# Electronic and magnetic properties of magnetic and chiral molecules from first-principles

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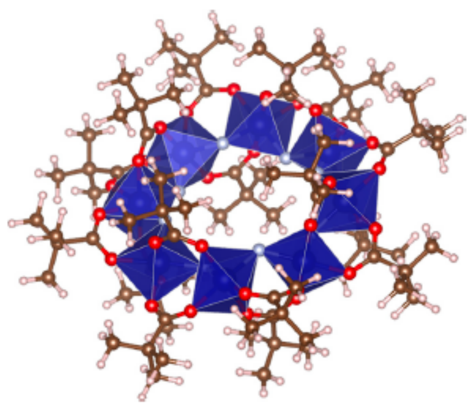
**Abstract.** Molecular magnets are systems of great technological appeal for a broad range of applications. In the first part of my talk I discuss the magnetic properties of two ring-shaped molecular magnets with eight transition metal atoms: $Cr_8$ and $V_8$, as obtained from ab initio Hubbard-corrected DFT calculations. Our results highlight a significant difference between the two systems, with V's partially occupied 3d states amplifying the effects of curvature on the magnetic properties through anisotropies and Dzyaloshinskii-Moriya chiral couplings. The second half of the work focuses on the relationship between structural chirality and its effects on electronic and transport properties. Fully relativistic ab initio calculations were able to reveal an interesting interplay between structural and electrons' chirality and, in particular, the possible occurrence of spin-polarised currents. This fundamental connection could contribute to explain the origin of Dzyaloshinskii-Moriya couplings and also the chirality-induced spin selectivity these systems exhibit in transport phenomena.

## Systems

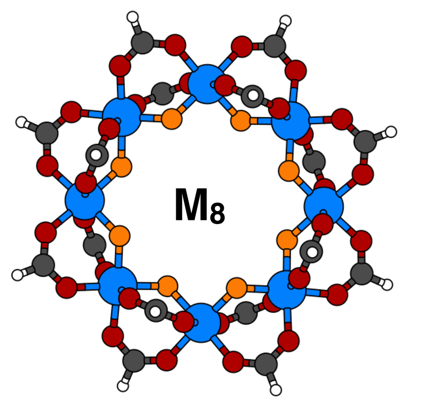
8 - transition-metal centers molecular rings

M = Cr or V (with octahedral coordination of O and F)

Spin localized on TM; inter site magnetic interactions through O and F bridges



Real system




Computational model

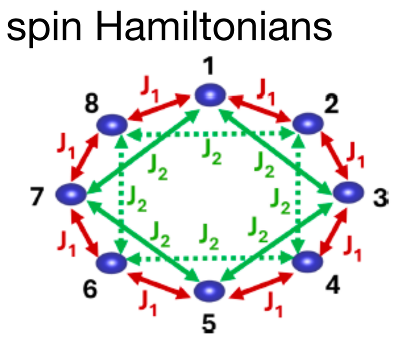
## Computational strategy

Based on interfacing DFT calculations with spin Hamiltonians

Spin model Hamiltonian: $$\hat{H} = \hat{H}_{ex} + \hat{H}_{BQ} + \hat{H}_{DM}$$

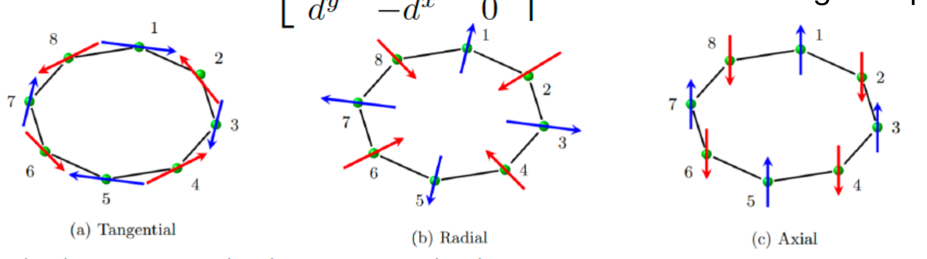
$$\hat{H}_{ex} = J^{(1)} \sum_i \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} + J^{(2)} \sum_i \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+2} \qquad \hat{H}_{BQ} = \sum_i J_{BQ_i} (\hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1})^2$$

