

ERC Consolidator Grant 2014
DECRESIM: A Chemical Approach to Molecular Spin Qubits:
Decoherence and Organisation of Rare Earth Single Ion Magnets
Part B2: *The scientific proposal*

Section a. State-of-the-art and objectives

Quantum theory started a century ago, but its development is still ongoing and there is still much that we do not understand. Meanwhile, we all live surrounded by advanced electronics that “*runs on quantum mechanics*”, from semiconductor electronics and lasers to giant-magnetoresistance-based hard drives and memories. We even have a number of spectacular technologies that depend very explicitly of quantum effects, such as medical MRIs, superconducting quantum interference devices (SQUIDs) or quantum dots. But there is ample room for research, development and innovation in the next-generation quantum technologies such as quantum computation/simulation, quantum key distribution/networks and quantum metrology, sensing and imaging, which all revolve around the coherent manipulation of the wave function and the concept of **quantum two-state system or qubit**.

Very **different physical, chemical or even biological systems can embody a qubit**, but not all are equally well suited, and it is at this point where chemical design may play a leading role. For decades, a large number of physicists –including giants such as Haroche and Cirac– have performed experiments on trapped ions and resonant cavities, showing the power of Optic and Atomic Physics to perform complex quantum manipulations that were beyond the capabilities of Solid State systems (such as quantum dots or SQUIDs). However, in recent times the spectacular results using Nitrogen-Vacancy defects in a diamond matrix, such as entangled qubits separated by 3 meters, or room-temperature entanglement with storage times (at room-temperature!) of the order of 1 milisecond,¹ have shown the potential of *Condensed Matter* systems, which is to say, systems in the domain of Chemistry and Materials Science. In the last few years, the study of quantum effects in a chemical context is also becoming a hot topic for biophysicists, as some natural biological processes –most notably, photosynthesis in plants and geolocation in birds– have been found to have a relation with quantum coherence.² This is of great interest, since it shows that quantum coherent processes in complex organized systems can be not only beautiful theoretical constructs but the solution chosen by evolution for a given practical task.

Whatever the hardware and the application, the key to quantum technologies are fundamental quantum effects such as the creation and protection of **quantum superposition and quantum correlations** (e.g. the so-called “*cat states*”, Fig. 1). In real systems these quantum states are very fragile in the sense that, after uncontrolled interaction with the environment, they lose any existing quantum superposition and/or quantum correlations. This phenomenon, called **decoherence**, is a **major obstacle** for quantum applications.³ This is a dramatic problem for solid state systems, which on the other hand have unique advantages from the point of view of the applications –such as stable circuits or scalability– that give them potential to be disruptive technologies.

Unfortunately, in most solid-state systems one finds an infinite hierarchy of interactions as one lowers the energy scale. This is a key issue for decoherence, because it means that one cannot simply lower the temperature to get rid of unwanted perturbations, and unwanted interactions destroy quantum effects. As a result, it will not be possible to exploit the advantages of solid state systems until we have a theoretical framework for quantum evolution that includes a realistic model for decoherence. Decoherence also happens to be a process of fundamental interest for physics, as it has been postulated to be an explanation for basic questions such as the arrow of time, the emergence of classical behaviour from quantum mechanics and the measurement problem.

Much is at stake. Understanding and eventually controlling the processes that give rise to quantum decoherence will lay the foundations of any conceivable advance in present or future *quantum technologies*, but the *fundamental questions* we are dealing with are also formidable: Do we really understand why quantum effects are not persistent in time? Is quantum mechanics valid in the macroscopic world?⁴

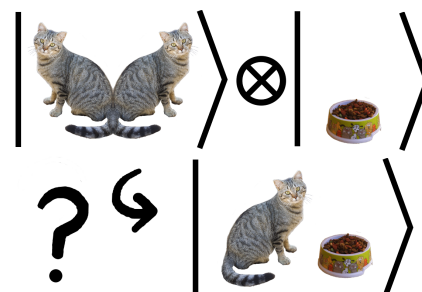


Fig. 1: Decoherence (not curiosity!) killed the *cat state*: uncontrolled interactions destroy any quantum superposition.

1 (a) Bernien et al., *Nature* 2013, 497, 86 ; (b) Dolde et al., *Nature Physics* 2013, 9, 139

2 N. Lambert, *Nature Physics* 2013, 9, 10

3 (a) W. P. Schleich, *Nature* 2000, 403, 256; (b) A. M. Zagoskin, “Quantum Engineering”, Cambridge Univ. Press, 2011
 4 P.C.E. Stamp, *Stud. Hist. Phil. Mod. Phys.* 2006, 37, 467

Indeed, there is an ongoing effort in understanding decoherence in order to design strategies that decrease its effect (see below for a partial summary of those). This project will establish firm handholds for **modelling decoherence to allow the chemical design of complex qubits structures**. Of course, to give practical answers we will need to choose and focus on a particular qubit architecture. In our case we will focus on molecular spin qubits, as this molecular approach appears to be very promising to chemically design and manipulate spins in solid matter. A major advantage of molecular spin qubits over other candidates stems from the power of Chemistry for a tailored and inexpensive synthesis of systems for their experimental study. For two decades, Molecular Magnetism has produced an array of tools to study, design and fine-tune magnetic molecules, and, in particular, **Single-Molecule Magnets** (SMMs) that vastly outnumbers the variations that can be performed on a particular type of crystalline defect in diamond.⁵ Experimentally, magnetic molecules have already been used to perform experiments on coherent oscillations,^{6(a)} and there have been recent theoretical studies about coherently manipulating a single qubit with electric fields.^{6(b)} Note that *Quantum Tunneling of the Magnetization*, which can be seen as a particular case of decoherence, is the main phenomenon in SMMs. Moreover, SMMs typically have a doubly (near-)degenerate ground state with a large separation to the first excited state, that is, a qubit, and a crucial parameter to describe this qubit is the *tunneling splitting* breaking its near degeneracy. Thus, **SMMs have a potential to be crucial in understanding and solving the decoherence problem for the Solid State**, much like in the first days of Quantum Computing, Nuclear Magnetic Resonance was key to implement the first quantum circuits.

It is thus SMMs that will be the subject of this project. In particular, we will focus on the so-called lanthanoid SMMs also known as Single-Ion Magnets (SIMs), a field shaped by seminal contributions of the PI. Thus, our general goal is to unravel the fine mechanistic details of relaxation and decoherence in Single Ion Magnets. This is a necessary step to measure, understand and improve their dynamical properties, either isolated or in complex, functional structures. In doing so we will offer answers to some central questions in Quantum Theory and Quantum Technologies.

