First principles studies of multiferroic materials

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Overview

1) Introduction to multiferroic materials
   • Why first principles calculations?
2) Density functional theory
3) Examples:
   a) BiFeO$_3$
      • Electric polarization
      • Strain dependence
      • Coupling between polarization and magnetism?
      • Computational design of new multiferroic materials
   b) Other examples...
What is a multiferroic?

Hans Schmid: “A material that combines two (or more) of the primary ferroic order parameters in one phase”

Important:
- switchable domains (change in point symmetry)
- not necessarily coupled!

In practice often:
multiferroic = (anti-)ferromagnetic + ferroelectric = magnetic ferroelectric
What is a multiferroic?
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In practice often:
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Related but different: **magneto-electric effect**
(electric field induces magnetization, magnetic field induces electric polarization)

\[
F(E, H) = F_0 - P_i^S E_i - M_i^S H_i - \frac{1}{2} \varepsilon_{ij} E_i E_j - \frac{1}{2} \mu_{ij} H_i H_j
- \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k + \ldots
\]
Magneto-electric multiferroics

Magneto-electric multiferroics = ferromagnetic + ferroelectric

- Ferromagnetic:

- Ferroelectric:

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First principles studies of multiferroic materials
Magneto-electric multiferroics

Magneto-electric multiferroics = ferromagnetic + ferroelectric

- Ferromagnetic:

- Ferroelectric:

- Domains:

- Hysteresis:

Non-volatile data-storage!
Magneto-electric multiferroics

- Coexistence of ferroelectric, ferroelastic and magnetic order


→ Interesting cross-correlations between polarization, magnetization, and strain!

Possible Applications:
- magneto-electric RAM (electric write/magnetic read)
- four-state memory
- ...
Some history

History of magnetoelectric (ME) effect

1894: First conjecture about ME effect by Pierre Curie

1956: Landau/Lifshitz formulate symmetry requirements for ME effect (concept of time reversal symmetry)

1959: Dzyaloshinskii predicts ME effect in Cr$_2$O$_3$

1960: Experimental confirmation by Astrov (ME)$_E$

1961: Reciprocal (ME)$_H$ effect measured by Rado et al.

But: small effects, mostly low temperatures, scarcity of materials, lack of microscopic understanding

Recently: improved theoretical understanding, thin film preparation, new experimental techniques

Known magnetic ferroelectrics:

1961: Smolenskii et al.: mixed perovskites (e.g. Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$, Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$)

1963: Smolenskii/Kiselev: BiFeO$_3$

1963: Bertaut et al.: hexagonal $RMnO_3$ (e.g. YMnO$_3$, HoMnO$_3$)

1966: Ascher/Schmid: Boracites $M_3B_7O_{13}X$ (e.g. Ni$_3$B$_7O_{13}I$)

1968: Eibschuetz/Guggenheim et al.: BaMF$_4$ (e.g. BaMnF$_4$, BaNiF$_4$)
Recent boom

Epitaxial BiFeO$_3$ Multiferroic Thin Film Heterostructures


→ Large polarization and (small) magnetization above room temperature

letters to nature

Magnetic control of ferroelectric polarization


→ Small Polarization created by non-centrosymmetric magnetic order
Classification of magnetic ferroelectrics

1) Ferroelectricity independent of magnetism
   - Boracites: \( \text{Ni}_3\text{B}_7\text{O}_{13}\text{I}, \text{Ni}_3\text{B}_7\text{O}_{13}\text{Cl}, \text{Co}_3\text{B}_7\text{O}_{13}\text{I} \), ...
   - “Doped” multiferroics: \( \text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3, \text{Pb(Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3 \), ...
   - “Lone pair” ferroelectrics: \( \text{BiFeO}_3, \text{BiMnO}_3, \) ...
   - “Geometric” ferroelectrics
     - proper: \( \text{BaMF}_4 \) (\( M=\text{Mn, Fe, Co, Ni} \))
     - improper: \( \text{Y MnO}_3, \text{HoMnO}_3, \) ... (hexagonal manganites)

2) Ferroelectricity induced by ...
   - ...magnetic order: \( \text{Tb MnO}_3, \text{Tb Mn}_2\text{O}_5, \text{Ni}_3\text{V}_2\text{O}_8, \text{Cu FeO}_2, \text{CoCr}_2\text{O}_4, \) ...
   - ...charge order”: \( \text{LuFe}_2\text{O}_4, \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) (?)

