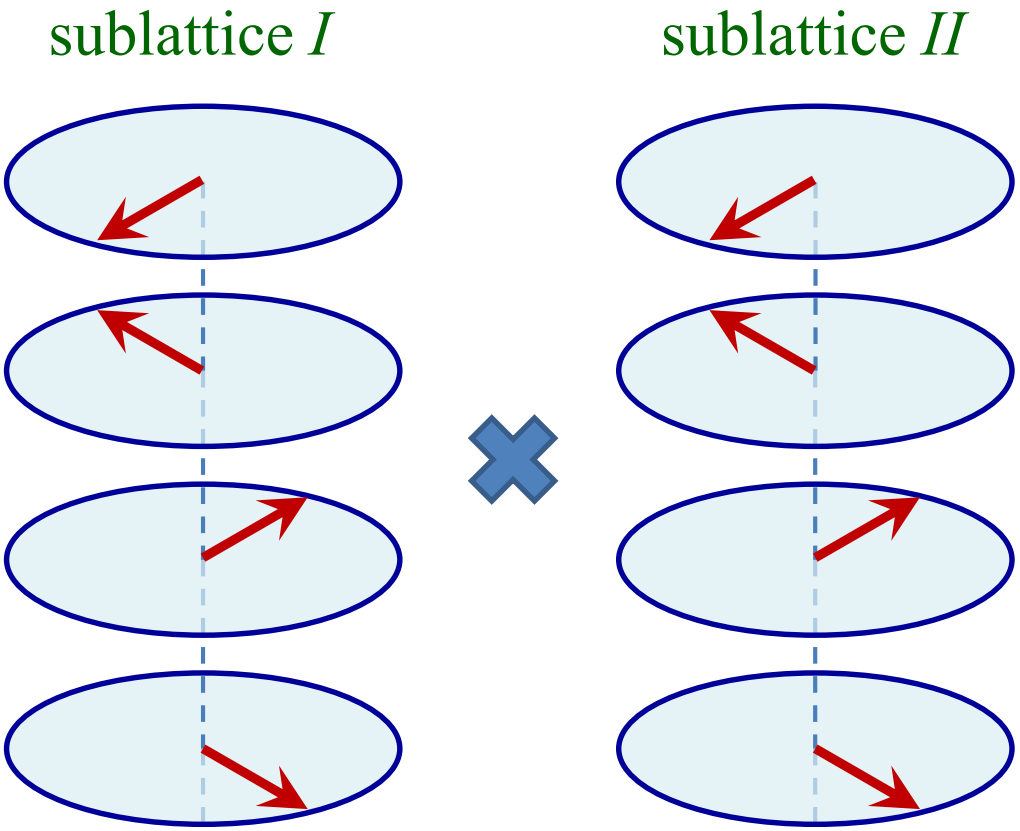


fourfold



Key mechanism: single-ion anisotropy deforms the spin spiral and breaks the inversion symmetry

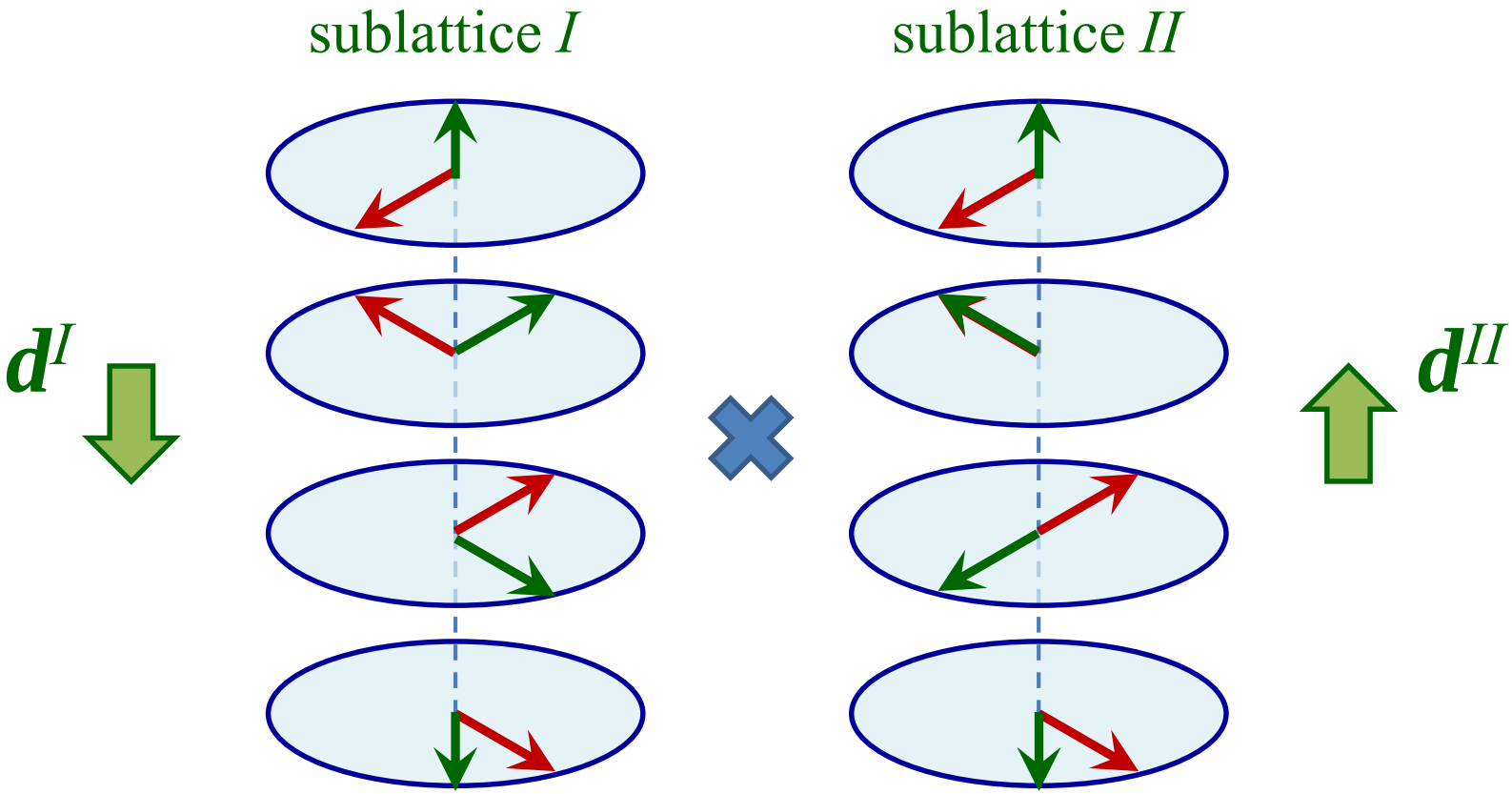
Example II: $MnWO_4$ (*P2/c* symmetry): Effect of isotropic exchange interactions



Spin spiral with the same chirality in both magnetic sublattices

Phys. Rev. B **87**, 144403 (2013)

Example II: $MnWO_4$ (*P2/c* symmetry): Isotropic versus Dzyaloshinskii-Moriya Interactions



the effects of isotropic and DM interactions are added

the effects of isotropic and DM interactions are subtracted

Sublattices become inequivalent → The unversion symmetry is broken

Phys. Rev. B **87**, 144403 (2013)