Let us recall the current state-of-the-art of our understanding. In SMMs, three main environmental decoherence mechanisms have been described. The electronic spins couple (1) to *phonons* (described as an oscillator bath), (2) to *nuclear spins* (described as a spin bath) (3) to *other electronic spins*, causing magnon waves (Fig. 2).⁷ Magnon waves have been shown to be quenchable at low temperatures and high tunneling splittings, which can in principle –but not yet in practice– be achieved by chemical design. The effect of nuclear spins can also be minimized by a combination of chemical design and isotopic purification, a demanding but well-defined path. It is also minimized at high tunneling splittings. In contrast, the mechanism of phonon-caused decoherence is least understood, as the system-dependent spin-phonon coupling has not been properly studied. Worse, the current understanding of phonon-caused decoherence is that it is almost completely insensitive to temperature, and that to decrease it we need lower, rather than higher, tunneling splitting. This means that the **critical parameters to be studied are the chemical design of the tunneling splitting and the spin-phonon coupling**. Advances in the understanding of the coupling between the state of the spin qubit and the lattice phonons would also have potential consequences in the recently invigorated field of spin caloritronics.⁸

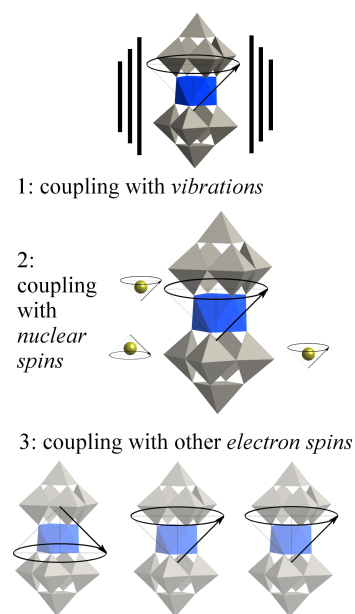


Fig. 2: Main sources of decoherence in a molecular spin qubit.

Weaker processes await being studied in detail after phonon decoherence can be decreased. In particular, part of the decoherence coming from the spin bath is caused not by magnetic spins, but from crystal defects that, being bi-stable quantum systems, behave quantum-mechanically as (non-magnetic) spins and are theoretically characterized as such. This process, which has not been properly studied yet, can be of general importance not only in crystals with recognized disorder: the tunneling of point defects, such as Schottky or Frenkel, is also expected to couple with the electronic spins via a higher-order process.

In any case, dealing with decoherence requires the knowledge of the affected energy levels and wavefunctions. The study of the electronic structure we will undertake will also serve to understand the characteristic properties of SIMs such as the slow relaxation of the magnetization. Note that the search for

⁵ The gigantic family of SMMs –the workhorse of Molecular Magnetism– is still growing by a new member every couple of days.

⁶ (a) C. J. Wedge et al., *Phys. Rev. Lett.* 2012, **108**, 107204 ; (b) F. Troiani, *Phys. Rev. B* 2012, **86**, 161409

⁷ (a) S. Takahashi et al., *Nature* 2011, **476**, 76; (b) P.C.E. Stamp, A. Gaita-Ariño, *J. Mater. Chem.* 2008, **19**, 1718

⁸ G. E. W. Bauer, *Nature Materials*, 2012, **11**, 391

lanthanoid SIMs in the last decade has been mostly trial and error, much like the search for transition-metal-cluster SMMs. Thousands of person-years have been consumed in several European projects and networks: MolNanoMag already in the 5thFP, then MagMaNet, QueMolNa... Great advances have been made,⁹ but we are still lacking a proper theoretical connection between the chemical structure and the desired dynamical physical property, e.g. the changes in a complex that are needed to achieve magnetic blocking at a higher temperature, or how to predictively control the quantum tunneling via the molecular structure: What should coordination chemists aim for, in terms of rigidity within the ligands and in the crystal structure, optimal shape, optimal functional groups or elements of the coordinating atoms, nature (or absence) of counterions, and also lanthanoid vs actinoid vs transition metal.

The current standard techniques to theoretically approach these questions are *ab initio* calculations, in particular Complete Active Space – Self-Consistent Field and Configuration Interaction. So far, these calculations are able to estimate the bulk magnetic properties including the magnetic anisotropy¹⁰ but they still face some problems, e.g. they fail to reproduce the low-energy structure as determined by spectroscopic techniques such as Inelastic Neutron Scattering, and also may present problems to estimate the full crystal-field gap.¹¹ Moreover, because of the computational cost, it is impractical to use them for predictive purposes. **Effective electrostatic point-charge models** are a promising alternative, as they can provide inexpensive predictive tools.¹⁰ Its current shortcoming is the small number of parameterized ligands so far, as this is an *empirical* method, not a *first principles* method. In this context, my team has very recently developed a software package using this electrostatic approximation called SIMPRE 1.1. This approach is based on a limited Hamiltonian acting on the ground state multiplet, which includes only the crystal field terms in the strong spin-orbit (LS) coupling approximation. This lowers the cost but limits the precision of the results in some cases.

Experimentally, the state-of-the-art in the field has also been influenced by the contributions of my theoretical team. A few years ago, my team reported the first two families of **Single Ion Magnets based on polyoxometalates (POMs)**.¹² These seminal contributions effectively opened up the field of SIMs to non-phthalocyaninato derivatives. Our recent efforts in this field have also resulted in papers opening new research fronts, including an attempt to rationalize of the synthesis of SIMs and the obtention of another SIM with an exotic 5-fold symmetry. Last year we also performed the first experimental study via generalized Rabi oscillation of the POM [GdW₃₀P₅O₁₁₀]¹²⁻.^{13(a)} In this experiment, it was possible to increase the number of coherent rotations tenfold through matching the Rabi frequency with the frequency of the proton. Achieving high coherence with lanthanoid POMs, we show their excellent potential, not only for the storage of quantum information, but even for the realization of quantum algorithms.

In the long run, little can be done with a single qubit, which means that we will need to think beyond a single molecule. Nevertheless, it is known that molecules containing more than one spin can be used to implement quantum gates¹⁴ or even a simple quantum algorithm such as Quantum Error Correction (QEC). This is an important point: **complex molecules can be designed to perform a practical function**, as a single encoded qubit allowing QEC effectively defeats decoherence.¹⁵ Nevertheless, so far these efforts have been largely limited to nuclear spins, rather than the electron spins of magnetic metal complexes. Notable exceptions include the suggestion to use the famous SMM Mn₁₂O₁₂(CH₃COO)₁₆(H₂O)₄ for a quantum algorithm,¹⁶ using antiferromagnetic chains to improve the properties of a single qubit¹⁷ or protocols for performing a single quantum gate with molecules containing either two lanthanoid ions^{18(a)} or a combination of fixed and mobile spins.^{18(b)}

The key point for quantum technologies, of course, will be the **organisation of such molecules** into actual devices. Although it has not been fully exploited in this field, a unique feature of molecules is the possibility of self-organization in arbitrarily complex structures, and this is precisely why Nature has chosen molecules as building blocks for life. Chemists in the nanosciences tend to wave the flag of the “bottom-up” approach, and defend the power of chemistry –or actually the power of Nature itself– to create perfectly “organized”

9 (a) J.D. Rinehart, *J. Am. Chem. Soc.* 2011, **133**, 14236 (b) R. Vincent, *Nature* 2012, **488**, 357

10 N. F. Chilton, *Nature Communications* 2013, **4**, 2551

11 (a) K. S. Pedersen, *Chem. Sci.* 2014, **5**, 1650 ; (b) Baldoví et al., submitted to *J. Am. Chem.Soc.*