$$\hat{H}_{DM} = \sum_i \mathbf{d} \cdot \left(\hat{\mathbf{S}}_i \times \hat{\mathbf{S}}_{i+1}\right) = \sum_i \hat{\mathbf{S}}_i \cdot J_{DM} \cdot \hat{\mathbf{S}}_{i+1} \qquad J_{DM} = \begin{bmatrix} 0 & d^z & -d^y \\ -d^z & 0 & d_x \\ d^y & -d^x & 0 \end{bmatrix}$$




Exchange couplings

Cylindrical coordinates actually used for spins

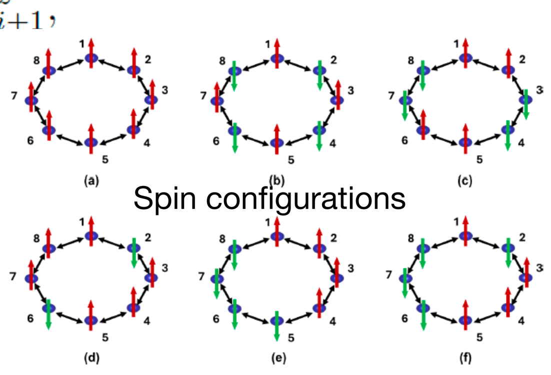



Example (nn exchange): $\hat{H}_{ex} = \sum_i J^t \hat{S}^t_i \hat{S}^t_{i+1} + J^r \hat{S}^r_i \hat{S}^r_{i+1} + J^z \hat{S}^z_i \hat{S}^z_{i+1},$

Effective couplings: from comparing DFT total energies

Both collinear and non-collinear spin configurations considered

DFT+U(+V) calculations from Quantum-ESPRESSO (1)



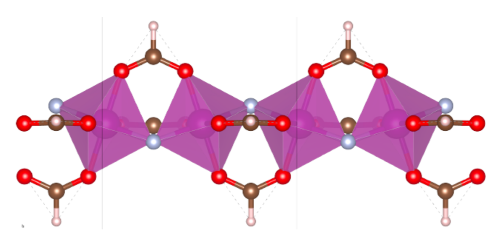

Spin configurations

Without the Hubbard correction delocalisation of 3d electrons results in a rough over-estimation of J. The problem gets fixed when using DFT+U(+V)

**Hubbard parameters:**

| | | $Cr_8$ | | $V_8$ | |
|---|---|---|---|---|---|
| | | DFT+$U$ | DFT+$U+V$ | DFT+$U$ | DFT+$U+V$ |
| LDA | $U$ | 5.26 | Cr-Cr 6.28 | 4.62 | V-V 5.66 |
| | $V$ | | Cr-F 1.54 | | V-F 1.48 |
| | | | Cr-O 1.40 | | V-O 1.37 |
| GGA | $U$ | 5.13 | Cr-Cr 6.11 | 4.51 | V-V 5.53 |
| | $V$ | | Cr-F 1.48 | | V-F 1.45 |
| | | | Cr-O 1.37 | | V-O 1.37 |

Hubbard parameters from a chain model of the systems



## Magnetic couplings

**Spin-collinear calculations: Exchange parameters**

| | $Cr_8$ | $V_8$ |
|---|---|---|
| $J_{LDA}$ | 16.043 | −38.370 |
| $J_{GGA}$ | 3.498 | −3.434 |

| Functional | $J$ | $Cr_8$ | $V_8$ |
|---|---|---|---|
| LDA+U | $J^{(1)}$ | 0.843 | −0.917 |
| | $J^{(2)}$ | −0.013 | 0.231 |
| GGA+U | $J^{(1)}$ | 0.628 | −0.937 |
| | $J^{(2)}$ | −0.011 | 0.098 |

While **$Cr_8$** has a **AFM** ground state, **$V_8$** shows consistently **FM** interactions with **large couplings between second nearest neighbour spins**