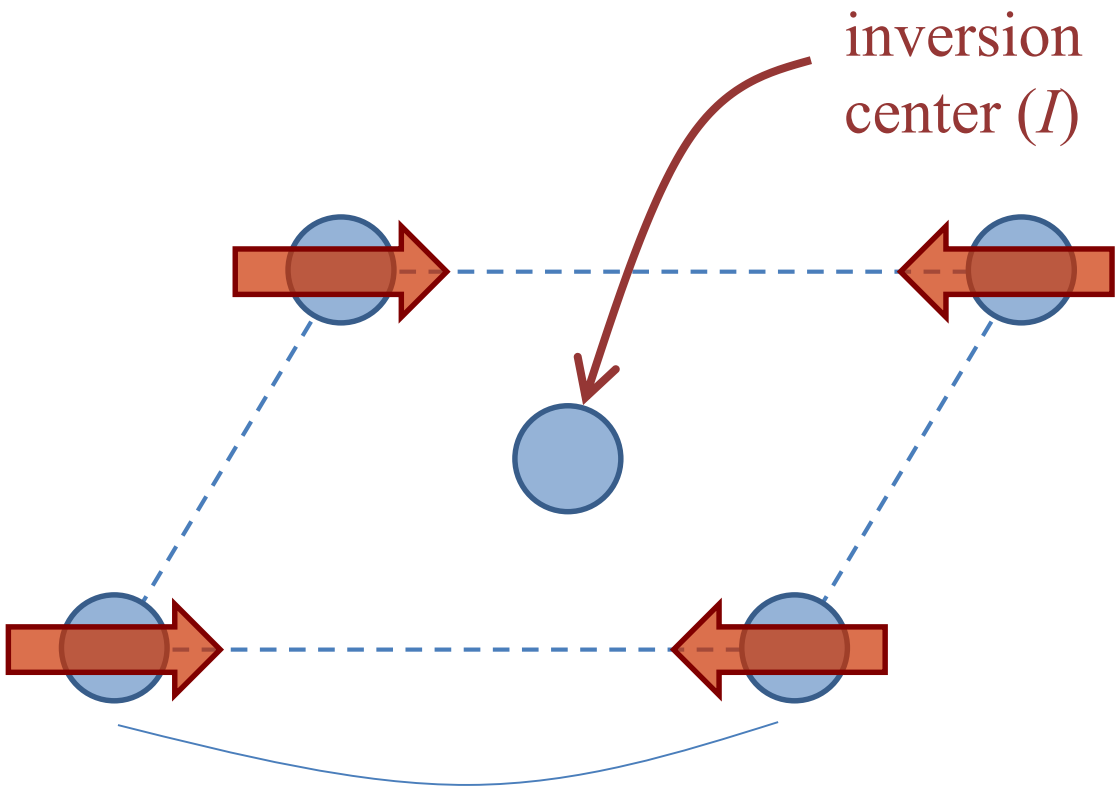
What is the origin of ferroelectricity
in the spin-spiral compounds?

Is it because of the spin-spiral structure itself
or
a deformation of this structure?

Why manganites?

Importance of the Hund's rule physics

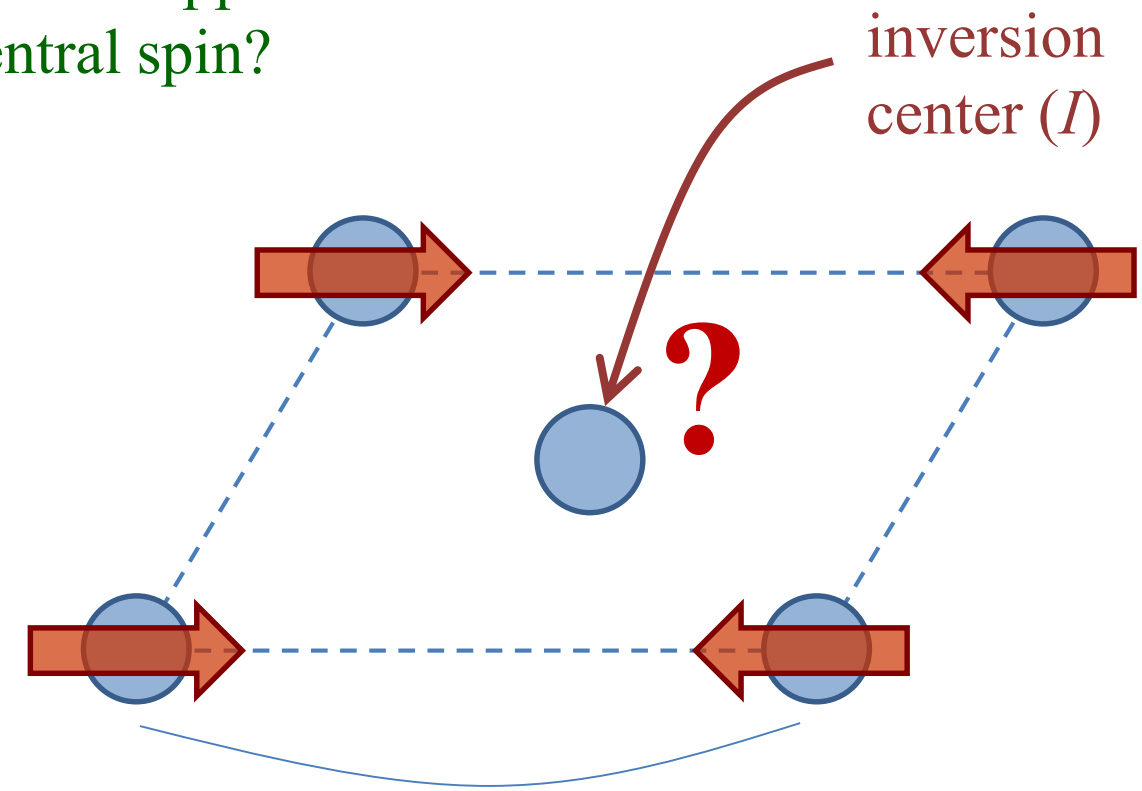
Origin of the Magnetic Inversion Breaking in Orthorhombic Manganites



Long-range antiferromagnetic interactions

Origin of the Magnetic Inversion Breaking in Orthorhombic Manganites

What will happen with the central spin?



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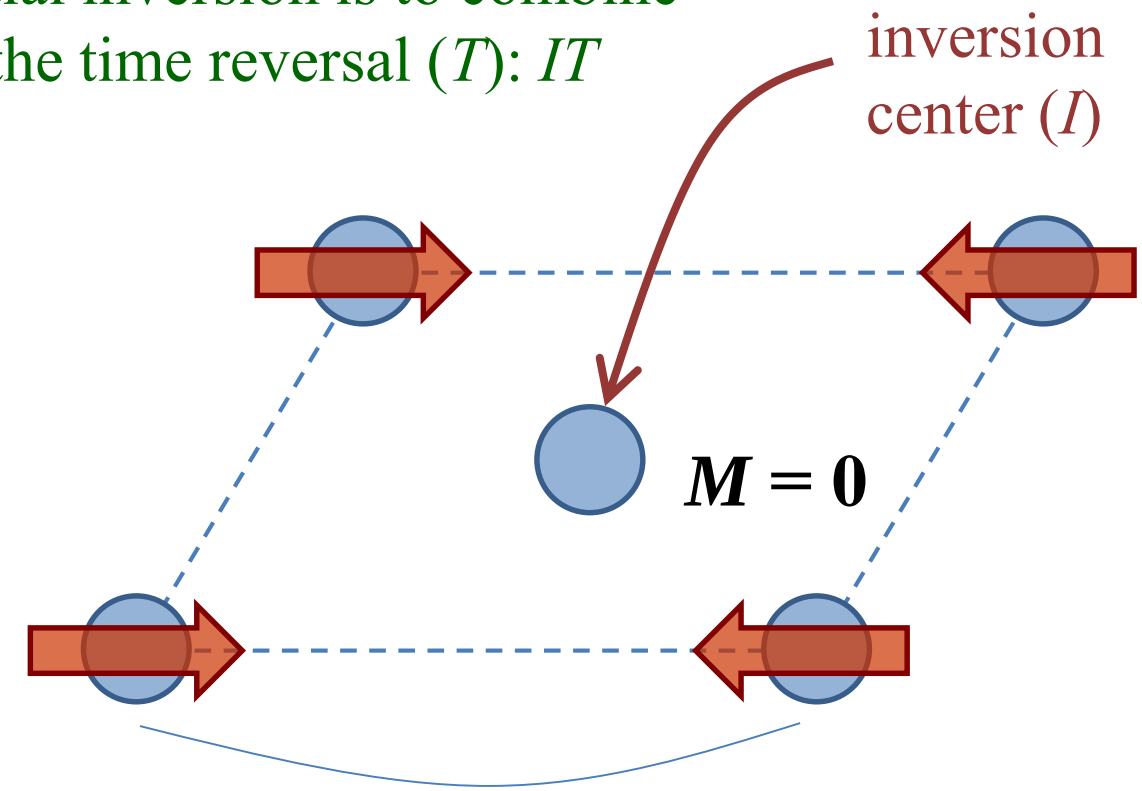
The only possibility to preserve the spatial inversion is to combine it with the time reversal (T): IT