12 (a) M. A. Aldamen et al, *J. Am. Chem. Soc.* 2008, **130**, 8874; (b) M. A. Aldamen et al, *Inorg. Chem.* 2009, **48**, 3467

13 (a) J. J. Baldoví et al., *Chem. Comm.* 2013, **79**, 8922 (b) S. Hill et al., in preparation

14 G. Aromí et al., *Chem. Soc. Rev.* 2012, **41**, 537

15 (a) K. Sato et al., *J. Mater. Chem.* 2009 **19**, 3739 ; (b) O. Moussa et al. *Phys. Rev. Lett.*, 2011 **107**, 160501

16 M. N. Leuenberger, D. Loss, *Nature* 2001 **410**, 789

17 F. Meier, D. Loss *Phys. Rev. Lett.* 2003 **90**, 047901

18 (a) F. Luis et al. *Phys. Rev. Lett.* 2011, **107**, 117203 ; (b) J. Lehmann et al, *Nature Nano.* 2007, **2**, 312

replicas of nano-objects. While this is true, the monotonous repetition of an object over a patterned 2D structure is not the end all-be all of organisation, and –notwithstanding heroic single-molecule experiments^{9(b)}– this is where we stand in the organisation of molecular spins.¹⁹ We have to take into account that even minimalistic systems such as cellular automata (Fig. 3), relying on the spacial and temporal repetition of basic units and interactions to achieve general computation capabilities, require some complexity, both to define the interaction rules and to initialize the system. In practice, **obtaining non-trivial nanostructures is an unresolved long-term requirement for functional quantum nano-devices.** In the mid-term, we should aspire to a molecular route to quantum cellular automata in 2D or 3D and in the long term a fully programmable organisation based on covalent 1D biopolymer chains would be ideal. Any of the three would be an unprecedented feat.

In this context, we recently presented a proposal that will be key to simplifying the organisation of spin qubits: the organisation of spin qubits in a Metal Organic Framework (MOF).²⁰ Our studies show that the different spin qubit types that need to be periodically arranged in space to advance toward quantum cellular automata will not necessarily have to be based each on a different lanthanoid metal. This would be very demanding, because lanthanoids are chemically very similar to each other. In fact, the same lanthanoid ion does not even need to be surrounded by ligands that are chemically very different: the small geometrical differences between crystallographically independent lanthanoids are sufficient to produce crystal fields that are distinguishable by EPR, in bulk. We recently published the synthesis and magnetic characterization of a MOF which achieves the regular repetition of three lanthanoid spin qubits, reminiscent of Lloyd's “global control” scheme for quantum computing.

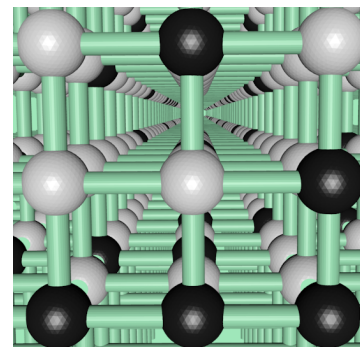


Fig. 3: $|0\rangle$ s and $|1\rangle$ s in MOF quantum cellular automata.

The general goal of this project will be to model decoherence in molecular spin systems of various nuclearities based on lanthanoid complexes. The concrete objectives will be:

#1 To unravel the mechanistic details of decoherence in molecular spin qubits based on **mononuclear lanthanoid complexes**. This study will establish criteria for the rational design of single spin qubits.

#2 To extend this study to the coupling between two or more spin qubits. This will allow us to explore the use of **polynuclear lanthanoid complexes** to achieve quantum gates or simple algorithms.

#3 To extrapolate to **infinite systems** formed by the complex organization of spin qubits. This exploratory goal will permit us to move beyond zero-dimensional systems, thus facilitating the advance towards complex quantum functions.

These three goals will be pursued by three distinct work packages. WP1 and WP2 are short- and medium-term goals and will be split in the following series of intermediate tasks:

- Complete a general library of parameterized ligands that is fit to reproduce the crystal-field Hamiltonian from the molecular structure of lanthanoid complexes.
- Program a software package for the screening of crystallographic databases, to find a collection of candidate structures matching the desired energy level scheme.
- Calculate the spin-phonon coupling terms in the Hamiltonian of lanthanoid complexes.
- Develop a platform able to predicting the time evolution of the wave function in these systems.
- Develop a formalism of decoherence that makes these predictions useful to interpret experiments.
- Test the developed theory in terms of magnetic relaxation.
- Test the developed theory in terms of decoherence, in a pulsed EPR setup.

WP3 is the start of a long-term goal for the complex organisation of spin qubits. We will explore organisation in MOFs and attached to programmable biopolymers. The two approaches are radically different from each other, with the last one pushing the boundaries of the so-called self-organisation of nano-objects.

19 A. Cormia et al., *Chem. Soc. Rev.*, 2011, **40**, 3076

20 J. J. Baldoví et al, *Chem. Eur. J.*, 2014, DOI: 10.1002/chem.201402255

Section b. Methodology

A large part of DECRESIM is theoretical, because first and foremost we need to understand decoherence processes in lanthanoid complexes. Nevertheless, theory cannot be developed in a vacuum: we need to test predictions, and, just as important, to find new phenomena that need explanation.

The first Work Package (WP1) will study decoherence focusing on the single-qubit case. This will allow the control of all variables, both in the theory and in the experiment. WP2 will extend this to the simplest multi-qubit cases: a small number of lanthanoids and their nuclear spins. With this we will be able to study and implement quantum gates and simple algorithms. WP3 has a more exploratory character: once coherent processes are under control for small clusters of qubits, we need to venture beyond the zero-dimensional systems and aim for complex organisation, a requirement to achieve complex functions.

WP1. A single molecular spin qubit: understanding decoherence

We will improve the current state of the theory with the double goal of the chemical design and for a proper understanding of the experiments. Experimental information on the properties of lanthanoid complexes is also crucial to test and

- Set up a predictive theoretical, design-oriented method that describes the time evolution in pulsed EPR experiments on molecular spin qubits.
- Implement a strategy that significantly extends quantum coherence in lanthanoid spin qubits.

fine-tune the theoretical models, from the crystal-field Hamiltonian to the coupling to the spin and phonon baths, from the magnetic behavior to the response in EPR experiments. Perhaps more importantly, new phenomena are often encountered experimentally which foster theoretical advances. This WP will be developed at the ICMol but will include external collaborations to access specialized equipment.

Task 1.1 From coordination environment to crystal field Hamiltonian in lanthanoid SIMs

The first goal is to be able to consistently produce a crystal-field (CF) Hamiltonian starting from the molecular structure. This is a necessary first stone to support DECRESIM, as the CF determines the most relevant energies and spin wavefunctions of our spin qubits, and relating this to the molecular structure is a requirement to perform the rational chemical design of molecular spin qubits with minimal decoherence. We will achieve this by using an effective electrostatic model, i.e. we will assume that the main effect of the ligands in the CF is electrostatic and that the covalent effects can be adequately reproduced by choosing an effective charge that is both smaller and at a closer distance to the metal ion (Fig. 4). The electrostatic treatment also makes this approach useful for simulating the effect of an external electric field. Preliminary calculations on complexes with highly polarizable ligands (anionic aromatic rings) show that this is a possible path for electrical control of the spin state.²¹

For the calculations, we will use SIMPRE 1.1, the software package developed by my team, to analyze available spectroscopic data²² and to distil optimal parameter values for all common ligands from the observed level splittings.

