Noncollinear treatment within DFPT and magnetic field perturbation

F. Ricci, S. Prokhorenko, M. J. Verstraete, M. Torrent and **E. Bousquet**

9th international ABINIT developer workshop, May 21 2019,
Louvain-la-Neuve, Belgium

Magnetism in DFT: Non-collinear case

Wave functions are described by spinors:

$$\phi_i(r) = \begin{pmatrix} \phi_{i\uparrow} \\ \phi_{i\downarrow} \end{pmatrix}$$

Such as the density is a 2×2 matrix:

$$\rho = \begin{pmatrix} \rho^{\uparrow\uparrow} & \rho^{\uparrow\downarrow} \\ \rho^{\downarrow\uparrow} & \rho^{\downarrow\downarrow} \end{pmatrix} = \frac{1}{2} \begin{pmatrix} n + m_z & m_x - i m_y \\ m_x + i m_y & n - m_z \end{pmatrix}$$

with n the electron density,

m_i the magnetization density along the direction i

Magnetism in DFT: Non-collinear case

The Hamiltonian is a 2×2 matrix:

$$H^{\alpha\beta} = T\delta_{\alpha\beta} + V(r)\delta_{\alpha\beta} + \int \frac{n(r')}{r - r'} dr' \delta_{\alpha\beta} + V_{xc}^{\alpha\beta}(r)$$

where

$$V_{xc}^{\alpha\beta}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho^{\alpha\beta}(r)}$$

DFPT within noncollinear magnetism framework

The problem: Most of the XC functionals are built at the collinear level

(only derivatives of n and m_z are accessible)

Solutions:

- Use noncollinear XC functionals (Eich, Gross, Vignale, *etc*)

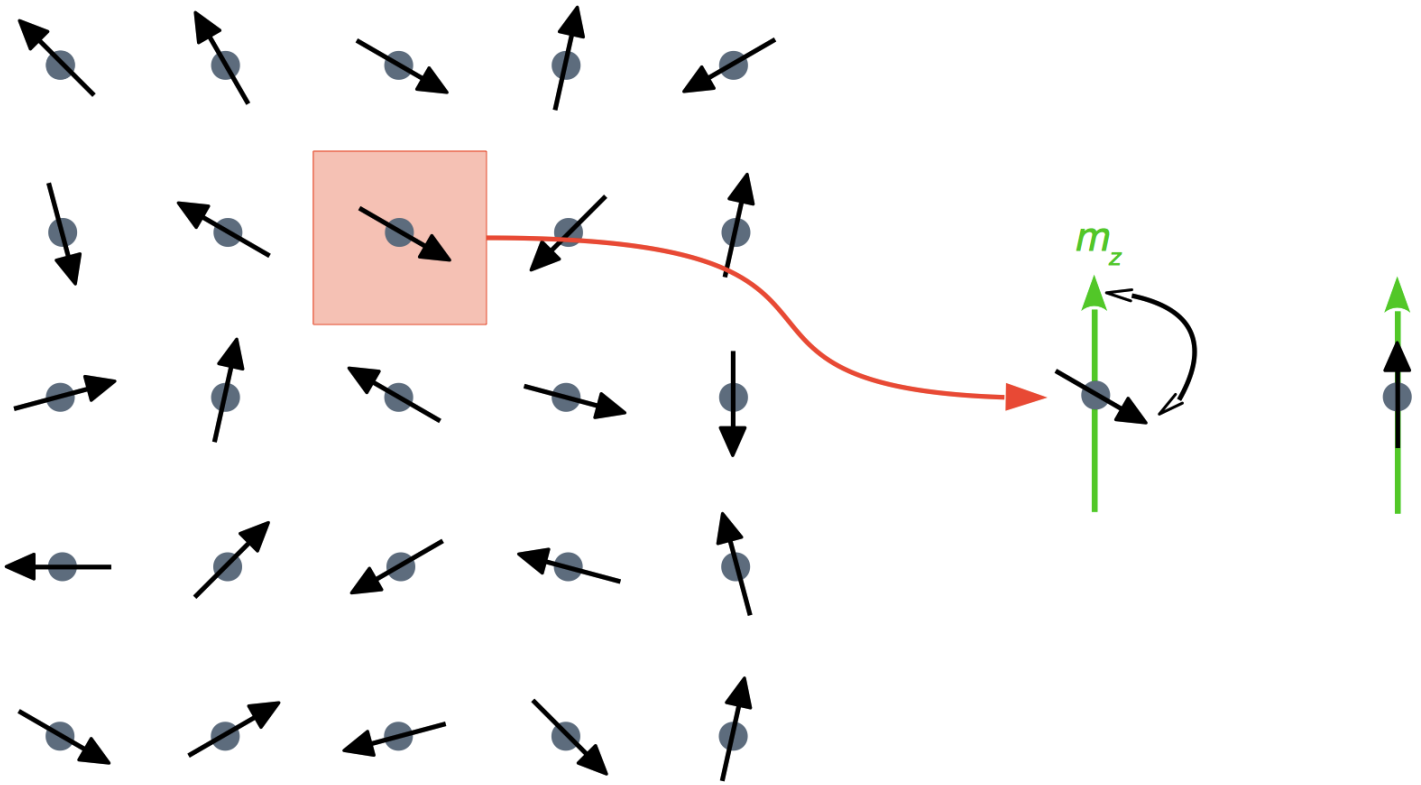
  PRL 111, 156401 (2013); PRB 88, 245102 (2013); PRB 87, 035117 (2013)