**Spin non-collinear spin calculations** (cylindrical coordinates)

**Exchange couplings (n.n.)**

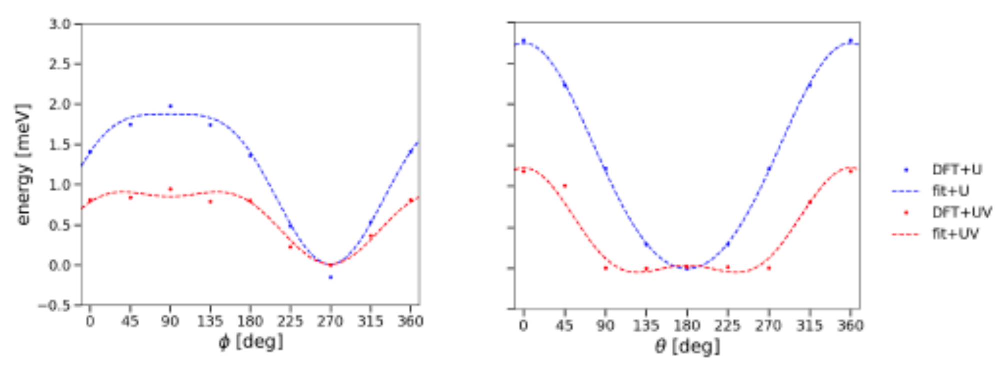
| $J_1$ (meV) | $Cr_8$-ring | | $V_8$-ring | |
|---|---|---|---|---|
| Parameter | +U | +U+V | +U | +U+V |
| $J^r$ | 0.596 | 0.848 | -0.643 | -0.403 |
| $J^t$ | 0.596 | 0.848 | -0.654 | -0.403 |
| $J^z$ | 0.843 | 1.198 | -0.913 | -0.585 |

**n.n.n. (and beyond)**

| LDA+U | $Cr_8$-ring | $V_8$-ring | | |
|---|---|---|---|---|
| Parameter | $J_2$ (meV) | $J_2$ (meV) | $J_3$ (meV) | $J_4$ (meV) |
| $J^r$ | -0.0003 | 0.120 | -0.020 | 0.024 |
| $J^t$ | -0.0005 | 0.163 | -0.017 | -0.019 |
| $J^z$ | -0.0150 | 0.207 | 0.013 | 0.001 |

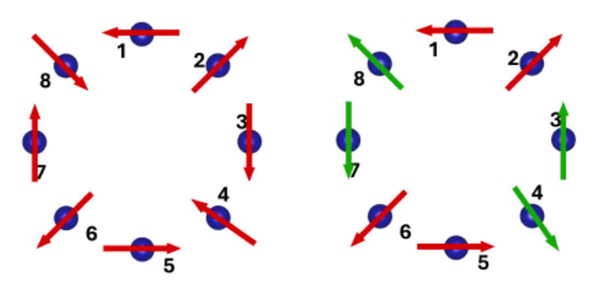
**Biquadratic couplings**

| | LDA+U | | LDA+U+V | |
|---|---|---|---|---|
| Parameter | $Cr_8$-ring | $V_8$-ring | $Cr_8$-ring | $V_8$-ring |
| $J_{Bq^r}$ | 0.004 | -0.230 | 0.005 | -0.175 |
| $J_{Bq^t}$ | 0.002 | -0.208 | 0.0002 | -0.227 |
| $J_{Bq^z}$ | 0.012 | 0.091 | -0.018 | 0.260 |




DFT energy fit upon rotating single spins around its reference orientation

**Dzyaloshinskii-Moriya couplings**



DM are obtained from comparing **helical** and **non helical** configurations

| | $Cr_8$-ring | | $V_8$-ring | |
|---|---|---|---|---|
| Parameter | +U | +U+V | +U | +U+V |
| $d^r$ | -0.193 | -0.007 | -0.381 | -0.433 |
| $d^t$ | -0.193 | -0.007 | -0.338 | -0.433 |
| $d^z$ | 0.594 | 0.853 | -0.515 | -0.939 |

DM interactions ($d^z$) are expected from rewriting couplings in cylindrical coordinates . However $V_8$ exhibits higher values than expected from geometrical reasons.