We will thus perform an effective point charge parameterization of the most common ligands in lanthanoid chemistry to account for the CF effect in these complexes. This is a task of general interest for the community working in coordination chemistry and physical properties of lanthanoid complexes, analogous to that of establishing the **spectrochemical series** for transition metal ions. In particular, we will parameterize:

- oxygen in water, in hydroxo or oxo groups and in carboxylates
- nitrogen in ligands based on pyridine
- carbon in organometallic (ferrocene-like) complexes

Next, we will produce SIMPRE 2.0, which will explicitly include spin-orbit coupling and thus will be used to refine the previous parameterization. This complete approach will be based on the full Hamiltonian within the whole $4f^n$ configuration, including the free ion terms in addition to the CF ones and incorporating the intermediate coupling and the J-mixing. From the diagonalization of the matrix Hamiltonian we will obtain the full set of energy levels and eigenvectors. This challenging improvement will considerably increase the cost of the exploration, as the matrices to diagonalize will be noticeably larger. It will also open the access to

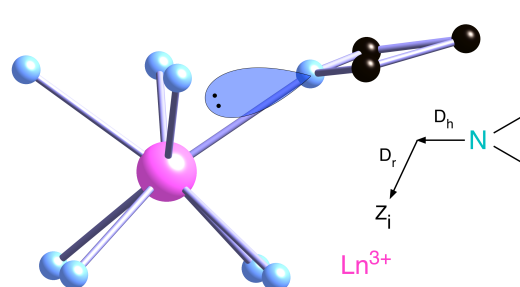


Fig. 4: Pyrazole ring of the phthalocyaninato ligand modelled by a point charge Z_i displaced D_h along the lone pair and D_r toward the ion.²³

²¹ J.J.Baldoví et al, in preparation.

²² See e.g. the 75th contribution in a lengthy series by H.D. Amberger et al., *J. Organometallic Chem.* 2011, **696**, 2829

²³ J.J.Baldoví et al., *Dalton Trans.*, 2012, **41**, 13705

the vast literature on optical transitions of lanthanoid complexes, thus allowing a refining of the previously obtained parameterization library.

Once the library is obtained, SIMPRE 2.0 will be used as **an inexpensive and predictive CF method**, a tool that **will have a great impact in the community**. This in turn will allow the **automated screening** of crystallography databases to select complexes with the desired properties. Furthermore, this will permit to envision the exploration of yet unsynthesized complexes, by *in silico* assembly, (DFT) relaxation and determination of their properties via SIMPRE 2.0, prior to a directed synthesis. Additionally, working with an effective Hamiltonian will ease the seamless integration of further effects (Task 1.2) and integration with methods of theoretical physics to predict time evolution of the quantum states (Tasks 1.3 and 1.4).

Task 1.2 Expand the Hamiltonian to include the coupling with the spin and oscillator baths

The second goal is to expand the CF Hamiltonian to deal with the main known decoherence processes: the coupling with the spin bath and the phonon bath.

The coupling with electron and nuclear spins will be included in the spin Hamiltonian as dipolar terms plus a superexchange tensor. In our model, this will be easily incorporated, as the hyperfine parameter is just an exchange term with a parameter that can be taken from the bibliography and the dipolar coupling is simply determined by the expectation value of the angular momentum in the three directions of space –observables that can be derived from the eigenvectors calculated by SIMPRE 2.0, see Task 1.1– and the crystallographic position of the nuclei.

In turn, the coupling with phonons is much more challenging: one needs to calculate, first, the response of the magnetic energy levels to geometrical distortions and second, which are the actual geometrical distortions acting on the system. While this challenge has never been undertaken for lanthanoid-based SIMs/qubits,²⁴ the PI has ample experience in coupling phonons into diverse kinds of spin Hamiltonians, whether the phonons are coupled with structural or electronic excitations.²⁵ An additional complication will be obtaining the phonon density of states, i.e. which phonons will be relevant at a given temperature.

The first problem will be partially solved by Task 1.1, which will facilitate the determination of the energy variation with any geometrical distortion. Additionally, we will need to add a **time-dependent Zeeman term**, as certain vibrations will periodically alter the alignment between the external magnetic field and the molecular magnetic anisotropy tensor. Indeed, a transversal lattice vibration which is seen as a rotation by the magnetic molecule causes the angle α between the molecular axis and the external magnetic field to be proportional to the phonon amplitude. For an external magnetic field along the easy axis of magnetization, this will result in a small perturbation (proportional to $\cos(\alpha)$) on the diagonal Zeeman terms but a dramatic effect on extradiagonal Zeeman terms caused by the time-dependent transverse field, proportional to $\sin(\alpha)$, which can then drive transitions.

An analysis of the **main molecular vibrational modes and their coupling with longitudinal and transverse phonons** of the lattice will be performed through standard DFT techniques.^{25(a)} The cost of the calculations will be decreased without any substantial loss of accuracy by the substitution of the lanthanoid cation by a diamagnetic ion such as Y^{3+} , with an identical charge and a similar radius but closed-shell.

Task 1.3 Predict the time evolution of the wave function

Once the main terms of the Hamiltonian have been evaluated, the third goal is to calculate the dynamical properties of the systems under study. Exciting results obtained recently by my team suggest that, once this theoretical handhold is in place, novel physical effects can be harnessed to significantly decrease decoherence in experiments (see Task 1.7).^{13(a)}

We will explore several approaches that are available for the so-called Central Spin problem, which studies the quantum evolution focusing on the Hamiltonian of a single effective spin in the center of an environment which introduces different interaction terms.

Ordered from the least to the most ambitious method, we will:

(a) obtain **dimensionless decoherence rates** (starting from a path integral approach and within the spin-boson model) as function of all relevant variables.⁷ This will allow us to effectively quantify decoherence for each system under study, or in general as a function of the chemical structure and composition. Furthermore, as the different contributions to decoherence are calculated separately, we will be able to distinguish and quantify the weight in total decoherence of the different processes, an invaluable aid for the molecular /

²⁴ The closest effort is the phonon module of [McPhase](#), which does not include any of the refinements detailed here.

²⁵ (a) A. Gaita-Ariño and M. Schechter, *Phys. Rev. Lett.*, 2011, **107**, 105504 ; (b) A. Gaita-Ariño et al., arXiv: submitted to *Phys. Rev. Lett.* ; (c) C. Bosch-Serrano et al., *Phys. Rev. B* 2012, **86**, 024432 ; (d) B. Tsukerblat et al., *Int. J. Quant. Chem.* 2012, **112**, 2957

crystalline design.

(b) apply **time-dependent perturbation theory**,²⁶ distinguishing between time-independent major terms such as the crystal field and minor perturbations such as the coupling with a fluctuating bath of nuclear spins. This will allow the detailed prediction of the time evolution of the quantum state of the systems, both for spontaneous decoherence processes and for induced coherent transitions. Artificially activating and deactivating terms in the Hamiltonian, it can serve the function of approach (a), but with a much richer result in terms of information, and also at a much higher computational cost.