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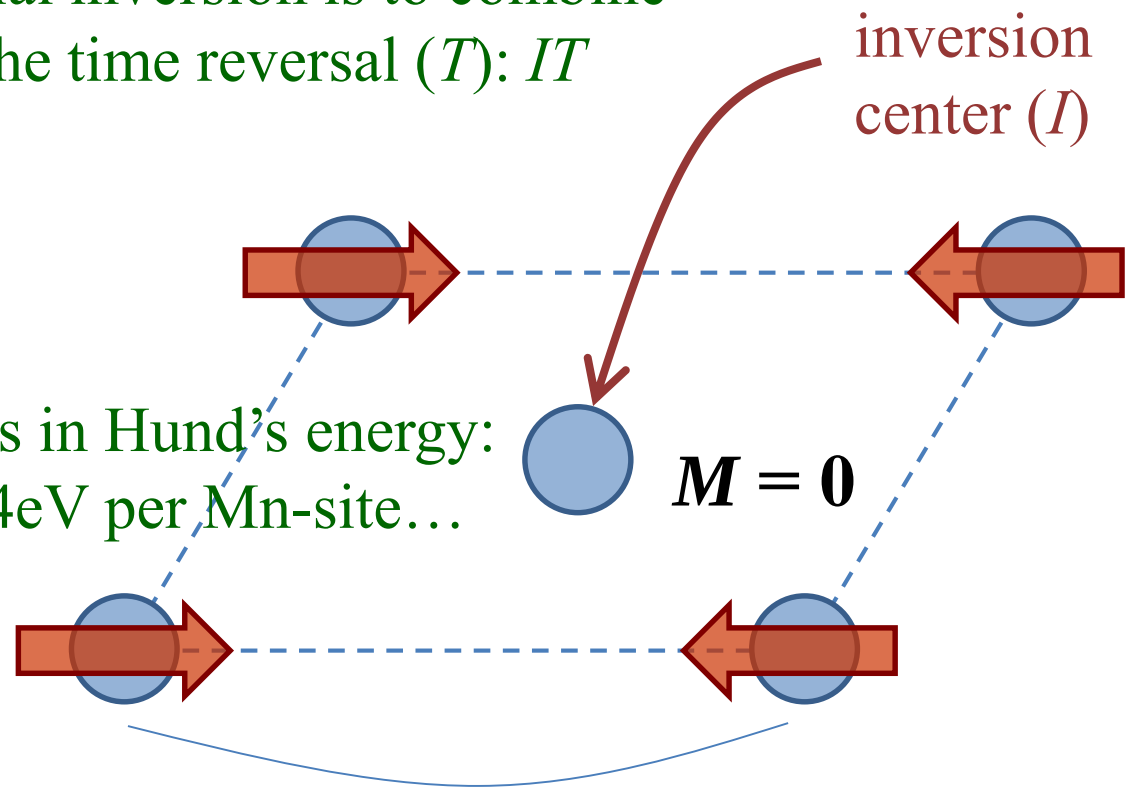
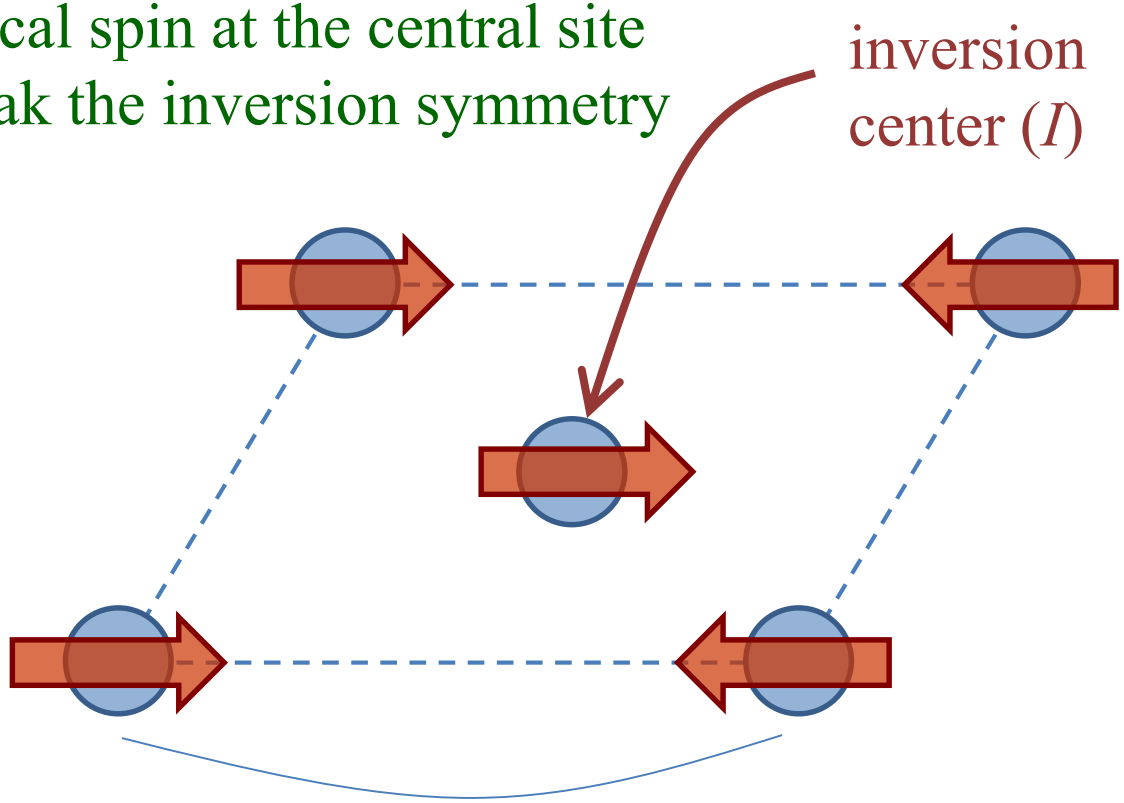


gigantic loss in Hund's energy: $J_H M^2/4 \sim 4$eV per Mn-site…

Long-range antiferromagnetic interactions

Origin of the Magnetic Inversion Breaking in Orthorhombic Manganites

It is more favorably energetically
to have local spin at the central site
but to break the inversion symmetry



Long-range antiferromagnetic interactions

Microscopic Model

Step I: from mean-field Hartree-Fock to Double Exchange model

$$\hat{H}_{ij}^{\mathrm{MF}} = \hat{t}_{ij} + \hat{\mathcal{V}}_i \delta_{ij} \quad \Rightarrow \quad \hat{H}_{ij}^{\mathrm{DE}} = \xi_{ij} \hat{t}_{ij} + \hat{\mathcal{V}}_i^{\uparrow} \delta_{ij}$$

where

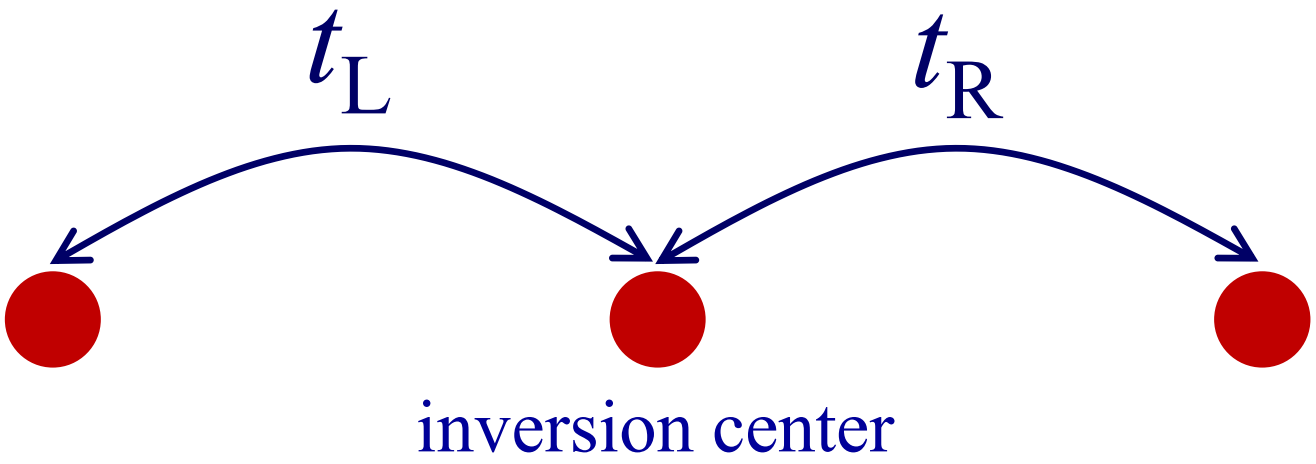
$$\hat{\mathcal{V}}_i = \begin{pmatrix} \hat{\mathcal{V}}_i^{\uparrow} & 0 \\ 0 & \hat{\mathcal{V}}_i^{\downarrow} \end{pmatrix}$$

$$\xi_{ij} = \cos\frac{\theta_i}{2}\cos\frac{\theta_j}{2} + \sin\frac{\theta_i}{2}\sin\frac{\theta_j}{2} e^{-(\phi_i - \phi_j)}$$

