

Development and Application of Ab-initio Methods for Strongly Correlated and Strongly Spin-Orbit Coupled Molecular Nanomagnets A Study in Existing and Novel Strategies

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Objectives

The present study has two objectives:

- 1 To test the limits of existing multiconfigurational /multireference ab-initio methods for strong spin-orbit coupled molecules and to use these methods to elucidate electronic structure in novel lanthanide complexes which act as Single molecule magnets.
- 2 To implement molecular integrals on a Gaussian Type Orbital(GTO) basis for selected scalar-relativistic and mean field spin-orbit coupling theories within the quantum chemistry package CERES(Computational Emulator of Rare Earth Systems) developed in our group and to test the code against existing software.

Talk Plan

- 1 Introduction
- 2 Ab-initio Methods for Molecular Magnetism
 - The Current Method of Choice: CASSCF
 - Configuration Averaged Hartree-Fock
- 3 Present Study
 - Development of CERES
 - Er(trensal)
 - Evans Systems
- 4 Timeline of Future Work

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What are Single Molecule Magnets(SMMs)

- These are molecules that are able to show bulk magnetic properties rooted in single molecular behavior such as magnetic hysteresis and quantum tunneling of magnetism at certain low temperatures¹.
- Inherent magnetic anisotropy + a high unquenched ground state magnetic moment \implies Lanthanide-SMMs(Ln-SMMs) very good candidates with higher energy barriers to magnetic relaxation. ².

¹Gatteschi, Dante, Roberta Sessoli, and Jacques Villain. Molecular nanomagnets. Vol. 5. Oxford University Press on Demand, 2006.;Gatteschi, D. and Sessoli, R. (2003), *Angewandte Chemie International Edition*, 42: 268297.

²N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, 125, 86948695.

Understanding their behavior

- It is expensive to synthesize and test every combination of the several factors at play.
- Relevant to be able to quantitatively predict with to high degree of accuracy, the energies of the lowest lying states in a given system.
- Model must avoid the use of phenomenological constants and be systematically improvable to greater levels of accuracy. This leads us to prefer ab-initio methods to calculate these levels.

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CASSCF/RASSI-SO

- Complete Active Space Self Consistent Field(SCF) and State Interaction with Spin Orbit coupling(CASSCF/RASSI-SO) is the Current method of choice.³
- Select a set of orbitals called the active space and optimize a set of molecular orbitals(MOs) for each possible electron configuration in it. This called the complete active space SCF.
- The cost of a CASSCF increases combinatorially as we increase the active space.

³Flanagan, Bernadine M., Paul V. Bernhardt, Elmars R. Krausz, Stefan R. Lthi, and Mark J. Riley., *Inorganic chemistry* 40, no. 21 (2001): 5401-5407

- The RASSI has limits on the number of optimized CASSCF wavefunctions it can mix via SOC(Spin Orbit Coupling)., due to the fact that that in general these CI(Configuration Interaction)-roots use different sets of orbitals which are not orthogonal⁴ to each other.
- One solution is to minimize the trace of each spin block(And thus the average energy) to get common MOs for each spin block called the state averaged(SA)-CASSCF, where we perform CI on each block using the resulting MO. Diagonalize the SOC operator on the basis of the resulting CASCI wavefunctions.⁵

⁴P.-. Malmqvist and B. O. Roos, Chem. Phys. Lett., 1989, 155, 189194.

⁵Van den Heuvel, Willem, Simone Calvello, and Alessandro Soncini.,
Physical Chemistry Chemical Physics 18.23 (2016): 15807-15814. 

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Configuration Averaged Hartree-Fock(CAHF)

- 1 CAHF: minimise trace of whole CI matrix obtain one set of orthogonal orbitals instead of as many sets as spin states.
- 2 CASCI-SO: set up determinant basis and diagonalize electron repulsion operator + SOC operator (mean field). This strategy has been implemented by our group in the new package CERES⁶ based on open-shell version⁷ of SYSMO code⁸.
- 3 And was used to demonstrate for first time that because of non-conservation of spin quantum number AND negligible mixing of 4f with ligands, CAHF/CASCI-SO has similar accuracy to CASSCF/RASSI-SO

⁶Van den Heuvel, Willem, Simone Calvello, and Alessandro Soncini., Physical Chemistry Chemical Physics 18.23 (2016): 15807-15814.;

⁷A. Soncini, J. Chem. Theory and Comput. 3, 2243 (2007).

⁸P. Lazzeretti, R. Zanasi, P. W. Fowler, E. Steiner, R. Havenith and A. Soncini, SYSMO quantum chemistry package, University of Modena.