(c) solve a **Master Equation** to calculate the evolution of the wavefunction²⁷, i.e. integrating to different final times with the complete Hamiltonian as defined in Tasks 1.1+1.2, without treating any of the processes as perturbations. This is essentially the same as approach (b), but without making assumptions about the energy ratios of different processes. This means a higher computational cost but also has the benefit of being able to explore the full parameter space, because for certain cases the “time-varying perturbation” will be a major term.

Task 1.4 Develop a proper phenomenology for decoherence

The T1-T2 phenomenology (spin-lattice and spin-spin relaxation times) is based on the classical Bloch theory, which is basically limited to the self-consistent description of a single spin in a classical fluctuating mean field. This is a treatment that is only adequate for “noise” decoherence, but leaves out “topological” decoherence and “precessional” decoherence. Topological spin bath decoherence results from the finite time (rather than infinitesimal) taken by each spin qubit transition. This term is proportional to the square of the (dipolar) hyperfine interaction and inversely proportional to the square of the distance to the first excited level, and is usually assumed to be small. Precessional decoherence, on the contrary, results from the spin bath absorbing phase from the central spin with every transition of the spin qubit, even if they are instantaneous. Usually this is the strongest contribution to decoherence from a spin bath, and it is caused by a phenomenon that is foreign to the T1-T2 phenomenology. The equations governing these phenomena are known, at least for some limiting cases,⁷ but the intermediate cases need to be solved, and a link with the experiment needs to be established with the development of standard experiments to extract decoherence information to obsolete/deprecate the current standard procedures (as spin echo experiments) in the context of spin qubits.

In doing so, we will develop a formalism that offers a proper description of pulsed EPR/NMR experiments considering all the internal phase information in the spin bath dynamics, including entanglement and the relative phases between spins. This theoretical development will permit the definition of experimental figures of merit to rationalize the progress and guide the optimization. More generally, this open problem is a theoretical challenge and its resolution will have consequences for all experimentalists characterizing molecular spin qubits by means of pulsed EPR experiments.

Task 1.5 Directed synthesis of lanthanoid complexes

Using the criteria defined in WP1, we will propose the types of compounds for which improved properties are expected. Experience shows that often, it will be possible to do that with little effort, as the vast majority of lanthanoid complexes have been obtained historically for their optical properties, so in most cases their magnetic properties remain unstudied. The ICMol hosts many researchers pursuing this goal using different chemical approaches, from polyoxometalates to phthalocyaninato complexes. In this project we will focus on polyoxotungstates, because several of their properties makes them ideal for our purposes, namely:

- the rigidity of the coordination sphere, compared with regular coordination chemistry compounds
- their almost complete lack of nuclear spins, being based on W (>85% free of nuclear spins) and coordinating through O (>99.95% free of nuclear spins)

Our team has a wide and recognised expertise in the characterization and modelization of POMs, making these systems ideal for DECRESIM. Our latest breakthrough was the directed synthesis (after the modelization of analogous compounds) of a Nd³⁺-based SIM. Early lanthanide SIMs are extremely rare, as most experimentalists focus on the more popular Tb-Er block. We showed -theoretically and experimentally- that early lanthanides constitute a virgin but fertile territory, and provided the tools to guide its exploration.

Task 1.6 Predict, delay or control magnetic relaxation

We will study the dynamical properties typical of SIMs: magnetic relaxation in presence and absence of magnetic field, at different temperatures and oscillating frequencies (or field ramps). These processes are

²⁶ as in e.g. J. H. Shim et al., *Phys. Rev. Lett.* 2012, **109**, 050401

²⁷ Using the procedure described in E. Barnes et al., *Phys. Rev. Lett.* 2012, **109**, 140403

governed by the electronic structure and its coupling to phonons, thus we will build upon results of Tasks 1.1 through 1.3 to study collective phenomena. In particular, we will perform studies based on:

-Landau-Zener experiments, which will be used for the characterization of the tunneling splittings and quantum interference phenomena²⁸ and has also been suggested by us for the manipulation of the spin state²⁹

-zero-field relaxation: in this experiment the spins are polarized and the magnetic field is suddenly switched off to study the decay of the magnetization. For the pure quantum regime, this results in a well-known square root of time law.³⁰

In all of these studies, we will also analyze the effect of isotopic enrichment, to quantify the influence the nuclear spins in relaxation processes. For some lanthanoids such as Dy or Er, preparing an isotopically pure sample allows to switch the lanthanoid nuclear spin on and off, keeping all the other parameters constant.

This magnetic studies, together with the theory developed in WP1, will allow us to advance beyond the identification of the energies and frequencies of primary and secondary relaxation processes,³¹ into mechanistic details that are needed to acquire some control and extend relaxation times. Beyond the importance of this results for DECRESIM, this will also be unvaluable to guide the rational design of SIMs that operate at higher temperatures and/or lower frequencies, and of lanthanoid complexes with better magnetocaloric properties.

Task 1.7 Manipulate quantum states by means of pulsed EPR

This task will build upon results of the whole WP1 including Task 1.4. We will use a pulsed EPR (X-band) already available in our laboratory, and additionally we will purchase a “super QFT” extension and a goniometer for the orientation of single crystal. The FT Q-Band gives improvement in resolution, accuracy, identification and signal intensity. The Q-band will allow us to access a wider frequency window (35GHz), corresponding to energies of 1.7K, which precisely correspond to the lowest multiplet of the lanthanoid complexes, embodying our spin qubits. With this equipment, we will both perform standard characterization and advance toward the coherent manipulation of molecular spin qubits, including simple quantum circuits, either in individual molecules or in complex organized networks (see WP3).

As in-house experiments, we will perform:

-Electron Spin Echo Envelope Modulation (ESSEM) both to create and to observe coherence-transfer echoes involving electronic and nuclear spins. This is the simplest way to access the nuclear spins of magnetic molecules. This is important because they are better protected from decoherence compared with the electrons. Among the multiple ESSEM experiments, we will focus on:

-bidimensional-three-pulse ESEEM, to obtain information on hyperfine, nuclear Zeeman and nuclear quadrupole parameters

-primary soft ESSEM, i.e. use of low microwave power to effect selective transitions, which allows enhanced access to information on spin dynamics

-Echo-detected transient nutations to observe Rabi oscillations, the most simple coherent manipulation; the number of observed Rabi oscillations can serve as a clock counter on the maximum number of quantum operations that can be performed on a (pseudo) pure quantum state of the system. We have already obtained spectacular preliminary results, decreasing decoherence (and thus maximizing the number of coherent oscillations) when operating in the right parameter regime (Fig. 5).^{13(a)}

As a collaboration with the National High Magnetic Field Laboratory (contact: Stephen Hill), we will extend our studies to Electron-Nuclear Double Resonance (ENDOR).