- Locally transform the noncollinear derivatives to a collinear regime

  Ricci, Prokhorenko, Torrent, Verstraete, Bousquet, PRB 99, 184404 (2019)

DFPT within noncollinear magnetism framework

Aligning the local magnetization with the local (z) quantization axis:



DFPT within noncollinear magnetism framework

We have implemented three possible methods (controlled by `ixcrot` flag):

- Method 1: Taylor expansion of the rotation matrix $U = U^{(0)} + \lambda U^{(1)} + \cdots$ $\longrightarrow$ `ixcrot = 1`
- Method 1': Analytical expression of $U^{(0)}$ and $U^{(1)}$ $\longrightarrow$ `ixcrot = 2`
- Method 2: Explicit analytical expression of XC $\longrightarrow$ `ixcrot = 3`

As of ABINIT v.8.10.2:

- Only LDA has been implemented and only norm-conserving psp
- Implementation done for atomic ($q = \Gamma$) and electric field perturbations

DFPT within noncollinear magnetism framework

Tests of atomic displacement perturbation in the collinear AFM Cr_2O_3:

Method	$\hat{\mathbf{m}}$	$E^{(2)}$ (FD)	$E^{(2)}$ (DFPT)	ΔV	# SCI
1			16.13785	$7\ 10^{-9}$	36
1'	$\hat{x}$	16.13695	16.14042	$3\ 10^{-9}$	39
2			16.13785	$3\ 10^{-5}$	80

- The three methods give similar results as the finite differences
- The method 2 is the slowest to converge (can be system dependent)

DFPT within noncollinear magnetism framework

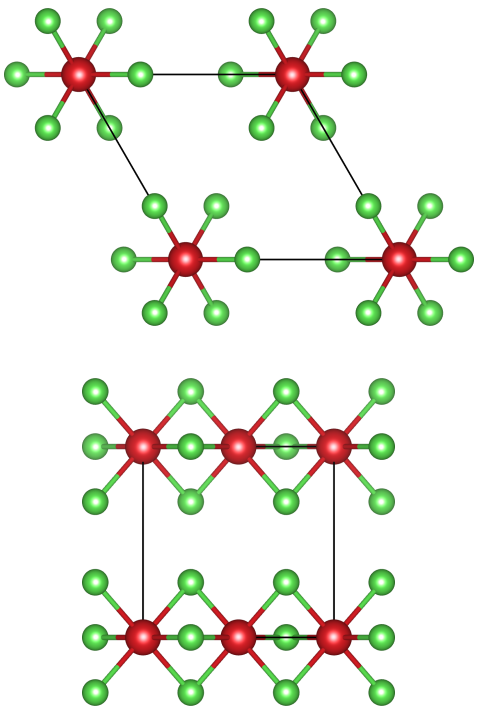
Phonon freq.: Very good agreements coll. vs noncoll. (as it should be!)