## References

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(2) E. Stocco et al., Phys Rev. B **111**, 214405 (2025); arXiv:2501.03393v2; M. B. Maccioni et al., "Understanding molecular magnets from non-collinear ab initio calculations", in preparation

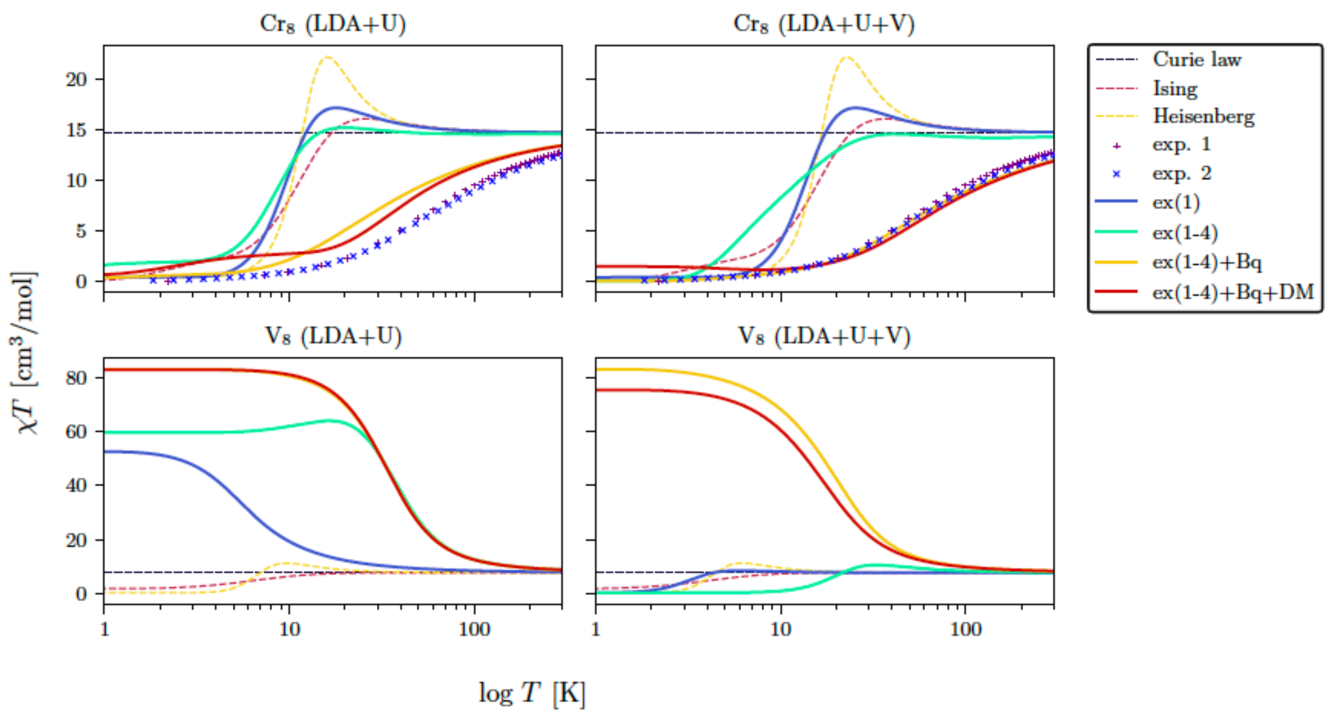
(3) S. K. Behera et al., "Relativistic Dynamics and Electron Transport in Isolated Chiral Molecules", in preparation; R. Sala et al., "Spin-orbit coupling and beyond in Chiral-Induced Spin Selectivity", arXiv:2601.20475

## Susceptibilities

Exact diagonalization of the quantistic Hamiltonian

$$\hat{H} = \hat{H}_{ex} + \hat{H}_{BQ} + \hat{H}_{DM}$$

Susceptibilities as thermal averages: $$\chi_{zz} = \mu_0 \beta \left[ \langle \hat{m}_z^2 \rangle - \langle \hat{m}_z \rangle^2 \right]$$