One multiferroic is not necessarily equal to another multiferroic!
**Why first principles calculations?**

**First principles:** start directly from fundamental laws of Physics, without model assumptions or fitting parameters

- Diverse materials science requires a theoretical approach that is able to resolve differences between different materials
- Provide reference values for experimental data (make predictions)
- Rationalize experimental observations
1) Introduction to multiferroic materials
   - Why first principles calculations?

2) Density functional theory

3) Examples:
   a) BiFeO$_3$
      - Electric polarization
      - Strain dependence
      - Coupling between polarization and magnetism?
      - Computational design of new multiferroic materials
   b) Other examples...
Density functional theory

Interacting many-body problem:

Effective single particle problem:

\[ V_{\text{eff}} = V_H + V_{\text{ion}} + V_{\text{xc}} \]

- Facilitates quantitative predictions of materials properties
- Provides powerful analysis-tool for electronic structure

Hohenberg/Kohn 1964, Kohn/Sham 1965, Nobel Prize in Chemistry 1998 for Walter Kohn

Claude Ederer
First principles studies of multiferroic materials
The problem:

\[ \hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i,I} \frac{Z_i e^2}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \]

Effort to calculate \( \Psi(\vec{r}_1, \ldots, \vec{r}_N) \) increases exponentially with N
→ only possible for small molecules (N \( \sim \) 10)
The Hohenberg-Kohn Theorems

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Effort to calculate \( \Psi(\vec{r}_1, \ldots, \vec{r}_N) \) increases exponentially with \( N \)
\( \rightarrow \) only possible for small molecules (\( N \sim 10 \))

Hohenberg/Kohn 1964:

- All ground state properties of an interacting many-electron system are uniquely determined by the electron density \( n(\vec{r}) \)
- The correct ground state density minimizes the total energy functional

\[ E[n] = T[n] + \int d^3 r V_{\text{ext}}(\vec{r})n(\vec{r}) + \int d^3 r d^3 r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\text{xc}}[n] \]

Density replaces many-body wavefunction as central quantity of interest

But how to obtain the density?
The Kohn-Sham equations

**Idea (Kohn/Sham 1965):** construct density from auxiliary non-interacting system with the same ground state density

**Interacting system:** \[ E[n] = T[n] + \int d^3 r V_{\text{ext}}(\vec{r}) n(\vec{r}) + \int d^3 r d^3 r' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{xc}[n] \]

**Non-interacting system:** \[ E[n] = T[n] + \int d^3 r V_{\text{eff}}(\vec{r}) n(\vec{r}) \]

\[ \frac{\delta E[n]}{\delta n(\vec{r})} = 0 \quad \rightarrow \quad V_{\text{eff}} = V_{\text{ext}} + \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \frac{\delta E_{xc}[n]}{\delta n(\vec{r})} \]
**The Kohn-Sham equations**

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Interacting system:  
\[ E[n] = T[n] + \int d^3r V_{\text{ext}}(\vec{r})n(\vec{r}) + \int d^3rd^3r' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\text{xc}}[n] \]

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\[ \left( -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}[n(\vec{r})] \right) \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}) \]

\[ n(\vec{r}) = \sum_{i, \text{occ}} \phi_i^*(\vec{r}) \phi_i(\vec{r}) \]

Still missing: expression for \( E_{\text{xc}}[n(\vec{r})] \)
The local density approximation (LDA)

\[ E_{xc} = \int d^3r n(\vec{r}) \epsilon_{xc}(n(\vec{r})) \]

Expected to be good for not slowly varying densities.

Exchange-correlation energy density of a homogeneous electron gas of density \( n \)
The local density approximation (LDA)

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Extremely successful!
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Exchange-correlation energy density of a homogeneous electron gas of density \( n \)

Expected to be good for not slowly varying densities.

Extremely successful!