	Collinear	non-coll. **1**	non-coll. **1'**	non-coll. **2**
	233.6	233.6	233.6	233.6
	236.0	236.0	236.0	236.0
	246.3	246.3	246.3	246.3
	279.5	279.5	279.5	279.5
	...	...	...	...
	536.9	536.9	536.9	536.9
	545.1	545.1	545.1	545.1
	566.8	566.8	566.8	566.8
LO_1	280.5	280.5	280.5	280.5
LO_2	416.5	416.5	416.5	416.5
LO_3	512.1	512.1	512.1	512.1
LO_4	590.3	590.3	590.3	590.3

$$\Delta\omega < 0.1 \text{ cm}^{-1}$$

DFPT within noncollinear magnetism framework

Ex where it is useful: noncollinear SOC spin-phonon coupling in $RuCl_3$:



Label	Collinear	non-collinear ($\hat{x}$)	non-collinear ($\hat{z}$)
Γ_2^+	20i	19i	21i
Γ_5^+	123	123	123
Γ_4^-	146	146	147
Γ_5^-	148	148	147
Γ_3^-	**169**	**166**	**158**
Γ_6^-	176	174	175
Γ_6^+	249	249	248
Γ_4^+	279	278	277
Γ_5^-	283	283	282
Γ_5^+	291	291	291
Γ_2^-	298	298	296
Γ_6^-	333	334	335
Γ_3^-	**355**	**347**	**351**
Γ_1^+	355	354	352

Only Γ_3^- label is affected by noncoll. (up to 9 cm^{-1})

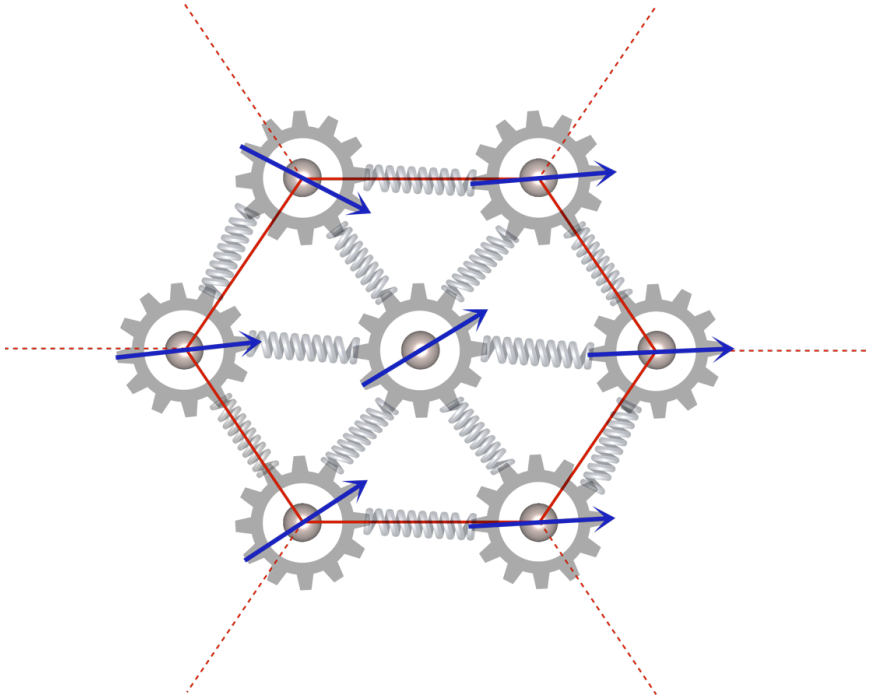
Why? ... On the TO-DO list!