- Biquadratic couplings seem crucial to recover the susceptibility of $Cr_8$ measured in experiments
- DFT+U+V is needed to achieve numerical accuracy

More details and results in Ref (2)

## Chirality in brief

Dirac equation (free electron): $\left(i\gamma^\mu \partial_\mu - m\right)\psi = 0$

Calculations were performed using the Dirac24 code, that bases DFT on the Dirac equation

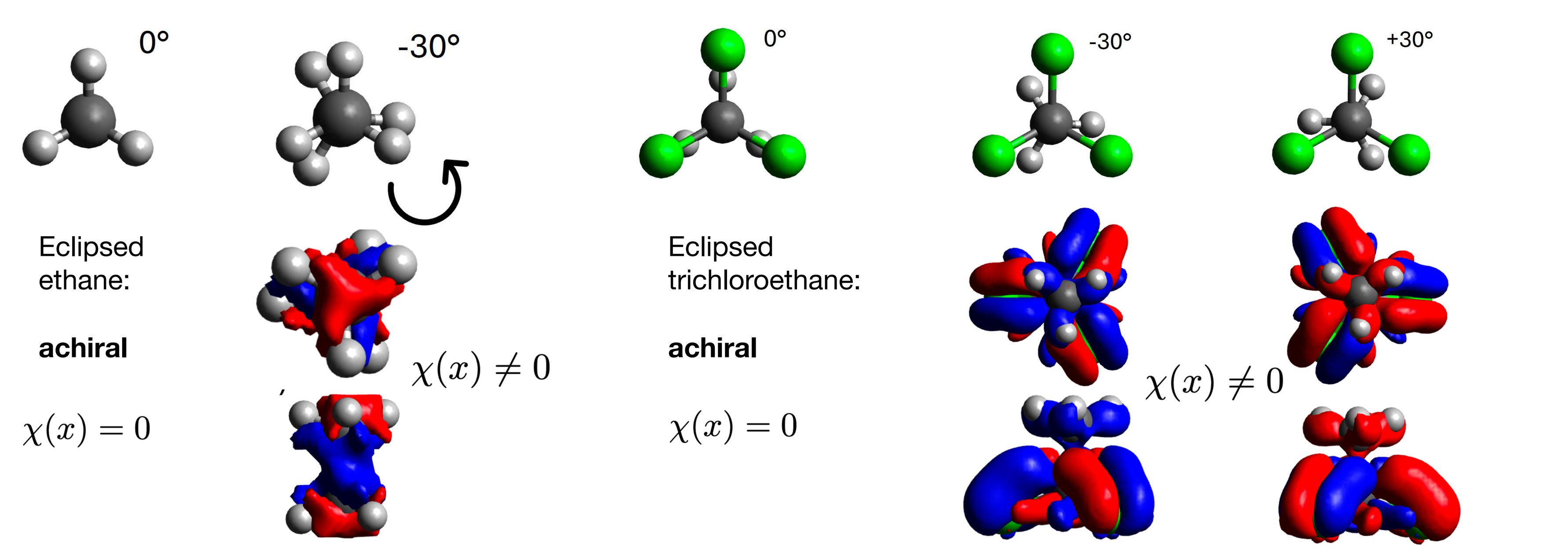
- Full account of single-electron spin-orbit coupling
- Density of electron chirality: $\chi(x) = \sum_{\mu\vartheta} \psi^*_\mu(x) \gamma^5_{\mu\vartheta} \psi_\vartheta(x)$ where $\gamma^5 \equiv i\gamma^0\gamma^1\gamma^2\gamma^3$