Problems:
- Underestimates band gaps in many semiconductors
- Not adequate for strongly correlated \( d \) or \( f \) electrons (eventually predicts metallic instead of insulating ground states)

→ Improved \( xc \)-functionals: Generalized Gradient Approximation (GGA), Exact exchange, hybrid functionals, GW, ...
Beyond LDA: correlated electrons

Hubbard model:  \[ \hat{H} = -t \sum_{i,j,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

- Competition between hopping (kinetic energy) and electron-electron interaction
- Contains main physics that dominates properties of many \textit{d} and \textit{f} electron systems
- But: extremely simplified, empirical parameters
Beyond LDA: correlated electrons

Hubbard model: \[ \hat{H} = -t \sum_{i,j,\sigma} (c^\dagger_{i\sigma} c_{j\sigma} + c^\dagger_{j\sigma} c_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \]

- Competition between hopping (kinetic energy) and electron-electron interaction
- Contains main physics that dominates properties of many \( d \) and \( f \) electron systems
- But: extremely simplified, empirical parameters

→ Combine Hubbard-type interaction with LDA/DFT: \textbf{LDA+U} (Anisimov et al. 1991)

\[
E = E_{\text{LDA}} + E_U - E_{dc}
\]

\[
E_U = \frac{1}{2} \sum_{\{\gamma\}} (U_{\gamma_1\gamma_3\gamma_2\gamma_4} - U_{\gamma_1\gamma_3\gamma_4\gamma_2}) n_{\gamma_1\gamma_2} n_{\gamma_3\gamma_4}
\]

- Leads to correct insulating ground state for many transition metal oxides
- Important: \( U \) dependence (basis set dependent parameter), double counting term \( E_{dc} \) (shifts relative to “uncorrelated” bands)
Quantities that can be calculated

- Charge density, total energies

\[ E = E\left[\{\vec{R}_I\}, n(\vec{r})\right] \rightarrow \text{energy differences between different structures, forces, phonons} \]

- Spin density for magnetic systems, energy differences between different magnetic configurations, magnetic anisotropy energies

- Single particle band-structure, electronic density of states, (zeroth approximation for electronic excitation spectra)

- Electric polarization, dielectric constants

In addition:

- Results can be analyzed in terms of fundamental quantities

- “Computer experiments”, with the possibility to control the position of each individual atom, switch off certain interactions, ...

- **Quantitative predictions** of materials properties
- **Powerful analysis-tool** for electronic structure
Overview

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BiFeO$_3$: A room temperature multiferroic

Epitaxial BiFeO$_3$ Multiferroic Thin Film Heterostructures

- ferroelectric below $T_E \approx 1100$ K
- antiferromagnetic below $T_M \approx 600$ K
- Controversial results about the “spontaneous polarization”:
  - 1970: $P = 6 \ \mu$C/cm$^2$ (single crystals) Teague et al., Solid State Comm. 8, 1073
  - 2003: $P = 60 \ \mu$C/cm$^2$ (thin films) Wang et al., Science 299, 1719

Large $P$: Effect of strain, defects, impurity phases, ... ???
Electric polarization

- Finite system: \[ \vec{P} = \frac{1}{V} \int d^3r \rho(\vec{r}) \vec{r} \] Not applicable within periodic boundary conditions (depends on unit cell choice).

King-Smith/Vanderbilt 1993, Resta 1994: “Modern theory of electric polarization”
- Polarization of a bulk solid is a multivalued quantity
- Only differences in polarization are meaningful quantities
Electric polarization

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\[ P = -1 \cdot \frac{a \cdot q}{2 \cdot V} \]
Electric polarization

- Finite system: \[ \bar{P} = \frac{1}{V} \int d^3 r \rho(\bar{r}) \bar{r} \]
  
  Not applicable within periodic boundary conditions (depends on unit cell choice).

**King-Smith/Vanderbilt 1993, Resta 1994**: “Modern theory of electric polarization”
- Polarization of a bulk solid is a multivalued quantity
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\[ P = 3 \cdot \frac{a}{2V} \]
Electric polarization

- Finite system: \[ \vec{P} = \frac{1}{V} \int d^3 r \rho(\vec{r}) \vec{r} \] Not applicable within periodic boundary conditions (depends on unit cell choice).