DFPT within noncollinear magnetism framework

F. Ricci, S. Prokhorenko, M. Torrent, M. Verstraete and E. Bousquet

PRB 99, 184404 (2019)

Editor's suggestion :-)



Future extension: strain perturbation, $q \neq 0$ phonons, PAW, GGA

DFPT with magnetic field perturbation

(works done by Sergei Prokhorenko)

Zeeman magnetic field response

Finite H field in DFT (Zeeman term in the potential)

$$V_H = -\mu_B \mu_0 \begin{pmatrix} H_z & H_x + iH_y \\ H_x - iH_y & -H_z \end{pmatrix}$$

Or adding Zeeman magnetic field perturbation into DFPT:

		1st order	2nd order			
perturbation			τ	η	$\mathscr{E}$	**H**
atom	τ	F	C	γ	Z^*	$\mathbf{Z}^*_\mathbf{m}$
strain	η	σ		c	e	**t**
E-field	$\mathscr{E}$	P			ε^∞	$\boldsymbol{\alpha}^\infty$
B-field	**H**	**M**				$\boldsymbol{\chi}$

q-dependent Zeeman magnetic field DFPT

First order self-consistent potential:

$$V^{(1)}(\mathbf{q}) = \sigma_0 \int \frac{n^{(1)}_{0,\mathbf{q}}(\mathbf{r}')e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \sigma + \sigma_j K^{i,j}_{xc} n^{(1)}_{i,\mathbf{q}}$$

$$\sigma_i = (\sigma_0, \sigma_x, \sigma_y, \sigma_z) \qquad \sigma_0 = I \qquad\qquad n^{(1)}_i = (n^{(1)}, m^{(1)}_x, m^{(1)}_y, m^{(1)}_z)$$

Remark: The time-reversal symmetry is broken by the B-field (for $q \neq 0$)

$V^{(1)}(\mathbf{q})$, $u^{(1)}_{n,\mathbf{k}+\mathbf{q}}$ and $V^{(1)}(-\mathbf{q})$, $u^{(1)}_{n,\mathbf{k}-\mathbf{q}}$ have to be evaluated separately

(in contrast to the phonon case)

q-dependent Zeeman magnetic field DFPT

SCF calculations:

- Compute $V^{(1)}(\mathbf{q})$ and $V^{(1)\dagger}(-\mathbf{q})$
- Find $u^{(1)}_{n,\mathbf{k}+\mathbf{q}}$ with $V^{(1)}(\mathbf{q})$
- Find $u^{(1)}_{n,\mathbf{k}-\mathbf{q}}$ with $V^{(1)}(-\mathbf{q})$
- Compute $n^{(1)}$ and $\mathbf{m}^{(1)} = \frac{1}{N_k}\sum_{n,\mathbf{k}} u^{(0)\dagger}_{n\mathbf{k}}\sigma u^{(1)}_{n,\mathbf{k}+\mathbf{q}} + u^{(1)\dagger}_{n,\mathbf{k}-\mathbf{q}}\sigma u^{(0)}_{n,\mathbf{k}}$

q-dependent Zeeman magnetic field DFPT

What can we get:

$$\chi_{\alpha\beta} \propto \frac{\partial^2 E}{\partial B_\alpha \partial B_\beta} = \frac{\partial m_\alpha}{\partial B_\beta}$$

but also through the integration of $m^{(1)}$:

$$\chi_{\alpha\beta} = \int m_\alpha^{(1)} dV \qquad \text{with } B_\beta$$

and thus all $\alpha = x, y, z$ of $\chi_{\alpha\beta}$ can be obtained with B_β perturbation

q-dependent Zeeman magnetic field DFPT

In practice in ABINIT:

- Only LDA (and `ixcrot = 3`) and norm-conserving psps
- Works for collinear and noncollinear (with SOC or not)

Important flags:

- GS WF obtained with `nsym = 1`, `kptopt = 3`, `istwfk = 1`
- `rfmagn = 1`
- `tim1rev = 0` (default for $\mathbf{q} \neq 0$ to split $\mathbf{k}+\mathbf{q}$ and $\mathbf{k}-\mathbf{q}$)
- `rfdir` for the direction of the field
- `qpt` for the direction of $\mathbf{q}$

q-dependent Zeeman magnetic field DFPT

Output of Fe BCC (spin along z, `rfdir` = 1 0 0, `qpt` = 0.1, 0.1, 0.1):

```
 ---------------------------------------------------------------------
 Integrals of the first order density n^(1) and magnetization m^(1):
 ---------------------------------------------------------------------

  Re[n^(1)] =  -0.50720427E-09   Im[n^(1)] =   0.15060236E-09
  Re[mx^(1)]=   0.17133315E+04   Im[mx^(1)]=   0.38180458E-11
  Re[my^(1)]=  -0.30894401E-09   Im[my^(1)]=   0.13968902E-08
  Re[mz^(1)]=  -0.11134313E-06   Im[mz^(1)]=  -0.44289496E-09

 ---------------------------------------------------------------------

( ... )

 etotal      8.5666576077E+02
```

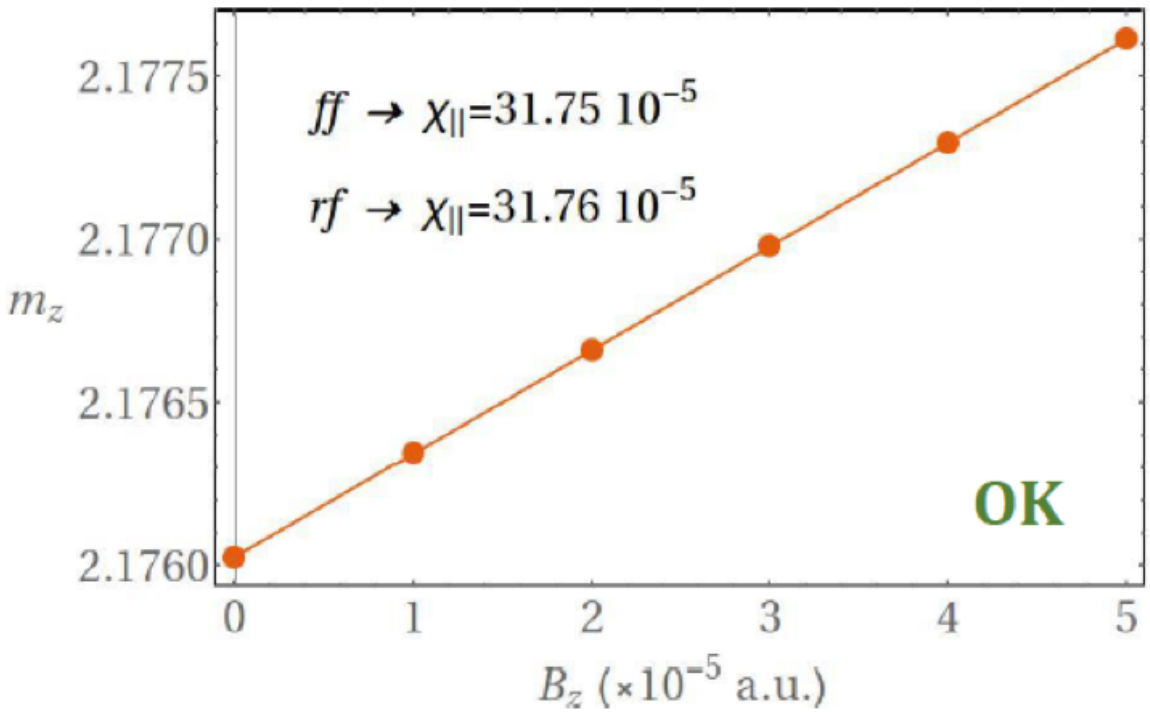
One has to check:

- Integration of $n^{(1)}$ should be 0 (charge conservation)
- $\chi_{\alpha\alpha} = 2 \times \frac{\partial^2 E}{\partial B_\alpha \partial B_\alpha}$ (`2*etotal = 0.17133315E+04 = Re[mx(1)]`)

q-dependent Zeeman magnetic field DFPT

Check with finite applied Zeeman field (`zeemanfield`):

at Γ (`qpt = 0.0 0.0 0.0`):