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Constraints with ORCA⁹

Some of the constraints are:

- 1 An inability to stitch a guess state for the molecule using the atomic Russell-Sauders states.
- 2 An inability to flexibly select multiple active spaces for CI-SOC.
- 3 A lack of incorporation of symmetry in CI or SCF (for higher than D_{2h}) leading to considerably longer computation times.

⁹F. Neese: The ORCA program system (WIREs Comput Mol Sci 2012, 2: 73-78).

Implementing 1-electron integrals in CERES

- We need to account for relativistic effects in CERES using a method such as Douglas-Kroll-Hess¹⁰ but CERES is built using libint¹¹ which **doesn't generate the requisite pVp integrals** $\langle \psi_a | pVp | \psi_b \rangle = pVp(i, j, k, l, m, n)$
- $\psi_a = x_A^i y_A^j z_A^k \exp(-ar_A^2)$ is a Cartesian Gaussian type orbital at a distance r_A from the nucleus
- (i, j, k) and (l, m, n) are their Cartesian Gaussian quantum numbers respectively.
- Where $\langle \psi_a | V | \psi_b \rangle = V_{i,j,k,l,m,n}$ is the **nuclear attraction integral which can be generated from libint.**

¹⁰Wolf, Reiher, and Hess., The J. of chem. phys. 117.20 (2002): 9215-9226.

¹¹Edward F. Valeev, <http://libint.valeev.net/>

Calculating Primitive Cartesian pVp integrals in a GTO basis

- For a Cartesian Gaussian $\psi_x^i = x_A^i \exp(-ax_A^2) \implies \psi_x^i \psi_y^j \psi_z^k = \psi_a$

$$-\frac{d\psi_x^i}{dx} = 2ax\psi_x^{i+1} - i\psi_x^{i-1}$$

- and using¹²,

$$\begin{aligned} \langle \Psi_a | pVp | \Psi_b \rangle &= \langle \nabla \Psi_a | V | \nabla \Psi_b \rangle \\ &= \left\langle \frac{d\psi_a}{dx} \middle| V \middle| \frac{d\psi_b}{dx} \right\rangle + \left\langle \frac{d\psi_a}{dy} \middle| V \middle| \frac{d\psi_b}{dy} \right\rangle + \left\langle \frac{d\psi_a}{dz} \middle| V \middle| \frac{d\psi_b}{dz} \right\rangle \end{aligned}$$

¹²Wolf, Reiher, and Hess., The J. of chem. phys. 117.20 (2002): 9215-9226.

Calculating Primitive Cartesian pVp integrals in a GTO basis

$$\begin{aligned}
 & pVp(i, j, k, l, m, n) \\
 &= 4abV_{i+1,j,k,l+1,m,n} - 2aIV_{i+1,j,k,l-1,m,n} - 2bIV_{i-1,j,k,l+1,m,n} + lV_{i-1,j,k,l-1,m,n} \\
 &+ 4abV_{i,j+1,k,l,m+1,n} - 2amV_{i,j+1,k,l,m-1,n} - 2bjV_{i,j-1,k,l,m+1,n} + mjV_{i,j-1,k,l,m-1,n} \\
 &+ 4abV_{i,j,k+1,l,m,n+1} - 2anV_{i,j,k+1,l,m,n-1} - 2bkV_{i,j,k-1,l,m,n+1} + nkV_{i,j,k-1,l,m,n-1}
 \end{aligned}$$

Where,

$i + j + k = L_a$ and $l + m + n = L_b$ are angular momentum quantum numbers of Gaussian primitives

Thus we can express pVp in terms of V of higher and lower angular momenta

To Summarize CERES Work

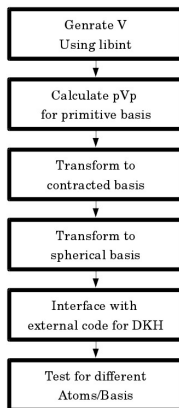


Figure: Summary of current implementation in CERES

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Er(trensals)¹³

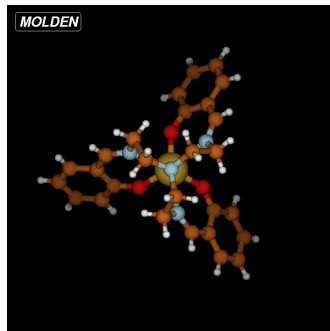
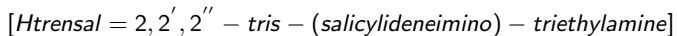


Figure: Structure of Er(trensals) (white, orange, blue, red and yellow correspond to H, C, N, O and Er)



¹³Pedersen et al. Chem. Sci. 5, 1650 (2014)

Background

- 1 The Er(trensal) system is ideal for study due to the presence of axial C₃ symmetry.
- 2 The salt has been experimentally analyzed¹⁴ and has been found to show slow magnetic relaxation at low temperatures.
- 3 Its spectrum has been recorded and can be readily be used to test prediction of theory.
- 4 The lowest spin-orbit multiplet $\frac{15}{2} I_4$ has J=15/2 which means it has 8 Kramers doublets.