**King-Smith/Vanderbilt 1993, Resta 1994:** “Modern theory of electric polarization”
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\[
P = (2n + 1) \cdot \frac{a}{2} \frac{q}{V}
\]
Electric polarization

- Finite system: \[ \vec{P} = \frac{1}{V} \int d^3 r \rho(\vec{r}) \hat{\vec{r}} \] Not applicable within periodic boundary conditions (depends on unit cell choice).

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\[ P = (2n + 1) \cdot \frac{a}{2V} \frac{q}{2V} \]

\[ P = (2n + 1) \cdot \frac{a}{2V} \frac{q}{V} - \delta \frac{q}{V} \]
Electric polarization

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\[ P = (2n + 1) \cdot \frac{a}{2V} \cdot \frac{q}{V} - \delta \frac{q}{V} \]

Spontaneous polarization:
\[ \Delta P = -\delta \frac{q}{V} \]
BiFeO₃: Electric polarization

Polarization in bulk periodic solid:

\[ P \sim \sum_n \int_{\text{BZ}} d^3k \langle u_{nk} | \frac{\partial}{\partial k} | u_{nk} \rangle \]

King-Smith/Vanderbilt 1993, Resta 1994

Problem: undistorted structure metallic in LDA → need LDA+U

Neaton, Ederer, Waghmare, Spaldin, Rabe, PRB 71, 014113 (2005)
BiFeO$_3$: Electric polarization

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King-Smith/Vanderbilt 1993, Resta 1994

Problem: undistorted structure metallic in LDA
→ need LDA+$U$
→ evaluate polarization for intermediate distortion

Large intrinsic polarization $P_s^{(bulk)} \approx 95 \mu\text{C/cm}^2$ ($\approx P_s^{(film)}$)

Neaton, Ederer, Waghmare, Spaldin, Rabe, PRB 71, 014113 (2005)
BiFeO₃: Electric polarization

Born effective charges: \( Z^*_\alpha = \frac{V}{e} \frac{\partial P}{\partial \vec{r}_\alpha} \)

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( Z^* )</th>
<th>formal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>+6.32</td>
<td>+3</td>
</tr>
<tr>
<td>Fe</td>
<td>+4.55</td>
<td>+3</td>
</tr>
<tr>
<td>O</td>
<td>-3.62</td>
<td>-2</td>
</tr>
</tbody>
</table>

Bi ion drives the ferroelectric distortion

See also: Seshadri/Hill: Visualizing the role of Bi 6s “lone pairs” in the off-center distortion in ferromagnetic BiMnO₃, Chem. Mater. 13, 2892 (2001)

\[ \vec{P} \approx \frac{e}{V} \sum_\alpha Z^*_\alpha \Delta \vec{r}_\alpha = 123.1 \mu C/cm^2 \]

Compare with BaTiO₃: (Ghosez/Michenaud/Gonze, PRB 58, 6224 (1998))

Ba: \( Z = 2.75 \), Ti: \( Z = 7.16 \), O: \( Z = -5.69/-2.11 \)

→ Ti drives the distortion

Neaton, Ederer, Waghmare, Spaldin, Rabe, PRB 71, 014113 (2005)
Strain effects in thin film ferroelectrics

Epitaxial thin film growth:
In-plane lattice constant determined by substrate:
→ epitaxial strain
→ can have drastic effects on ferroelectric properties


BiFeO$_3$: Effect of epitaxial strain

Strain dependence:

...but only weak effect in BiFeO$_3$

\[ \Delta P = \left( \frac{2c_{31}}{n} - \frac{c_{33}}{n} \right) \varepsilon \]

$c_{33}$, $c_{31}$: piezoelectric constants
$n$: Poisson ratio
$\varepsilon$: epitaxial strain

Ederer/Spaldin PRB 71, 224103 (2005)
Ederer/Spaldin PRL 95, 257601 (2005)

Theory predictions:
- Large intrinsic bulk polarization
- Very weak epitaxial strain dependence
BiFeO$_3$: More recent experiments


![Graph](image1)

**FIG. 1.** (Color online) First full $P$-$E$ hysteresis loop of the single crystal of BiFeO$_3$ at room temperature. The remnant polarization $P_{[012]}$ is 60 $\mu$C cm$^{-2}$ and the coercive field is 12 kV/cm. The inferred full saturation polarization along the [001]$_{hex}$ direction is close to 100 $\mu$C cm$^{-2}$. (Insert) Raw $I$(V) data.