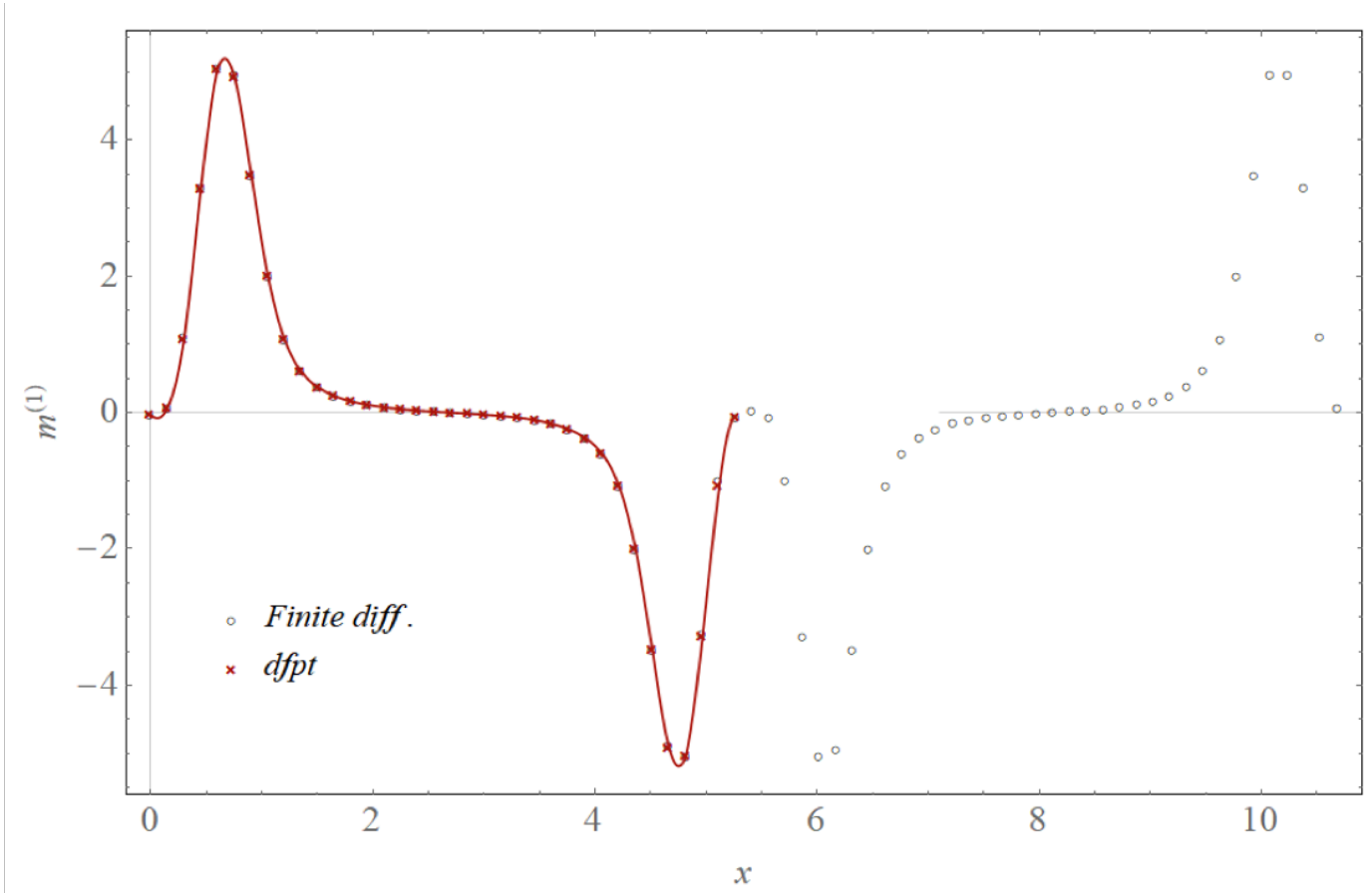


`WARNING:` At Γ, for collinear and noncollinear FM without SOC the transverse response is infinite!