HF potential

ξ_{ij}=1 for FM bonds, ξ_{ij}=0 for AFM bonds

Basic Mechanism of the Inversion Symmetry Breaking



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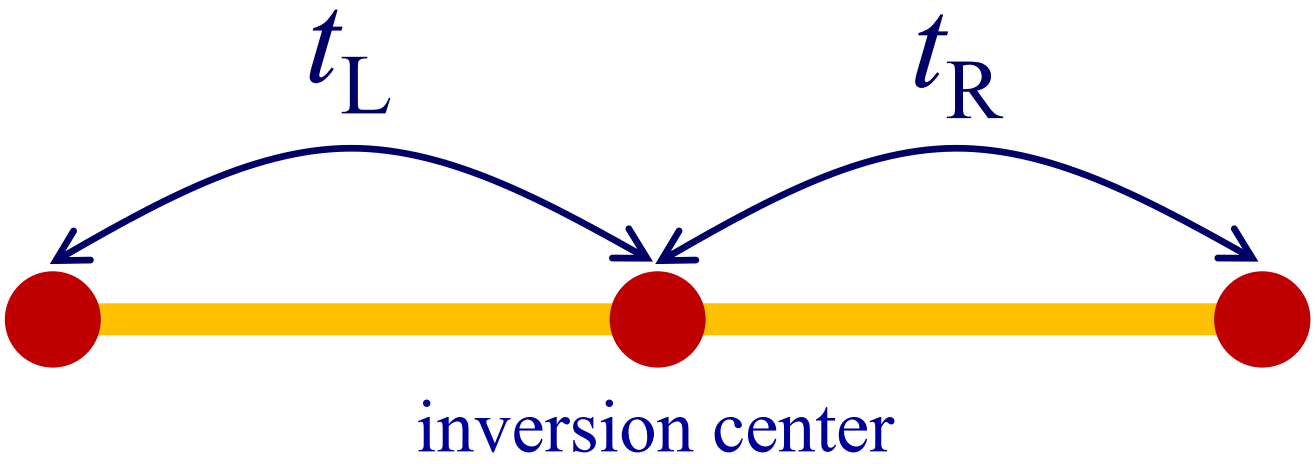
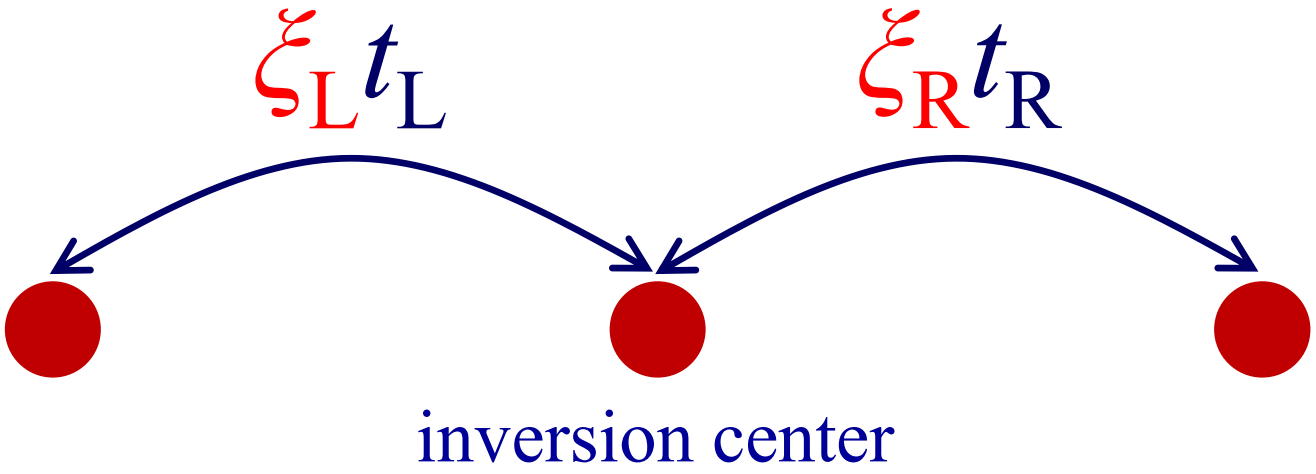


- $t_R = t_L$
- bonds are equivalent
- inversion symmetry is preserved

Basic Mechanism of the Inversion Symmetry Breaking



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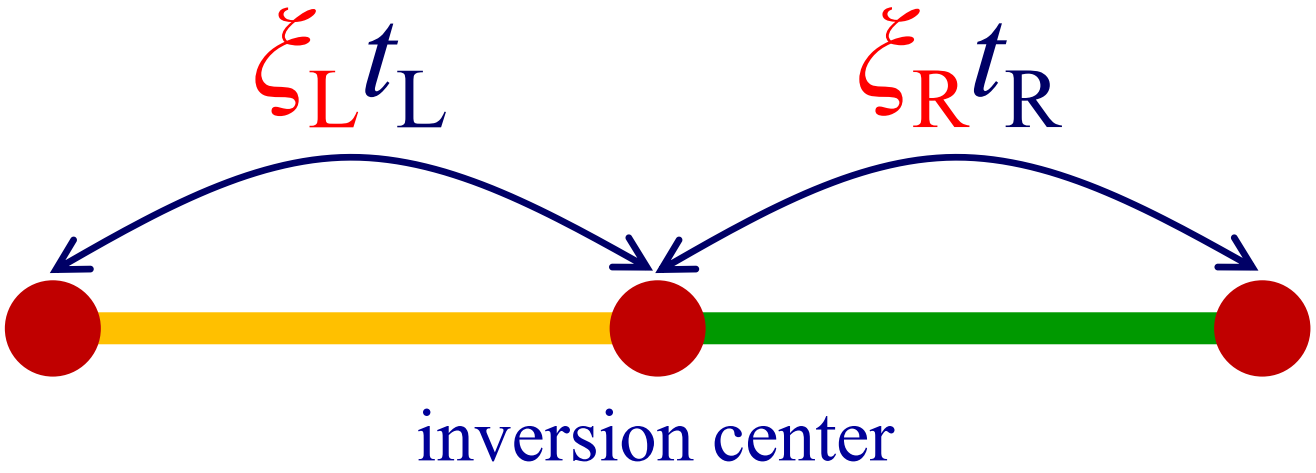
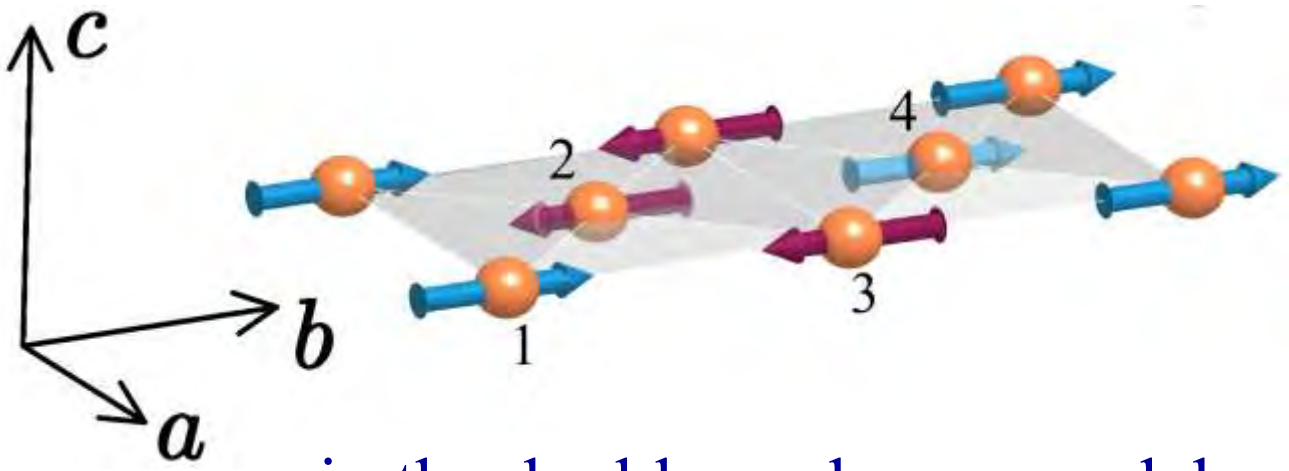