![Graph](image2)

**Fig. 2.** (Color online) (a) In-plane ($a=b$, purple circles) and out-of-plane ($c$, blue squares) lattice parameters, (b) $c/a$ ratio, and (c) $P_t$ (red circles) and $E_c$ (blue squares) of the BiFeO$_3$ films with varying thickness. The dotted rectangle represents the fully-strained thickness range. The dash-dotted horizontal lines are guides to the eye.

**Consistent with results of first principles calculations**
BiFeO$_3$: Magnetic properties

**Bulk:** G-type AFM + cycloidal rotation ($\lambda=640\text{nm}$)

**Thin films:**


Small magnetization but no cycloidal rotation (Bea et al., Phil Mag. 87, 165 (2007))

From: Lebeugle et al., PRL 100, 227602 (2008)
Weak ferromagnetism in BiFeO$_3$

Calculations show:
Antiferromagnetic sub-lattices are canted by $\approx 1^\circ$

Dzyaloshinskii-Moriya interaction (Moriya 1960):

$$E_{DM} = -\frac{1}{2} \vec{D} \cdot (\vec{M}_{Fe1} \times \vec{M}_{Fe2}) = -\vec{D} \cdot (\vec{L} \times \vec{M})$$

$$\vec{M} = \vec{M}_{Fe1} + \vec{M}_{Fe2} ; \quad \vec{L} = \vec{M}_{Fe1} - \vec{M}_{Fe2}$$

$M \approx 0.1 \mu_B/Fe$
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\[ \vec{M} = \vec{M}_{\text{Fe1}} + \vec{M}_{\text{Fe2}} ; \quad \vec{L} = \vec{M}_{\text{Fe1}} - \vec{M}_{\text{Fe2}} \]

How is the canting coupled to the structural distortions?

Electric-field-induced magnetization switching?

\[ \Rightarrow \text{Electric-field-induced magnetization switching?} \]
Magneto-structural coupling in BiFeO$_3$

BiFeO$_3$: two different structural modes!

1. Counter-rotations of oxygen octahedra around [111]
2. Polar displacements along [111]

Both symmetry analysis and first principles calculations show:

DM interactions is generated by oxygen octahedra rotations!

Ederer/Spaldin, PRB 71, 060401 (2005)
Magneto-structural coupling in BiFeO$_3$

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Ederer/Spaldin, PRB 71, 060401 (2005)

Symmetry analysis: $L$ in BFO does not break space inversion symmetry!

$$E \sim \vec{P} \cdot (\vec{L} \times \vec{M})$$

$L$ has to change sign under both time and space inversion
Effect of octahedral rotations

- ionic displacements corresponding to octahedral rotations:

- $DM = 0$ if midpoint between magnetic sites is inversion center
- octahedral rotations lift inversion center between B sites
  $\rightarrow$ weak magnetism is induced
Effect of octahedral rotations

- Ionic displacements corresponding to octahedral rotations:
  - $DM = 0$ if midpoint between magnetic sites is inversion center
  - Octahedral rotations lift inversion center between B sites $\rightarrow$ weak magnetism is induced

Solution:
- Put magnetic cation on A-site, (e.g. FeTiO$_3$)
  $\rightarrow$ L is odd under space inversion
- C. J. Fennie, PRL 100, 167203 (2008)
Ferroelectric/magnetic domains in BiFeO$_3$

Polarization along \{111\} direction $\rightarrow$ 8 different FE domains

Piezoelectric force microscopy (PFM):

Zavaliche et al., APL 87, 182912 (2005)
Polarization along \{111\} direction → 8 different FE domains

Piezoelectric force microscopy (PFM):

Correlation with magnetic domains?