q-dependent Zeeman magnetic field DFPT

Check with finite applied Zeeman field (`zeemanfield`):

at `qpt = 0.5 0.0 0.0`:

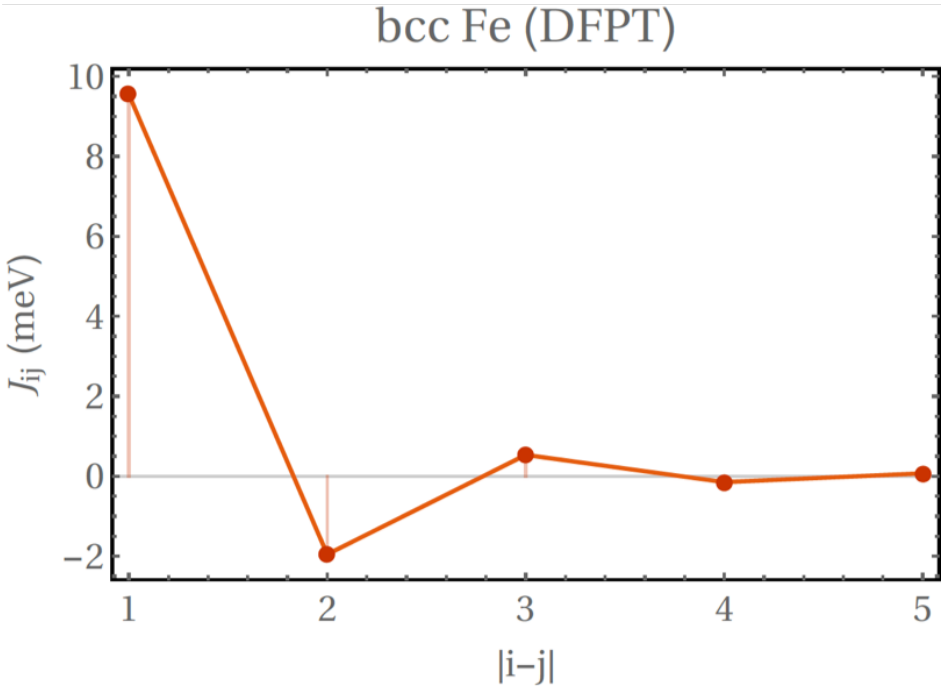


q-dependent Zeeman magnetic field DFPT

Side application: Computing the Heisenberg superexchange interactions

$$H = \sum_{i,j} J_{ij} S_i S_j - \sum_i S_{ix} B_x e^{iqr_i} \Leftrightarrow \sum_{q'} J_{q'} S_{q'} S_{-q'} - S_{qx} B_x$$

$$\longrightarrow S^{(1)}_{qx} = \frac{1}{J_q} \longrightarrow \text{Reciprocal space } J_q \longrightarrow \text{Real space } J$$



q-dependent Zeeman magnetic field DFPT

Future extensions:

- Extending it to frequency dependent (to get $\chi(\mathbf{q},\omega)$)
- Extending it to PAW
- Implementing the $2n+1$ theorem to get all cross responses between B and strain, E-field or atomic displacement perturbations

Other developments:

- Local spin rotation perturbation (on-site magnetic perturbation)

ANNEX

DFPT within noncollinear magnetism framework

Method 1: Use of a rotation transformation matrix U

$$\sum_{\alpha\beta} U^{\dagger}_{i\alpha}\ \hat{\rho}^{\alpha\beta}\ U_{\beta j} = \rho_{ij}\ \delta_{ij} \qquad \sum_{\alpha\beta} U^{\dagger}_{i\alpha}\ V_{\alpha\beta}\ U_{\beta j} = V_i\ \delta_{ij}$$

$$V_{\alpha\beta} = V^{(0)}_{\alpha\beta} + \lambda\ V^{(1)}_{\alpha\beta} + o(\lambda^2)$$

$$\sum_{\alpha} \left(U^{(0)}_{i\alpha} + \lambda U^{(1)}_{i\alpha}\right)^{\dagger} \left(U^{(0)}_{i\alpha} + \lambda U^{(1)}_{i\alpha}\right) = \delta_{ij}$$

after some maths, one can get

$$V^{(1)}_{\alpha\beta} = \sum_{ij} U^{(0)}_{\alpha i} \left[V^{(1)}_i \delta_{ij} - \sum_{\alpha} U^{\dagger(1)}_{i\alpha} U^{(0)}_{\alpha j} \left(V^{(0)}_j - V^{(0)}_i \right) \right] U^{\dagger(0)}_{j\beta}$$