## Calculations and results

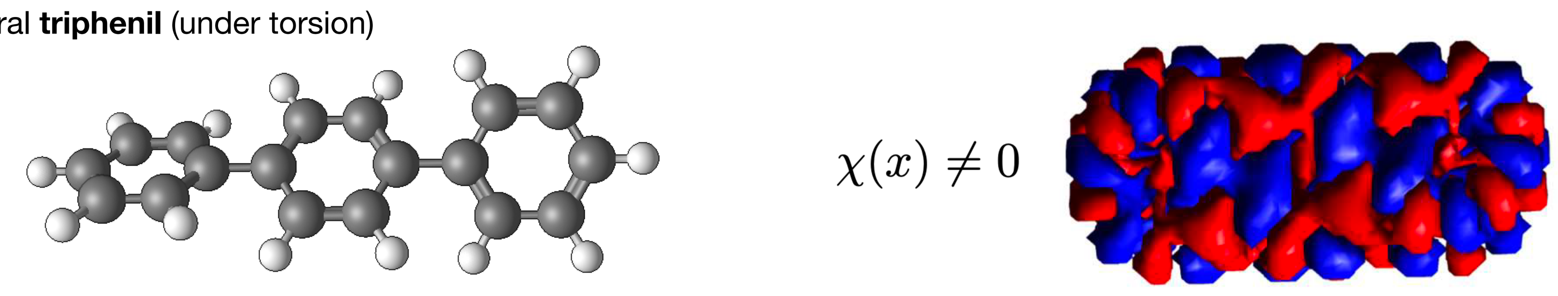
Are structural and electronic chirality related?

Molecules with tunable structural chirality: $CH_3$-$CH_3$ (ethane) and $CH_3$-$CCl_3$ (trichloroethane)

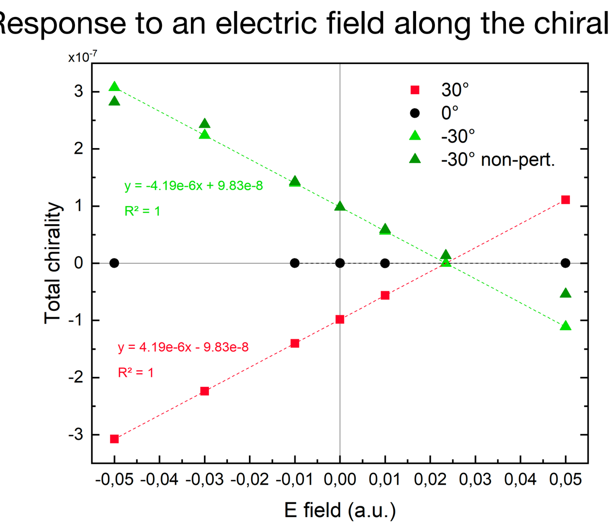
Chirality density $\chi(x)$ isosurfaces:



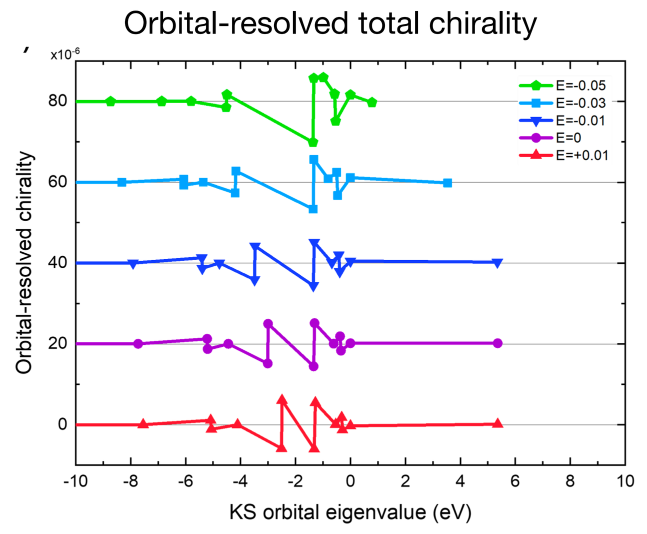

Chiral **triphenil** (under torsion)




Response to an electric field along the chiral axis




Orbital-resolved total chirality




Non-equilibrium conditions probably crucial to enhance chirality

The electronic chirality is sensitive to external electric fields in presence of dipoles.

More details and results in Ref (3)

## General Discussion

- Spin-orbit coupling seems unable to induce the spin-momentum locking of chirality-induced spin selectivity (CISS) and to be unrelated to "exotic" magnetic couplings as DM
- Other degrees of freedom probably have to be explicitly included in energy functionals. What about currents and spin-currents?

## Acknowledgements

Computing

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