AFM domains (?):

FE domains:

X-ray linear dichroism (XLD) depends on orientation of antiferromagnetic axis:

Zavaliche et al., APL 87, 182912 (2005)
Magnetic anisotropy in BiFeO$_3$

\[
\Delta E \approx 2 \text{meV (LSDA)}
\]

In-plane 6-fold degeneracy (bulk):
Magnetic anisotropy in BiFeO$_3$

$E_{\text{Fe}1/2} \parallel [111]$

$\Delta E \sim 2\text{meV (LSDA)}$

$M_{\text{Fe}1/2} \perp [111]$

In-plane 6-fold degeneracy (bulk):

Magnetic moments want to be perpendicular to $P$

$\rightarrow$ changing the direction of $P$

will affect magnetic order

71° switching

109° switching
Electric-field switching of AFM domains

- (001)-oriented films have small monoclinic distortion
- 6-fold degeneracy is broken
- Calculation: monoclinic strain favors [110] direction

71° switching → AFM axis preserved
109° switching → AFM axis changed

Electric-field switching of AFM domains

- (001)-oriented films have small monoclinic distortion
- 6-fold degeneracy is broken
- Calculation: monoclinic strain favors [110] direction

71° switching → AFM axis preserved
109° switching → AFM axis changed

→ in agreement with exp. observations

Why is it interesting?

Exchange bias coupling to a ferromagnet:

→ effective electric-field switching of magnetization

Magnetoelectric RA M

Very recent work

Exchange bias demonstrated recently for BiFeO$_3$/CoFeB heterostructures:
Bea et al., PRL 100, 017204 (2008)

“Electric field control of local ferromagnetism using a magnetoelectric multiferroic”,
Computational design of novel multiferroics

**Bi$_2$FeCrO$_6$: A ferrimagnetic ferroelectric**

Layered double perovskite structure:

Predicted ground state properties:

- $P_s \approx 80 \mu C/cm^2$
- $M = 2 \mu_B$/formula unit

Baettig/Spaldin, APL 86, 012505 (2005); Baettig/Ederer/Spaldin, PRB 72, 257601 (2005)
**Computational design of novel multiferroics**

**Bi$_2$FeCrO$_6$: A ferrimagnetic ferroelectric**

Layered double perovskite structure:

Predicted ground state properties:
- $P_s \approx 80 \mu$C/cm$^2$
- $M = 2\mu_B$/formula unit

Systematic LSDA+$U$ study for BiFeO$_3$ - Bi$_2$FeCrO$_6$ - BiCrO$_3$ to estimate $T_C$

$$E = E_0 - \sum_{i,j} J_{ij} \hat{s}_i \hat{s}_j$$

Mean-field approximation for $T_C$

Baettig/Spaldin, APL 86, 012505 (2005); Baettig/Ederer/Spaldin, PRB 72, 257601 (2005)
Overview

1) Introduction to multiferroic materials
   - Why first principles calculations?
2) Density functional theory
3) Examples:
   a) BiFeO$_3$
      - Electric polarization
      - Strain dependence
      - Coupling between polarization and magnetism?
      - Computational design of new multiferroic materials
   b) Other examples…
Magnetically induced ferroelectricity

• Two examples
  
  a) Spiral multiferroics: \( \text{TbMnO}_3 \)

  b) Ferroelectricity from collinear magnetic order: \( \text{HoMnO}_3 \)
Orthorhombic manganites

$RMnO_3$ ($R=$La, Pr, Nd, ... , Ho)

Orthorhombically distorted perovskite structure ($Pnma$ symmetry):

T. Kimura et al.: PRB 68, 060403(R), 2003:
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Example 1: $TbMnO_3$ - representative for “spiral multiferroics” (non-collinear)

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Example 2: $HoMnO_3$ - collinear magnetic order breaks inversion symmetry
letters to nature

Magnetic control of ferroelectric polarization

T. Kimura¹, T. Goto¹, H. Shintani¹, K. Ishizaka¹, T. Arima¹ & Y. Tokura¹

- Small Polarization below $T_C \sim 28K$
- Polarization can be rotated from $c$ to $a$ by magnetic field
Ferroelectricity induced by spiral magnetic ordering

Mostovoy, PRL 96, 067601 (2006)

Free energy (Lifshitz invariant):

\[ F_{LI} = \gamma \vec{P} \cdot \left( (\vec{M} \nabla) \vec{M} - \vec{M} (\nabla \vec{M}) \right) \quad \rightarrow \quad \vec{P} = \frac{\gamma}{\alpha} \left( (\vec{M} \nabla) \vec{M} - \vec{M} (\nabla \vec{M}) \right) \]