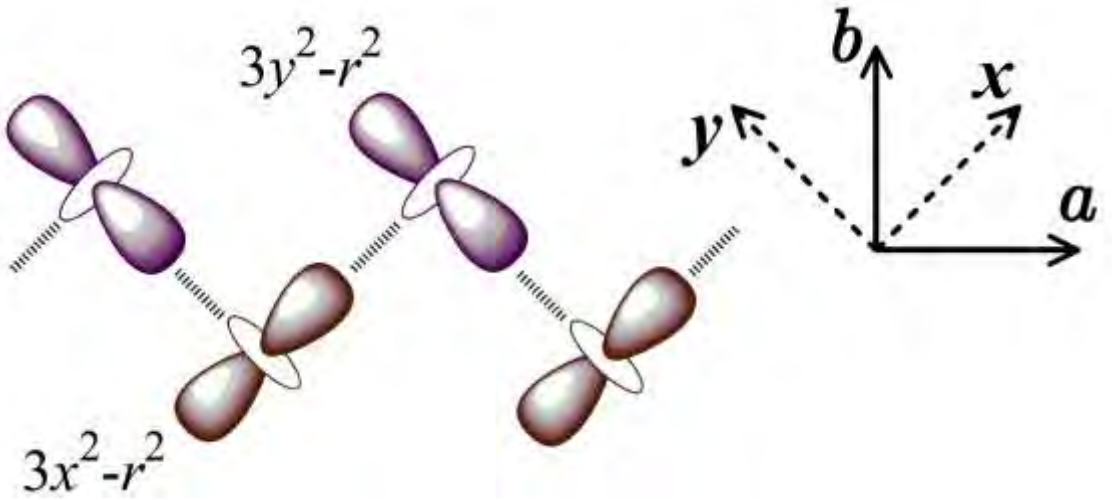
- $\xi_R \neq \xi_L$
- bonds are inequivalent
- inversion symmetry is broken

Simplest Example: E-phase



$YMnO_3$
$HoMnO_3$

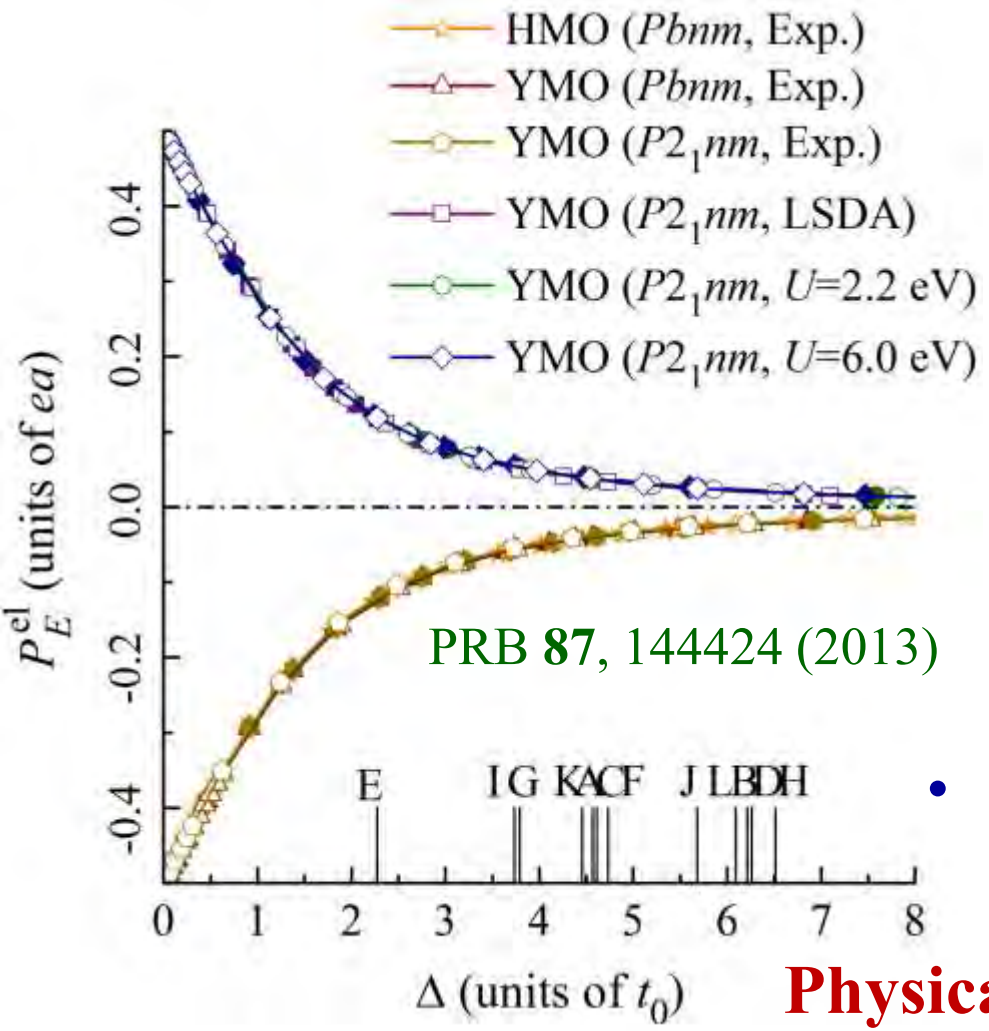
in the double exchange model:



see also

P. Barone, K. Yamauchi, and S. Picozzi,
Phys. Rev. Lett. **106**, 077201 (2011)

Contribution of e_g bands to the polarization in the E-phase



PRB **87**, 144424 (2013)

$\hat{t}$ and △ from "downfolding" of the HF Hamiltonian;

Then,

$$\mathbf{P} = -\frac{ie}{(2\pi)^3}\sum_{n=1}^{M}\int_{\mathrm{BZ}}\langle n\mathbf{k}|\nabla_{\mathbf{k}}|n\mathbf{k}\rangle d\mathbf{k}$$

The value of P is controlled by
1. e_g-level splitting △;
2. lattice parameters a, b, and c

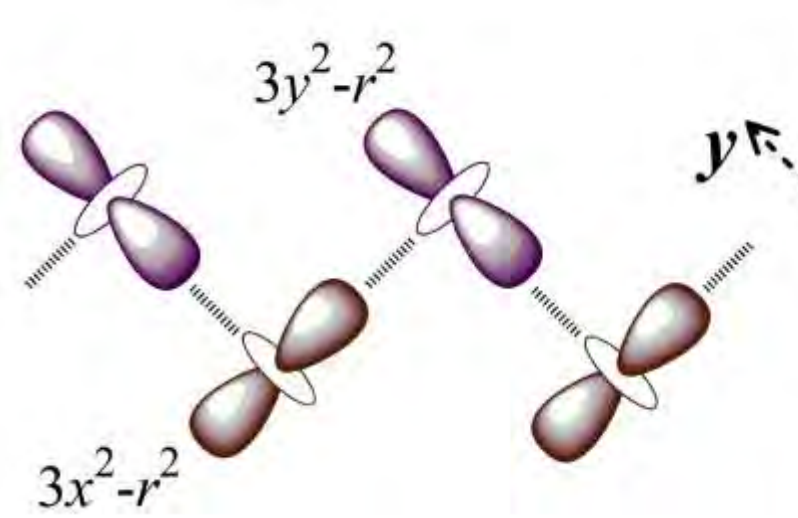
- does not depend on buckling of Mn-O-Mn bonds

Physically relevant limit: "Large △"

Universal dependence on △, obtained for different crystal structures ($HoMnO_3$ and $YMnO_3$, both experimental and theoretically optimized)

Useful consequence:

(analogy with superexchange interactions)



$$\mathbf{P} = -\frac{e}{V}\sum_{n=1}^{M}\int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$

Atomic limit: **P** = 0

Phys. Rev. B **87**, 144424 (2013)

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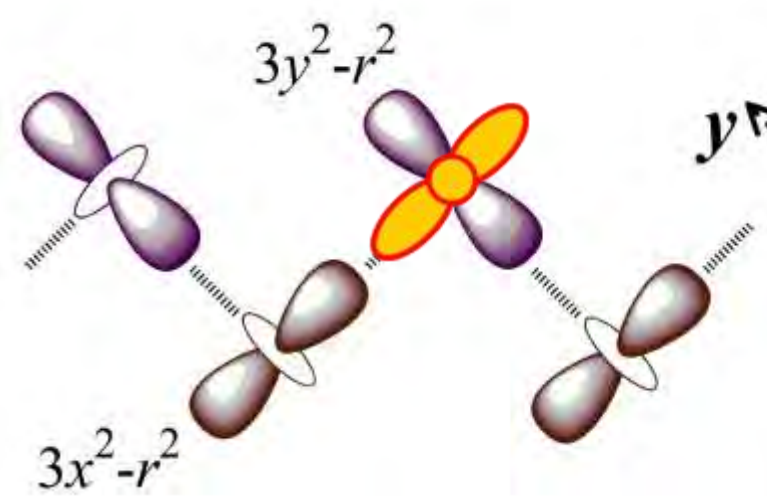


$$\mathbf{P} = -\frac{e}{V}\sum_{n=1}^{M}\int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r}$$

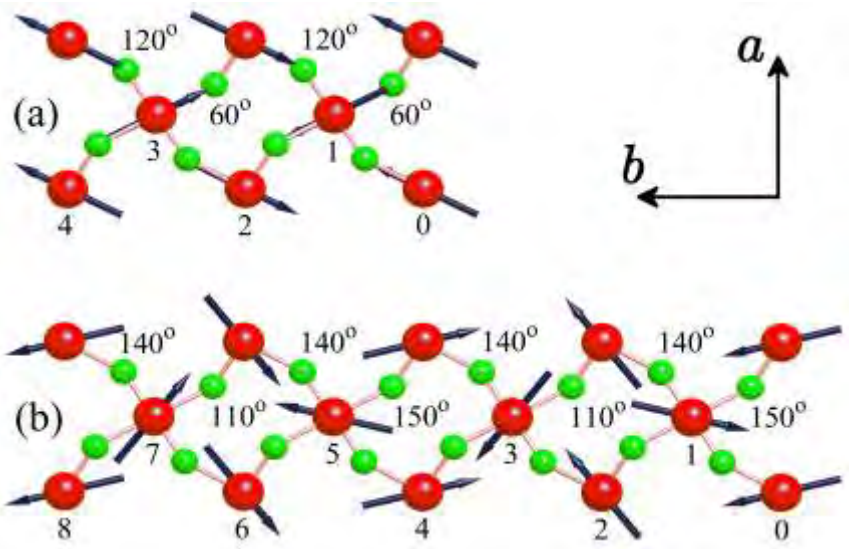
Atomic limit: $\mathbf{P} = 0$

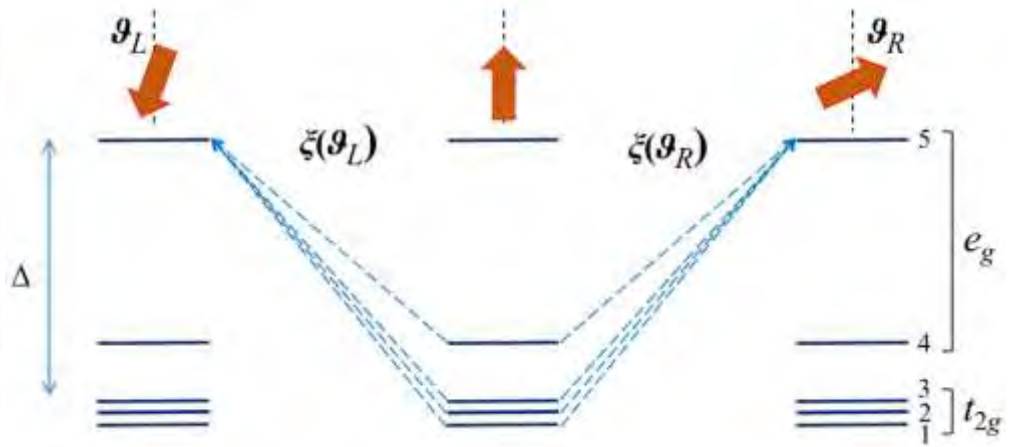
Perturbation theory for Wannier functions: $W_{ij} \sim \frac{t_{ij}}{\Delta}$

Asymmetric Wannier-weight transfer ➔ finite **P**

Phys. Rev. B **87**, 144424 (2013)

DE model: general expression





$$\frac{1}{\Delta^2}\sum_{m\le 4}|\mathrm{t}_{ij}^{5m}|^2$$

lattice model
perturbation theory

$\sim \mathbf{e}_j\cdot\mathbf{e}_j$

$$\mathbf{P} = -\frac{e}{V}\sum_{n=1}^{M}\int \mathbf{r}\, w_n^2(\mathbf{r})\, d\mathbf{r} \quad \Rightarrow \quad \mathbf{P}_i = \frac{e}{V}\sum_j \Delta\boldsymbol{\tau}_{ji}|\xi_{ij}|^2 w_{ij}^2$$

$$P^a = \frac{1}{2L}\sum_{i=0}^{2L-1}(-1)^i \mathbf{e}_i\cdot\mathbf{e}_{i+1}P_E \qquad \text{where} \qquad P_E = \frac{ea}{V_0}\left(w_{01}^2 - w_{10}^2\right)$$

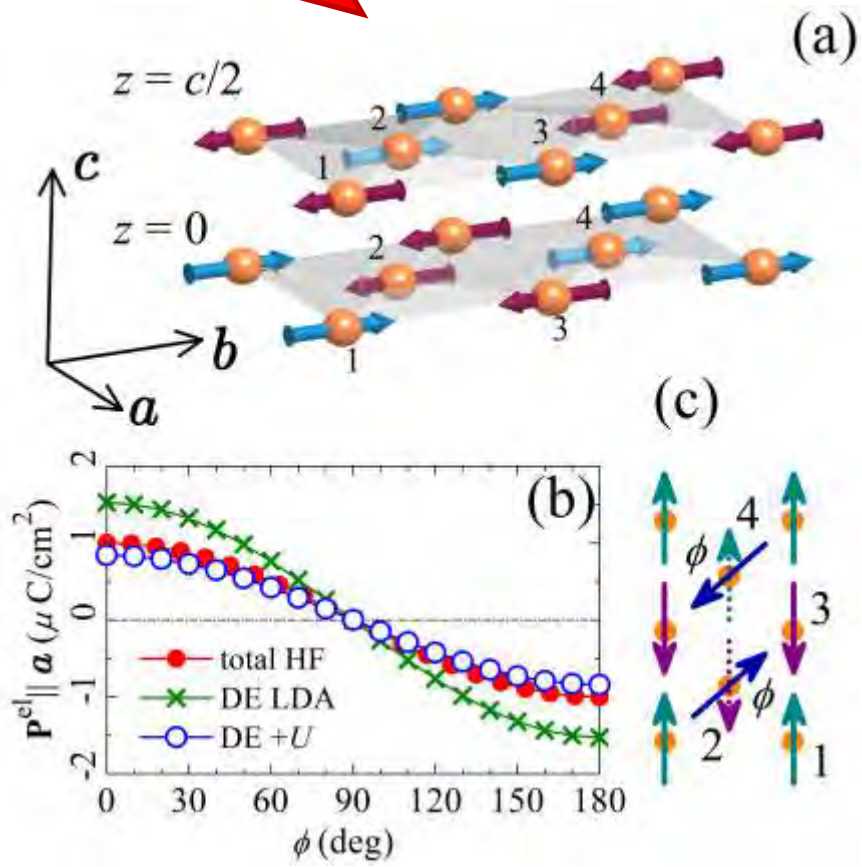
polarization of (zigzag) E-type AFM phase