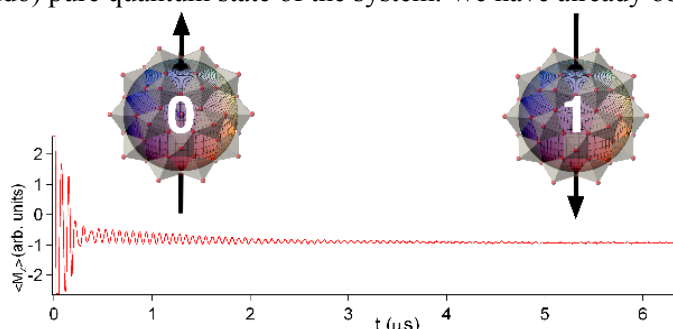


Fig. 5: The number of coherent oscillations was increased tenfold in a sample of $[YW_{30}P_5O_{110}H_2O]K_{14} \cdot nH_2O$ doped with Gd^{3+} .^{13(a)}

28 (a) W. Wernsdorfer and R. Sessoli, *Science* 1999, **284**, 133 ; (b) N. A. Sinitsyn and N. Prokof'ev, *Phys. Rev. B* 2003, **67**, 134403

29 A. Palić et al., *Phys. Rev. B* 2011, **84**, 184426

30 (a) L. Thomas et al, *Phys Rev. Lett.* 1999, **83**, 2398 (b) W. Wernsdorfer et al, *Phys Rev. Lett.* 1999, **82**, 3903

31 J. D. Rinehart et al., *J. Am. Chem. Soc.* 2010, **132**, 7572

WP2. Interactions: from the single quantum bit to the quantum gate

While WP1 deals with mononuclear, isolated lanthanoid complexes as single spin qubits, WP2 considers more than one lanthanoid in close proximity, which creates the possibility of quantum gates and even simple algorithms.

- Design, prepare and characterize lanthanide complexes embodying more than one spin qubit.
- Implement quantum gates and simple algorithms in a pulsed EPR setup.

There is a large methodological overlap between WP2 and WP1, both theoretical and experimental: almost every technique that is useful for WP1 is equally useful for WP2 and *vice versa*. For this reason, here we merely point out the main differences.

Task 2.1: Extend coherent manipulations to two-qubit quantum gates and simple algorithms

Given the wide field of chemical possibilities, the choice of suitable systems will be guided by the theoretical studies performed in WP1 in order to minimize decoherence. In this respect, POMs might offer limited possibilities for the goal of connecting lanthanides via weak magnetic superexchange. We will thus resort to the more ample possibilities of polydentate organic ligands, which are being used successfully for this purpose.³² In particular, we will focus on dinuclear and trinuclear lanthanoid complexes based on either quinolinato-like (Q) ligands or on triethylenetetraamine, such as $[\{\text{Tb}(\text{TETA})\}_2\text{Tb}(\text{H}_2\text{O})_8]^+$ (Fig. 6). For both ligands, we have already obtained promising preliminary result with the coupling of three Tb^{3+} ions. In the case of $[\{\text{Tb}(\text{TETA})\}_2\text{Tb}(\text{H}_2\text{O})_8]^+$, it has even been possible to experimentally tune the coupling between the metal ions.³³

We recently showed that the ground energy level structure of a molecule containing three exchange-coupled $^{159}\text{Tb}^{3+}$ ions is equivalent to nine electron-nuclear qubits.³⁴ We derived the relation between spin states and qubit states for a reasonable parameter range, and studied the possibility to implement Shor's QEC code on such a molecule. In particular, we quantified the accuracy of our scheme by the quantum fidelity between separable and mixed quantum states and we calculated how this depends on molecular parameters such as the magnetic exchange J and the quantum tunneling Δ (Fig. 7). We also discussed recently developed molecular systems that could be adequate from an experimental point of view.

In addition, we will study other multi-qubit schemes. For example, we will combine a 4-degenerate electronic state with the 8-degenerate nuclear spin state of Ho to produce 5 qubits, which may be useful for fault-tolerant Quantum Error Correction codes. Possible systems for this scheme include the cubical POM structures described by Kortz³⁵ of formula $[\text{HoPd}_{12}(\text{AsPh})_8\text{O}_{32}]^{5-}$ and octahedral Elpasolite salts $\text{Cs}_2\text{NaY}_x\text{Ho}_{(1-x)}\text{Cl}_6$, $\text{Cs}_2\text{NaY}_x\text{Ho}_{(1-x)}\text{F}_6$. In fact, we have already started the theoretical treatment and the experimental magnetic characterization of these structures.³⁶

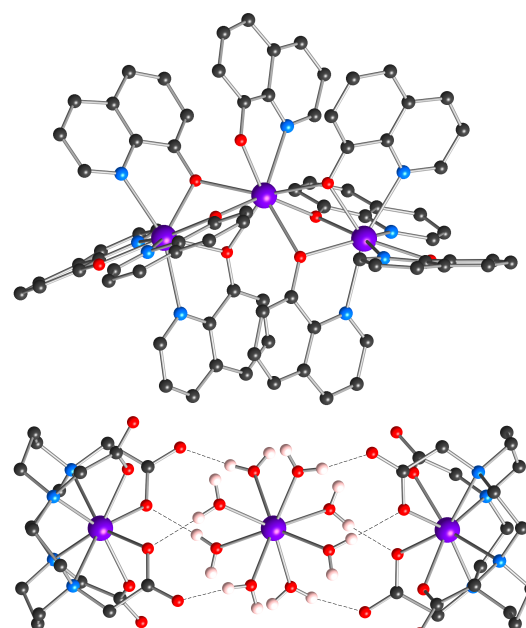


Fig. 6: (up) Covalent complex Tb_3Q_9 (Q=quinolinato)
(down) Supramolecular trimeric complex $[\{\text{Tb}(\text{TETA})\}_2\text{Tb}(\text{H}_2\text{O})_8]^+$

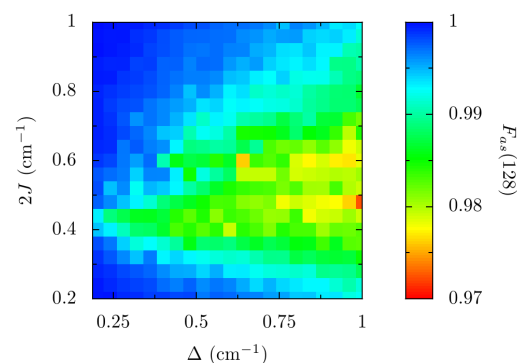


Fig. 7: Quantum fidelity vs. molecular parameters: maximal fidelity is achieved at low Δ , high J .

32 N. F. Chilton et al, *Inorg. Chem.* 2014, **53**, 2528

33 G. Mínguez-Espallargas et al, in preparation

34 J. J. Baldoví et al., arXiv, submitted to *Phys. Rev. A*

35 M. Barsukova et al., *Chem. Eur. J.* 2010, **16**, 9076

36 (a) J. J. Baldoví et al, *Inorg. Chem.*, 2012, **51**, 12565, (b) J. J. Baldoví et al, in preparation

WP3. Organisation of spin qubits

Theoretical proposals, when disconnected from the experiment, often make non-realistic assumptions. Thus, for the theoretical study of spin qubits organised in complex structures we will work in parallel with the experiments. The empirical input will allow the development of theoretical proposals that can actually spark follow-up experiments. In particular, we will work on different extensions of the Lloyd's scheme, originally based on an $(-ABC-)_n$ chain,³⁷ either to higher dimensionality, to a coding that is more complex: a larger alphabet and/or the possibility of choosing different sequences.

