

## Proposed Teaching Activity

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**Course Title:** *Ab initio modelling of molecular magnetism: The case of Lanthanide-based Single Molecule Magnets*

**Duration:** 2 weeks: 8 lectures (4 theoretical + 4 hands-on computational experiments), arranged into four 2-hour sessions, as detailed in the Course Plan below.

**Prerequisites:** Basic quantum mechanics/atomic theory notions, and statistical mechanics. Basic knowledge of Python 2.7 is not necessary, but can help the student in setting up calculations and elaborate the output data in an independent manner.

**Software for computational experiments:** CERES ab initio package, developed by the Soncini Research Group at the University of Melbourne, will be provided and installed by the lecturer.

**Synopsis:** Lanthanide-based Single-Molecule Magnets (Ln-SMMs) are inorganic or metallo-organic complexes containing lanthanide ions, which display hysteretic spin-dynamics below a finite blocking temperature, originating at the single-molecule level, which makes them promising candidates for the storage and processing of information at the single-molecule level. The origin of this behavior is fundamentally rooted in the complex electronic structure of the Ln-SMM, arising from the interplay between strong electron correlation, strong spin orbit coupling, and lanthanide ion-organic ligand so-called “crystal field” interactions. In this cycle of lectures and computational experiments we will explore “hands-on” theoretical and computational models for the accurate determination of the magnetic levels and crystal field states of lanthanide complexes, and use the results to (i) discuss the origin of the slow spin relaxation behavior at the root of single molecule magnetism (ii) calculate experimental observables such as equilibrium magnetization and molar susceptibility as function of temperature and magnetic field (iii) analyse the role of magnetic coupling in the formation of chiral/toroidal spin states in molecules.

**Learning outcomes:** The student will learn how to set up and solve complex multiconfigurational and strong spin orbit coupled ab initio quantum chemistry computational models to determine the magnetic states of Ln(III)-based single-molecule magnets, and assess their static and dynamic magnetic properties at finite temperatures. These models will in particular assist the student both in the identification of magneto-structural correlations determining single-molecule magnet behavior, and in the direct accurate evaluation of experimental observables useful to model several experiments, such as DC- and AC-magnetometry, EPR and paramagnetic NMR spectroscopies, inelastic neutron scattering, 4f electron density determination via X-ray diffraction, and XMCD experiments.

## Course Plan:

### Week I

#### Theoretical Seminars (2 hours-session):

##### *Lecture 1: atomic and crystal field theory models of electronic structure of Ln(III)-complexes*

- Introduction to calculations of magnetic states and interactions in molecular systems.
- Introduction to Ln(III)-based molecular magnetism.
- Introduction to the electronic structure of Ln(III) free ions: interplay between strong electron correlation and strong spin orbit coupling.
- Ab initio vs Russel-Saunders term description of strong electron correlation
- Ab initio vs L.S description of spin-orbit coupling, and the Lande' interval rule.
- The molecule: an overview of crystal field theory.

##### *Lecture 2: ab initio models of the electronic structure of Ln(III)-complexes*

- Introduction to the ab initio approach: Configurationally Averaged Hartree-Fock (CAHF) + Complete Active Space Configuration Interaction with Spin-Orbit coupling (CASCI-SO) strategy developed at University of Melbourne, and implemented in CERES.
- Modelling magnetic experiments: magnetization (M) vs field (H), and susceptibility  $\chi$  (and  $\chi T$ ) vs temperature (T), as probes of the magnetic levels in SMMs.
- Signatures of isotropic and anisotropic magnetism.

#### Computational Seminars/Experiments (2 hours-session):

- Model systems explored:
  1. Dy(III) free ion
  2. Er(III) free ion
  3. Dy(III)(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>
  4. Er(III)(acac)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>
  5. [Dy(III)(Cp<sup>†††</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (record magnetic hysteresis observed at 60K)
  6. [Tb(III)Pc<sub>2</sub>]<sup>-</sup>: An Ising doublet SMM due to high symmetry (quasi-D<sub>4d</sub>)
- Set up CAHF module input in CERES for the 6 models.
- Set up CASCI-SO module input in CERES for the 6 models.
- Calculate and analyse results for models 1 and 2, identify ab initio J-multiplet degeneracies and compare SOC splitting with what expected from Landé-interval rule.
- Calculate and analyse ab initio "g-tensor" (Landé g<sub>J</sub> value) and  $\chi T$  vs T for models 1 and 2, and compare with expectations from simple atomic theory.
- Calculate and analyse ab initio crystal field levels, Kramers doublets g-tensors and  $\chi T$  vs T for crystal field levels in models 3-4: comment on quasi-orthogonality of anisotropy axes in Dy and Er analogues.
- Calculate and analyse ab initio crystal field levels, Kramers doublets g-tensors, and  $\chi T$  vs T for model 5, and discuss high SMM performance in terms of results.
- Calculate and analyse ab initio crystal field levels, Ising doublets g-tensors, and  $\chi T$  vs T for model 6, and discuss high SMM performance in terms of results. Can you identify the M quantum numbers only based on calculated g-tensors?
- Calculate and analyse the electron charge density for ground Kramers doublet in model 2 and 3. We'll discuss these results next time!

## **Week II**

### Theoretical Seminars (2 hours-session):

*Lecture 3: Role of electrostatics in determining strongly axial magnetic anisotropy in Ln(III) complexes. Role of strong on-site axiality in determining toroidal (a.k.a. anapolar) spin textures in polynuclear Ln(III) complexes.*

- Calculation of the charge density associated to a pure  $|\pm M\rangle$  spin-orbit doublet using the Sievers model.
- Generalization to an arbitrarily mixed crystal field state.
- Electrostatic model for the magnetic anisotropy of Ln(III)-based molecular nanomagnet.
- High-resolution X-ray scattering measurement of 4f-electron density: a proof of principle of the Sievers electrostatic model.
- Toroidal moments arising in polynuclear Ln(III) complexes with special anisotropy axes configurations and Ln-Ln exchange and dipolar interactions.

*Lecture 4: Exchange coupling in nanomagnets with multiple localized magnetic moieties.*

- Basic theory of exchange coupling between two magnetic centers: the two electrons in two metal orbitals model.
- Kinetic and potential exchange mechanisms, and their generalization for orbitally degenerate metal centers.
- Spin-polarization mechanisms in organic radicals.
- A special example of exchange interaction with crucial consequences for molecular spintronics: 4f electrons- $\pi$  radical interaction in the double-decker  $[\text{LnPc}_2]^0$  family of molecules.

### Computational Seminars/Experiments (2 hours-session):

- Model systems explored:
  1.  $\text{H}_2$  molecule
  2. phthalocyanine radical
  3.  $[\text{Tb(III)Pc}_2]^0$  (SMM, & probed as spintronics device e.g. on graphene, CNTs)
  4.  $[\text{Dy(III)Pc}_2]^0$  (SMM)
  5.  $[\text{Ho(III)Pc}_2]^0$
- Set up CAHF module input in CERES for the 5 models (define three different configurational averaging spaces for models 1, 2 and 3-5).
- Set up CASCI-SO module input in CERES for the 5 models (define three different full CI active spaces for models 1, 2 and 3-5).
- Calculate and analyse results for simple model 1 and discuss signatures of potential and kinetic exchange.
- Calculate and analyse results for model 2 and discuss signatures of spin-polarization.
- Calculate and analyse results for model 3-5: is the 4f-radical interaction ferromagnetic or antiferromagnetic? Why? How does the interaction scale in varying the Ln ion? Why?