¹⁴Flanagan, Bernadine M., Paul V. Bernhardt, Elmars R. Krausz, Stefan R. Lthi, and Mark J. Riley., Inorganic chemistry 40, no. 21 (2001): 5401-5407.; Lucaccini, Eva, et al., Chemical Communications 50.14 (2014): 1648-1651.

Current Method

- It so happens that it is possible to do a CAHF calculation using the software package ORCA but such a calculation using it on Lanthanide systems has not been attempted so far.
- In ORCA the MRCI routine helps in expanding the CI matrix to include excitation to selected orbitals outside the active space.
- This leads us to use a CAHF/MRCI-SO in this study with single excitations.

Computational Details

- SARC2-QZV-DKH2 basis sets¹⁵ contracted to [18s12p9d4f] used for the Er atom (SARC2)
- A similar calculation was also run with the old SARC basis for Er atom which was contracted to [18s12p9d3f]
- A SARC basis¹⁶ (optimized for DKH) contracted to [3s2p1d] was used for N, C and O
- H used a SARC basis contracted to [2s1p].

¹⁵Aravena, Daniel, Frank Neese, and Dimitrios A. Pantazis., Journal of chemical theory and computation 12.3 (2016): 1148-1156.

¹⁶D. A. Pantazis, X. Y. Chen, C. R. Landis and F. Neese, J. Chem. Theory Comput. 4, 908 (2008); D. A. Pantazis and F. Neese, J. Chem. Theory Comput. 5, 2229 (2009)

Preliminary Results vs Observed Values¹⁷

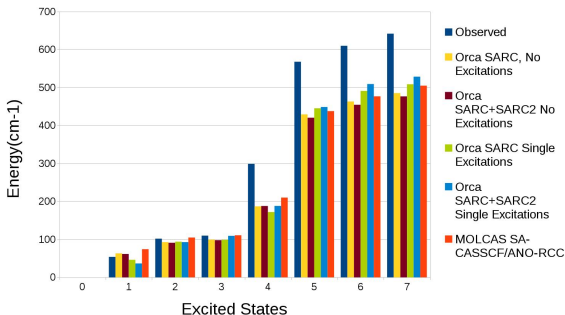


Figure: Energy of lowest 8 Kramers doublets obtained by different levels of theory and choice of basis compared with experimentally observed values (Relative to Ground State).

¹⁷Flanagan, Bernadine M., Paul V. Bernhardt, Elmars R. Krausz, Stefan R. Lüthi, and Mark J. Riley., *Inorganic chemistry* 40, no. 21 (2001): 5401-5407.

In Summary

- 1 Prediction of gaps for higher excitations needs to be improved.
- 2 Use of SARC2 basis improved prediction for higher states.
- 3 Need to improve method of selecting active space possibly use multiple active spaces in CERES.
- 4 in ORCA we can extend our current model by selecting larger active space or including double excitations.

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The Evans System

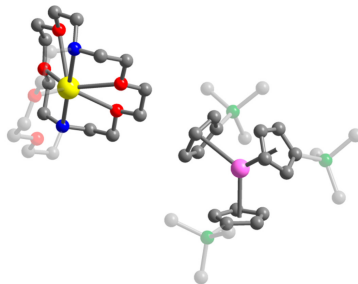


Figure: Structure of $[K(2.2.2 - cryptand)][Cp_3Ho]$

The system and the model

- Recent synthesis of the $[Cp_3Ln]$ system by Evans et al.¹⁸
- Current studies indicate that this compound has the the Ln in the +2 oxidation state. This is thought to consist of the 4f electron occupation as in +3 ion, and the extra electron in the 5d orbitals, exchange coupled to the 4f electrons.
- Aside from being a theoretical curiosity this molecule has also been revealed to be have the highest magnetic moment currently reported in Ln-SMMs.

¹⁸Jeffrey R. Long et al., J. Am. Chem. Soc. 2015, 137, 9855.;William J. Evans et al., Chem. Sci. 2015, 6, 7267.; David Mills et al., Inorg. Chem., DOI: 10.1021/acs.inorgchem.6b00808

The system and the model

- We could use a CAHF method(with possible MRCI) with more than one active space to describe the electronic structure of this system.
- The goal of CERES is to be able to calculate such systems with all the relevant effects taken into consideration.