Set up an experimental research line on the complex organisation of spin qubits.

Organisation is a high-risk, high-benefit part of this project. The goal is broad and ambitious, as we will go beyond the current state of the art. We will deal with the risk by exploring two promising methods for the organisation of spin qubits which are radically different from each other: insertion into Metal-Organic Frameworks and attachment to programmable biopolymers. In a sense, this will constitute a safely adventurous quest, because initially none of the tasks will require heavy investment in equipment, chemicals nor personnel, and depending on success in intermediate critical steps, we will pursue the most productive path(s). In all of WP3 we will build over WP1, WP2: initially we will work with the lanthanoid complex (or cluster) that allows for an easiest manipulation, but after a given strategy has proven successful (as in the case of Task 3.1, see details below) we will optimize it by choosing or designing a lanthanoid complex that will minimize all known decoherence processes. Postdoctoral fellows with a strong experimental background in the different fields will deal with the day-to-day problems of the material processing in WP3.

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Task 3.1 Organisation in Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs) are ideal three-dimensional crystalline structures for the organisation of molecular spin qubits, due to their chemical flexibility.

In this project we will extend this new concept to organize other SIMs (note also that we are not limited to 3D, as there are 1D and 2D MOFs). We will focus on lanthanoid MOFs for which there is already a large number of examples. The Cambridge Structure Database (CSD) identifies approximately 8000 polymeric lanthanide structures, some of which will undoubtedly be adequate for our purposes. We will thus acquire a full academic license of CSD and its associated products (including *Mogul*) to perform an in-depth search. We will exploit the scripting possibilities of *Mogul* and use it as first stage for a massive exploration considering all the final search criteria, which will be defined by Task 1.2 and couple this with an automated study of each structure using SIMPRE 2.0, the optimized methodology developed in Task 1.1. Note that we will consider not only the single-ion behavior but also relevant environmental factors such as:

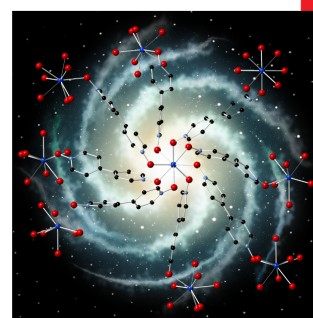
- number of crystallographically different lanthanoids in a given structure
- distance and estimated coupling (e.g. via dipolar interactions) between magnetic centers
- density and nature of nuclear spins in natural isotopic abundance / in the most favourable isotopic purification

We will tune the optimization criteria so that the automated search results in about a hundred candidates, a number that can be managed by a human operator. The next step will involve reading in detail about each compound, structure and synthesis. Indeed, we will then be able to manually reduce the list using chemical criteria, such as the reported or expected ease of synthesis and manipulation, the possibility to obtain high-quality single crystals or the chemical stability.

This selection will allow us to focus on organized lanthanoid MOFs with minimal decoherence. With those, we will propose pulsed-EPR sequences based on the three-dimensional extension of Lloyd's one-dimensional proposal, with the final perspective of advancing toward a quantum cellular automata. As already pointed out, we have already started to use MOFs in this context. In fact, in collaboration with Dr. Mínguez-Espallargas, a postdoc specialist working in magnetic MOFs, we have shown that a spatially regular organisation of three different spin qubits, reminiscent of Lloyd's "global control" scheme for quantum

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SIMs to be in (3D) order
The formation of a single-ion magnetic metal-organic framework (SIM-MOF) is presented, which enormously simplifies the challenging issue of making SIM-MOFs. The incorporation of bulky polynuclear ligands into the cavities does not interfere with the slow magnetic relaxation, demonstrating the robustness of the frameworks and opening the possibility of incorporating non-exact centers.

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Fig. 8: Inner cover with the first complex MOF organisation of SIMs in $[\text{Ln}(\text{bipyNO})_4](\text{TfO})_3$.

37 S. Lloyd, *Science* 1993, **261**, 1569

computing, formed by lanthanides in the nodes can be chemically constructed (Fig. 8).³⁸ Independently, another group has announced the quantum tunneling of the magnetization in an Fe-based Single-Ion Magnet – Metal Organic Framework.³⁹

While the case of the Nitrogen-Vacancy centers in diamond seems to favour absolute rigidity, this study will allow us to establish rational chemical criteria for the design of lanthanoid complexes with the desired spin-phonon coupling. Do we want an absolutely rigid lattice, a rigid coordination sphere with flexible side groups, or perhaps rigid complexes, such as POMs, with loose counterions? To answer these questions, the analysis of the spin-phonon coupling will need to go a step beyond what was explained in Task 1.2. In particular, we will explore, following the theoretical method by Efros and Shklovskii,^{40(a)} whether Metal-Organic-Frameworks (MOFs) are **optimal structures to minimize decoherence caused by spin-phonon coupling**, as one can expect intuitively. In particular, this would happen because of the energy separation between the binding energy in the MOF structure (covalent) compared with the solvent and counterions in the cavity. Thus, low-energy phonons taking place in the cavities (dominated by weaker intermolecular interactions) could gap higher-energy vibrations happening in the MOF structure. This effect, analogous to the one described in the study of universality of low-temperature thermal and mechanical behavior in disordered solids,^{40(b)} would result in an extremely reduced density of states for the relevant phonons i.e. those that couple more strongly to the spin state. In turn, this would minimize phonon-based decoherence, which, as explained in the introduction, is one of the most challenging open problems in this field.

Task 3.2 Organisation via biopolymers

The programmable structures of biopolymers, such as proteins or DNA, have an unmatched potential as scaffold for the organisation of quantum nanoobjects such as molecular spin qubits. Note that not only these covalent skeletons are used by Nature to store and manipulate information: there are also examples where they are involved in processes where coherent quantum effects (at room temperature!) play a biological function.² In the long term, we propose using specific DNA sequences to attach different complexes – embodying distinct qubits or qubit groups– in different positions, in a *programmable* fashion. This would result in the possibility of choosing richer codes to implement a scheme analogue to the one proposed by Lloyd. Having a larger alphabet and, specially, the possibility of going beyond a regular repetition, would reduce the number of quantum steps and the needed precision. In the short and medium term we need to study how to minimize decoherence and how to control the qubit-qubit interactions in these environments.

Recently, a simple method was reported for preparing recombinant histone octamers by overexpressing all four histones from a single polycistronic vector followed by standard chromatography under native conditions.⁴¹ This procedure, a great advance over the previous state of the art, can be used to prepare histone proteins with arbitrary modifications with standard molecular biology equipment as found in the ICMol. Thus, as biostructure for Task 3.1 we will use **recombinant histone proteins**. The N-terminal end of histones –not essential for DNA binding– will be cut off and substituted by a tail that will be used to attach the lanthanoid complexes carrying the spin qubits. This modification will also allow recognition by nucleosome-positioning DNA sequences, via salt gradient dialysis assembly. Eventually, chimeric arrays will be used to organize the lanthanoid-bearing histones in specific sequences. The goal will be “writing” a code in DNA where different sequences will recognize different histones (Fig. 9), thus allowing the “programmable” organization of our spin qubits. A first exploration of the whole procedure (without the qubits) will take place with a commercial Chromatin Assembly Kit from Millipore.