Example - frustrated Heisenberg spin chain:

\[ H = \sum_{n} \left( J \vec{S}_n \cdot \vec{S}_{n+1} + J' \vec{S}_n \cdot \vec{S}_{n+2} \right) \]

Periodicity depends on relative strength of various coupling constants
→ often incommensurate
Microscopic mechanism

- **Spin-current model**
  Katsura/Nagaosa/Balatsky, PRL 95, 057205 (2005)
  “electronically driven”

- **Inverse DM interaction**
  Sergienko/Dagotto, PRB 73, 094434 (2006)
  “lattice driven”

\[ E_{DM} = D_{12} \cdot (\vec{S}_1 \times \vec{S}_2) \]

\[ D_{12} \sim \vec{x} \times \vec{r}_{12} \]

In both cases:

\[ \vec{P} \sim \lambda \vec{r}_{12} \times (\vec{S}_1 \times \vec{S}_2) \]

Spin-orbit coupling → \( P \) typically \( \mu C/m^2 \) (BaTiO\(_3\): 25 \( \mu C/cm^2 \))
First principles calculations

Malashevich/Vanderbilt, PRL 101, 037210 (2008):

- Simplified commensurate spin order $k=1/3$ (exp. $k=0.28$)
- Highly accurate calculations including spin-orbit coupling (SOC)

Results:
- Without SOC: $P = 0$
- With SOC, no ionic relaxation: $P = 32 \, \mu\text{C/cm}^2$
- SOC + ionic relaxations: $P = -467 \, \mu\text{C/cm}^2$
- Exp.: $P = -600 \, \mu\text{C/cm}^2$

Polarization mainly “lattice-driven”, but not fully compatible with simple DM model.
Alternative mechanism without SOC


$E$-type AFM in orthorhombic manganites (e.g. HoMnO$_3$)

Relevant free energy invariant:

$$F = c(E_1^2 - E_2^2)P_a$$

$$\rightarrow P_a = \frac{c}{\alpha}(E_1^2 - E_2^2)$$

$\text{Mn}^{3+}: d^4$

t$_{2g}$ \hspace{1cm} eg

Double exchange model (virtual hopping):

$$H = -\sum_{i,j,\sigma} d_{i\sigma}^\dagger t_{ij}(\{Q_{i\alpha}\})d_{j\sigma} + J \sum_i \vec{S}_i \cdot \vec{s}_i + \sum_{i\alpha} \kappa_{i\alpha}Q_{i\alpha}^2 + H_{JT}$$

$\Rightarrow$ FM bonds: $\alpha_p > \alpha_0$ (less distorted)

$\Rightarrow$ AFM bonds: $\alpha_{ap} < \alpha_0$ (more distorted)
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\begin{align*}
\text{Mn}^{3+}: d^4 & \\
E & \\
eg e_g & \\
\neg t_{2g} & \\
\bar{S} & \\
\end{align*}

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\( \text{Mn}^{3+}: d^4 \)

\( \left( \begin{array}{c} e_g \\ t_{2g} \end{array} \right) \)

\( \tilde{S} \)

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$$F = c(E_1^2 - E_2^2)P_a$$

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Mn$^{3+}$: d$^4$

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Interplay of hopping, octahedral rotations and E-type AFM leads to electric polarization
HoMnO₃: First principles calculations

Picozzi et al., PRL 99, 227201 (2007)

Sizable polarization $\sim 6\mu\text{C/cm}^2$
(not spin-orbit related!)

Not confirmed by experiment, yet, but difficult to prepare single domain state.
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Similar mechanism might be at work in $R$Mn$_2$O$_5$
($R=$Tb, Ho, Y, ..)
Summary

• First principles calculations allow to make quantitative predictions of materials properties and provide a powerful analysis tool
• Examples:
  √ Polarization in bulk BiFeO$_3$ is large and only slightly affected by epitaxial strain
  √ Weak magnetization in thin films is coupled to antiferrodistortive counter-rotations of oxygen octahedra
  √ Electric field induced switching of AFM domains can be explained by change in magneto-crystalline anisotropy
  √ New “designer multiferroics” can be predicted
  √ Polarization in TbMnO$_3$ mostly lattice-driven
  √ “Exchange-striction” can cause significant polarization even for collinear magnetic order