Timeline of Future Work

| | CERES | ORCA |
|---------------------------------|---|---|
| First Six Months of Second Year | Finish Debugging pVp + implement DKH and link with SCF of CERES | Use multiple active space CAHF for Evans Molecule and possibly MRCI with ORCA |
| Month 6 till end of Second Year | Implement Effective Nuclear Charge for SOC + Write paper for new version of CERES | Write paper for multiple active space calculation on evans molecule |
| First Six Months of Third Year | Implement AMFI for CERES + Use CERES to explore Evans complex and trensal complex + Compare with ORCA Results | |
| Month 6 till end of Third year | Try to implement Ln-Dimers using CERES + Write Thesis | |

Thank You!

Extra Slides

Dirac Theory

⇒ When the electron moves at relativistic velocities, one must solve the four dimensional Dirac equation where the Hamiltonian contains odd operators that couple the upper and lower components to each other and even operators that couple the upper and lower components to themselves.

⇒ Under the DKH transformation¹⁹, a series of similarity transforms expand the odd operators into even and odd operators of higher orders of $1/c$.

$$H_{BD} = UH_{Dirac}U^\dagger = \dots U_4U_3U_2U_1H_{Dirac}U_1^\dagger U_2^\dagger U_3^\dagger U_4^\dagger \dots = \sum_{k=0}^{n_{dkh}} \epsilon_{n_{dkh}}$$

¹⁹Reiher, Markus, and Alexander Wolf., The Journal of chemical physics 121.5 (2004): 2037-2047.; Wolf, Alexander, Markus Reiher, and Bernd Artur Hess., The Journal of chemical physics 117.20 (2002): 9215-9226.; Reiher, Markus, and Alexander Wolf., The Journal of chemical physics 121.22 (2004): 10945-10956.

DKH Transformation

The lowest order DKH Energies are then given by:

$$\epsilon_0(i) = E_i - mc^2$$

$$\begin{aligned} \epsilon_1(i) &= A_i(V_{ij} + P_i V_{ij} P_j)A_j + iA_i\sigma(P_i \times V_{ij} P_j)A_j \\ &= (\textit{spin - free}) + (\textit{spin - dependent}) \end{aligned}$$

And so on. Where,

$$A_p = \sqrt{\frac{E_p + mc^2}{2E_p}}, E_p = \sqrt{p^2c^2 + m^2c^4}$$

Algorithm for Implementation of 1-electron Hamiltonian

the DKH Hamiltonian requires us to know the matrix of nuclear attraction integrals $\langle V \rangle$, the kinetic energy integrals $\langle T \rangle$ and the $\langle pVp \rangle$. Then the following algorithm²⁰ can be implemented.

- 1 The integrals are transformed into a basis where the matrix 'T' is diagonal using a unitary transform $\Omega T \Omega^\dagger$.
- 2 Use the same transform Ω to transform the above three sets of integrals into p^2 space.
- 3 Add all up to the n^{th} order to get H_{DKHn} energies in p^2 space using the appropriate formulae.
- 4 Transform H_{DKHn} back to position space using $\Omega^\dagger H_{DKHn} \Omega$

It can also be shown for a basis $\{\Psi_j\}$. That:

$$\langle \Psi_a | pVp | \Psi_b \rangle = \langle \nabla \Psi_a | V | \nabla \Psi_b \rangle$$

²⁰Wolf, Alexander, Markus Reiher, and Bernd Artur Hess., The Journal of chemical physics 117.20 (2002): 9215-9226.

Transformation into Spherical and Cartesian Gaussians

The transformation into a spherical basis from a Cartesian Gaussian is given by²¹ :

$$G_{lm}(\mathbf{r}, \mathbf{a}, \mathbf{A}) = N_{lm}^S \sum_{t=0}^{[(l-|m|)/2]} \sum_{u=0}^t \sum_{v=v_m}^{[|m|/2-v_m]+v_m} C_{tuv}^{lm} G_{2t+|m|-2(u+v), 2(u+v), l-2t-|m|}(\mathbf{r}, \mathbf{a}, \mathbf{A})$$

Where,

$$N_{lm}^S = \frac{1}{2^{|m|} l!} \sqrt{\frac{2(l+|m|)!(l-|m|)!}{2^{\delta_{0m}}}}$$

$$C_{tuv}^{lm} = (-1)^{t+u-v_m} \left(\frac{1}{4}\right)^t \binom{l}{t} \binom{l-t}{|m|+t} \binom{t}{u} \binom{|m|}{2v}$$

$$v_m = \begin{cases} 0 & m \geq 0 \\ 1 & m < 0 \end{cases}$$

²¹"Molecular Electronic-Structure Theory", by Helgaker, Jorgensen and Olsen.