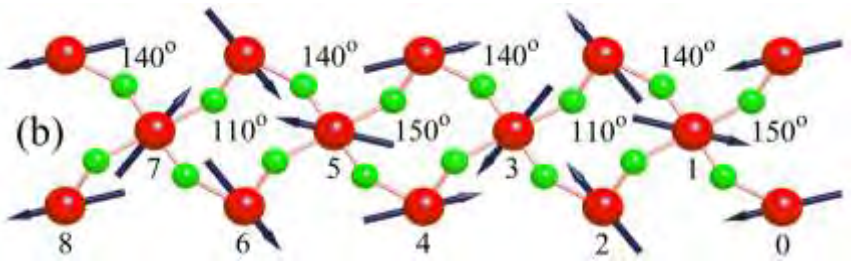
Phys. Rev. B **90**, 184425 (2014)

twofold

$$P^a = \frac{1}{2L}\sum_{i=0}^{2L-1}(-1)^i \mathbf{e}_i \cdot \mathbf{e}_{i+1} P_E$$

fourfold





$$\varphi_i = \boldsymbol{q}\cdot\boldsymbol{R}_i + \alpha_i$$

Parameters	$TbMnO_3$	$HoMnO_3$	$YMnO_3$
$\Delta\alpha_0 = \Delta\alpha_4$	18	15	13
$\Delta\alpha_1 = \Delta\alpha_5$	7	5	5
$\Delta\alpha_2 = \Delta\alpha_6$	−32	−25	−23
$\Delta\alpha_3 = \Delta\alpha_7$	7	5	5

$$P^a = \frac{1}{2L}\sum_{i=0}^{2L-1}(-1)^i \cos\left(\frac{\pi n}{L} + \alpha_{i+1} - \alpha_i\right) P_E$$

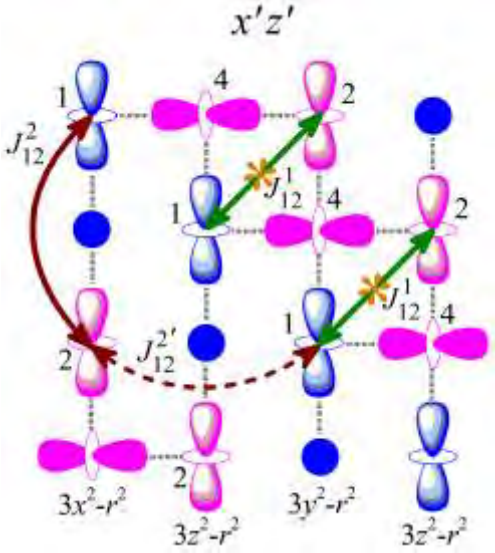
Phys. Rev. B
87, 144424 (2013);
90, 184425 (2014)

P/P_E

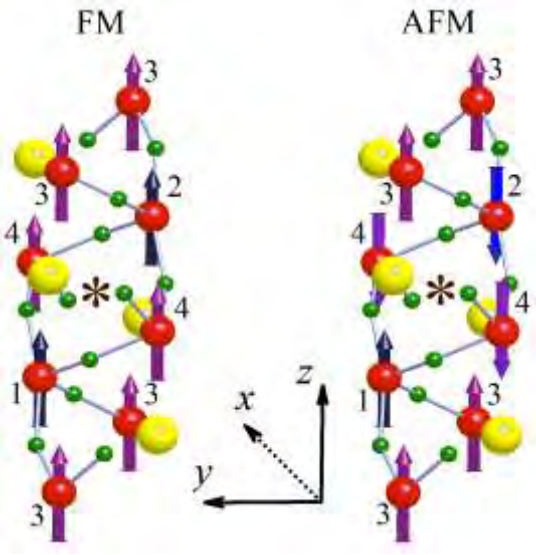
	$TbMnO_3$	$HoMnO_3$	$YMnO_3$
HF	0.138	0.110	0.101
DE	0.115	0.081	0.077

Ferroelectricity and Ferromagnetism

Example: $BiMnO_3$ ($C2/c$ symmetry)

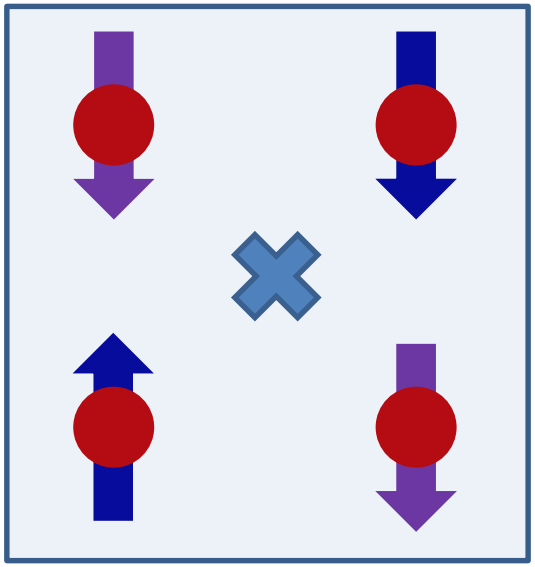


orbital ordering and exchange interactions

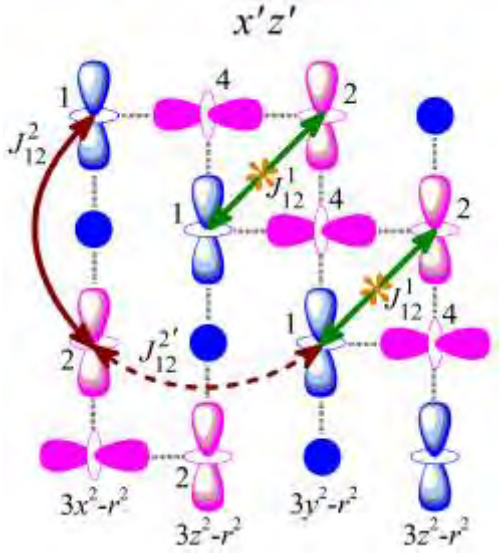


possible spin structures

main pattern

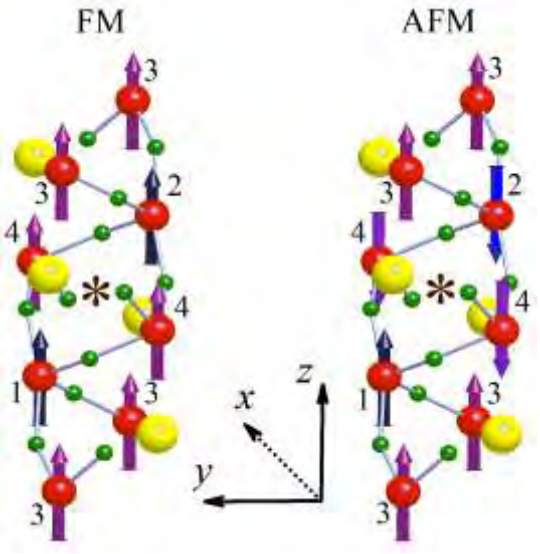


Example: $BiMnO_3$ ($C2/c$ symmetry)