This method is independent on the XC functional (LDA, GGA, *etc*)

DFPT within noncollinear magnetism framework

Method 1': Using analytical expression of $U^{(0)}$ and $U^{(1)}$

$$U^{(0)} = \exp\left[-i\frac{\theta}{2}(\boldsymbol{\sigma}\cdot\hat{n})\right] = \cos\left(\frac{\theta}{2}\right) - i\sin\left(\frac{\theta}{2}\right)(\boldsymbol{\sigma}\cdot\hat{n})$$

with $\hat{n}$ the rotation axis direction and θ the rotation angle:

$$\hat{n} = \frac{\hat{z}\times\mathbf{m}}{|\hat{z}\times\mathbf{m}|} \qquad \theta = \arccos\frac{m_z}{m}$$

And the same can be done for $U^{(1)}$ .....

DFPT within noncollinear magnetism framework

$$U^{(1)} = -\frac{\sin(\theta/2) + i\cos(\theta/2)(\boldsymbol{\sigma}\cdot\hat{n})}{2}\theta^{(1)} - i\sin(\theta/2)(\boldsymbol{\sigma}\cdot\hat{n}^{(1)})$$

$$\hat{n}^{(1)} = \left(\frac{-m_x^2 m_y^{(1)} + m_x m_y m_x^{(1)}}{\left(m_x^2+m_y^2\right)^{3/2}};\ \frac{m_y^2 m_x^{(1)} + m_x m_y m_y^{(1)}}{\left(m_x^2+m_y^2\right)^{3/2}};\ 0\right)$$

$$\theta^{(1)} = \frac{-\left(m_x^2+m_y^2\right)m_z^{(1)} + \left(m_x m_x^{(1)} + m_y m_y^{(1)}\right)m_z}{|m|^2\sqrt{m_x^2+m_y^2}}$$

DFPT within noncollinear magnetism framework

Method 2: Explicit evaluation of the XC potential:

$$\hat{V}^{(1)}_{\alpha\beta} = \frac{B^{(0)}_{xc}}{m}\left(\boldsymbol{\sigma}_{\alpha\beta} - \frac{(\boldsymbol{\sigma}_{\alpha\beta}\cdot\mathbf{m})\mathbf{m}}{m^2}\right)\cdot\mathbf{m}^{(1)} + v^{(1)}_{xc}\,\mathbf{I}_{\alpha\beta} + B^{(1)}_{xc}\frac{(\boldsymbol{\sigma}_{\alpha\beta}\cdot\mathbf{m})}{m}$$

which, for LDA gives:

$$V^{(1)}_{xc} = \frac{1}{2}\left(\frac{\partial^2 E_{xc}}{\partial\rho^2_\uparrow}\rho^{(1)}_\uparrow + \frac{\partial^2 E_{xc}}{\partial\rho^2_\downarrow}\rho^{(1)}_\downarrow + \frac{\partial^2 E_{xc}}{\partial\rho_\uparrow\partial\rho_\downarrow}(\rho^{(1)}_\uparrow + \rho^{(1)}_\downarrow)\right)$$

$$B^{(1)}_{xc} = \frac{1}{2}\left(\frac{\partial^2 E_{xc}}{\partial\rho^2_\uparrow}\rho^{(1)}_\uparrow - \frac{\partial^2 E_{xc}}{\partial\rho^2_\downarrow}\rho^{(1)}_\downarrow + \frac{\partial^2 E_{xc}}{\partial\rho_\uparrow\partial\rho_\downarrow}(\rho^{(1)}_\downarrow - \rho^{(1)}_\uparrow)\right)$$