orbital ordering and exchange interactions

P = 0



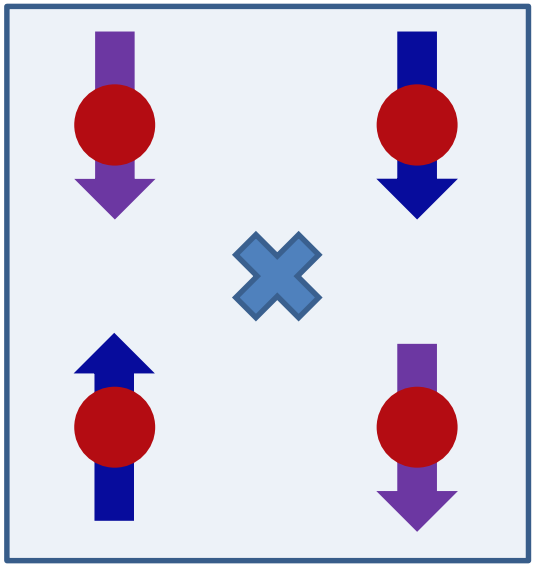
possible spin structures

$P_x = 0.79\ \mu C/cm^2$

$P_y = 0$

$P_z = 0.04\ \mu C/cm^2$

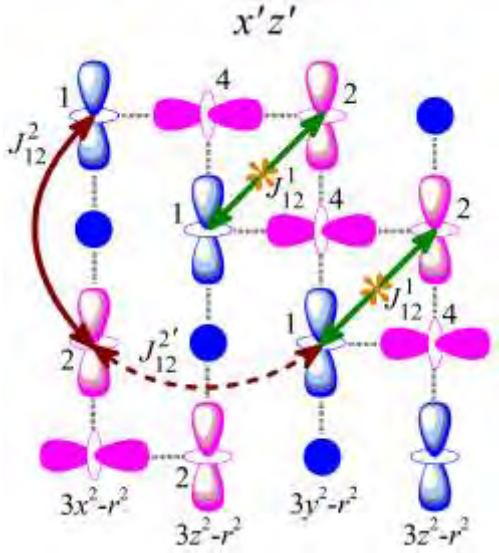
main pattern



change of electronic structure

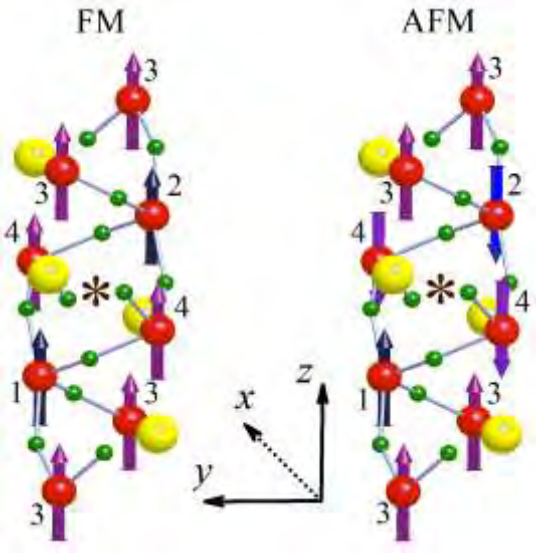
electric polarization

Example: $BiMnO_3$ ($C2/c$ symmetry)



orbital ordering and exchange interactions

P = 0



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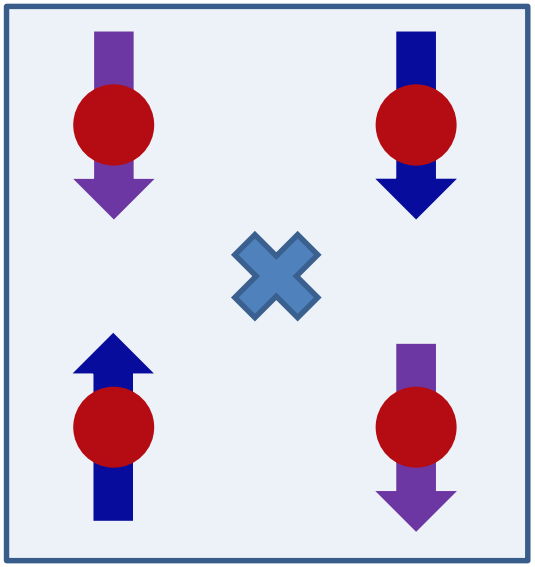


change of electronic structure

electric polarization

change of electronic structure

Dzyaloshinskii-Moriya interactions;
Weak ferromagnetism?

Local mapping onto spin model

A.I. Liechtenstein *et al*, J. Magn. Magn. Matter. **67**, 65 (1987); PRL **76**, 4825 (1996)

$$E = -\sum_{i>j} J_{ij} \boldsymbol{e}_i \cdot \boldsymbol{e}_j + \sum_{i>j} \boldsymbol{d}_{ij} \cdot [\boldsymbol{e}_i \times \boldsymbol{e}_j]$$

energy of spin system

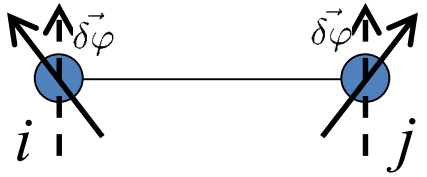
$$\frac{1}{2}\left(\boldsymbol{f}_i^j - \boldsymbol{f}_j^i\right) = [\boldsymbol{d}_{ij} \times \boldsymbol{e}^0] + \frac{1}{2} J_{ij} \left(\delta \boldsymbol{e}_j - \delta \boldsymbol{e}_i\right)$$

force

The same for electron system, using perturbation theory:

$$\frac{1}{2}\left(\boldsymbol{f}_i^j - \boldsymbol{f}_j^i\right) = \frac{1}{\pi} \mathrm{Im} \int_{-\infty}^{\varepsilon_F} d\varepsilon \mathrm{Tr}\left\{\hat{\boldsymbol{\sigma}} \left(\hat{\mathcal{G}}_{ij}(\varepsilon) \delta \hat{v}_j^p \hat{\mathcal{G}}_{ji}(\varepsilon) \hat{b}_i - \hat{\mathcal{G}}_{ij}(\varepsilon) \hat{b}_j \hat{\mathcal{G}}_{ji}(\varepsilon) \delta \hat{v}_i^p\right)\right\}$$

$$J_{ij} = \frac{2}{\pi} \mathrm{Im} \int_{-\infty}^{\varepsilon_F} d\varepsilon \mathrm{Tr}_L \left\{\hat{\mathcal{G}}_{ij}^{+}(\varepsilon) \hat{b}_j \hat{\mathcal{G}}_{ji}^{-}(\varepsilon) \hat{b}_i\right\}$$

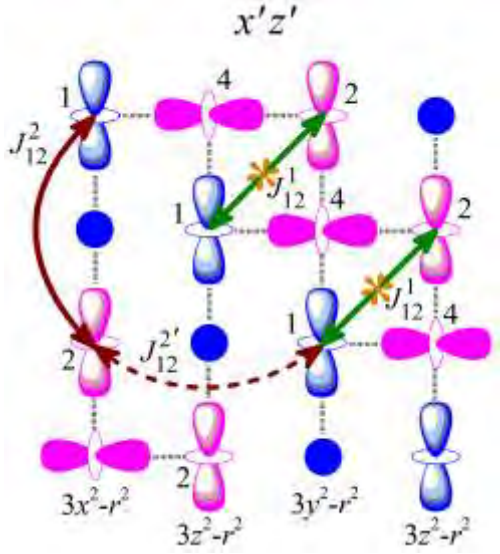


$$\delta\vec{v}^{\,p} = \left[1 - \mathbb{U}\mathbb{R}\right]^{-1} \delta\vec{v}^{\mathrm{SOC}}$$

self-consistent linear response for the spin-orbit coupling

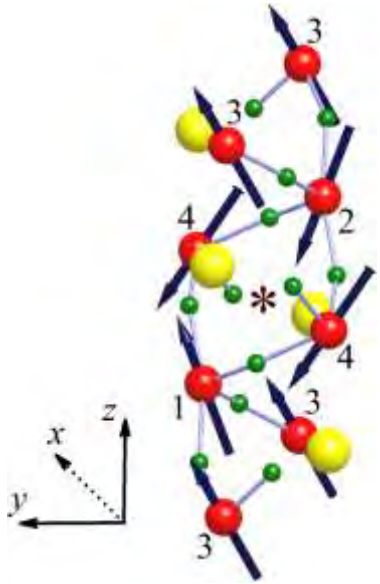
Phys. Rev. B **90**, 024417 (2014).

Example: $BiMnO_3$ ($C2/c$ symmetry)



Isotropic and Dzyaloshinskii-Moriya interactions in the AFM structure (in meV)

k	J	d
1	−1.28	(−0.311, 0.040, 0.122)
2	−3.03	(−0.689, −0.007, 0.328)



Magnetic ground state with the spin-orbit interaction

Mn-site	M_X	M_Y	M_Z
1	-0.08	1.45	-3.69
2	0.08	1.45	3.69
3	0.97	2.02	3.27
4	-0.97	2.02	-3.27

Phys. Rev. B **82**, 094425 (2010); **90**, 179909(E) (2014); **90**, 024417 (2014).

Conclusions

- spin spirality and spontaneous polarization:
  key mechanism is the ***deformation*** of the spin spiral
- microscopic model:
  DE physics + large "JT-distortion";
  one mechanism for different magnetic structures;
  $\mathbf{P} \sim \mathbf{P}_E$
- ferroelectricity and ferromagnetism:
  yes, it is possible ($BiMnO_3$)

Thank you!