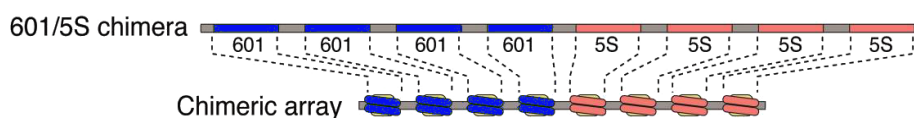


Fig. 9: Nucleosomal array using nucleosome-positioning DNA-sequences, from [37].

38 J. J. Baldoví et al, *Chem. Eur. J.*, 2014 (DOI: 10.1002/chem.201402255, cover confirmed on May 8th)

39 Y. Tian et al., *Phys. Rev. Lett.* 2014, **112**, 017202

40 (a) A. L. Efros et al., *J. Phys. C* 1975, **8**, L49 ; (b) M. Schechter and P. C. E. Stamp, *Phys. Rev. B* 2013, **88**, 174202

41 Y. Shim et al., *Anal Biochem.* 2012, **427**, 190.

The experimental steps identified as critical are the following:

Critical step 1: Obtention of a lanthanoid-binding histone. The obtention of a histone protein with the desired peptidic extension will occur via a bacterial expression⁴¹ with a plasmid containing the DNA sequence of the histone plus a Lanthanide Binding Tag (LBT).⁴² Lanthanoid complexes attached to biomolecules are used as local probes to study their structure or dynamics, either with luminiscence or in NMR experiments.⁴³ The histone-LBT-lanthanoid complex can be critical for the elucidation of nucleosome assembly and epigenetic inheritance,⁴⁴ and thus will awake an interest well outside the scope of DECRESIM.

Critical step 2: Characterization of the spin qubit. The sample quantities (of the order of 1 mg, and with a magnetic density of about 1 lanthanoid ion per 110 kDa) and the expected difficulty to obtain crystals, will require the use of highly sensitive techniques, namely EPR, available at the ICMol, or micro-SQUID, available at the Instituto de Ciencia de Materiales de Aragón.

Critical step 3: Recognition of the histone-LBT-Ln complex by DNA. The different flexibility and intrinsic shape of different DNA sequences, and the fact that the LBTs will be adjacent to the histone core will enable, in principle, selective recognition between DNA and lanthanoid-bearing histones. We will apply antibody techniques to study the affinity of nucleosome-positioning DNA sequences –e.g. sea urchin 5SrDNA or *in vitro* selected 601, 603 sequences– for different recombinant histones and for wild type histones.⁴⁵

The result will be a linear sequence of different lanthanoid complexes. Determining the magnetic and optical properties of the thus organised lanthanoid complexes will enable the theoretical formulation of proposals profiting from the programmable character of this linear sequence of molecular spin qubits.

Risk/gain assessment

Task 1.1 will provide a novel and inexpensive approach to estimate the crystal field (CF) of lanthanoid complexes. Possible risks include the impossibility to accurately reproduce the effect of the charge by a single point charge. If the achieved accuracy and predictive power are high enough, this tool will be of great value, well beyond this project. It can thus be described as a *medium-risk, high-gain* component of DECRESIM.

Task 1.2 will enable the rational design of systems with minimal phonon-caused decoherence, a currently open problem. The Task will be based on a new approach regarding the spin-phonon coupling and will solve an open problem. Given the expertise of the PI, it poses *no significant risk*.

Task 1.3 will use parameters obtained in the two previous Tasks to describe the time evolution of the quantum state of particular systems. The methods are ambitious, so it is a *medium-risk, medium-gain* component.

Task 1.4 will result in an improved formalism for the description of decoherence (beyond T1/T2) in pulsed EPR experiments. Again, this formalism will be useful well beyond the scope of DECRESIM. Given the expertise of the PI, it poses *no significant risk*.

Tasks 1.5 and 1.6 are based on standard techniques and even includes alternatives of different difficulty, so there is *no significant risk* associated to either of them.

Task 1.7 is *more challenging*, as it will also require the setup of new equipment. Preliminary results obtained and prospects for collaborations will mitigate the risk

Significant breakthroughs can be expected, associated with WP1, namely:

- (a) the **theoretical framework for decoherence on lanthanoid complexes**, covering all the way from the chemical structure to the time evolution of the wavefunction, and
- (b) the **directed synthesis and characterization of new molecular spin qubits**, which will be possible thanks to the proper understanding of the mechanisms for decoherence and relaxation.

Task 2.1, will require to go a step beyond and extend the results of WP1 from a single lanthanoid ion –or a single molecular spin qubit– to multiple spin qubits, thus it is a *high risk* Task. An expected ground-breaking result is the **experimental execution of a simple quantum algorithm** using trinuclear lanthanoid complexes.

Work Package 3, where DECRESIM tackles not only the theoretical frontier but also the experimental frontier, is defined as two possible strategies, with markedly differentiated risk (3.1 << 3.2).

42 M. Nitz et al., *Angew. Chem. Int. Ed.* 2004, **43**, 3682

43 (a) J. R. Morrow et al., *Met Ions Life Sci.* 2012, **10**,171 (b) A. W. Barb et al., *Protein Sci.* 2012, **21**, 1456

44 (a) B. Zhu and D. Reinberg, *Cell Research* 2011, **21**, 435 (b) L. Y. Kadyrova et al. *Cell Cycle* 2013, **12**, 3286

45 J.-I. Nishikawa et al, *Nucleic Acids Res.* 2013, **41**, 1544

The approach taken in Task 3.1 is low risk as it has already produced preliminary results: it constitutes a safe backup plan, see below.

Task 3.2 is a high-risk/high-gain task. A fundamentally new experimental approach is used for the ultimate organisation goal of magnetic molecules or indeed any nanoobject: the use of **programmable biostructures**. Notice that intermediate steps of Tasks 3.2, such as the obtention of a lanthanoid-binding histone, and the recognition of the modified histones by specific DNA sequences constitute major results by themselves.

Action plan associated with the identified risks

Task	Risk	Action plan
1.1	medium	If a single effective charge per ligand is not sufficient to simulate the CF effect, we will try to use more than one charge: a proximal one for the covalent effect and a distant one for the electrostatic effect. In case of need, we will also resort to mixed theoretical methods: treat a minimalistic system (metal ion + single ligand) with the highest (DDCI) ab initio method, and use this as reference for the parametric fitting. If intrinsic limitations of the CF method do not allow for sufficiently precise predictions, we will switch to the now-standard CASSCF-CASCI methods as an alternative. This will include switching to a postdoctoral fellow with the required expertise. The effects of this methodological change will be (1) enhanced accuracy, (2) lower efficiency of any automated exploration.
1.2	medium	If the vibronic coupling produces time-independent matrix Hamiltonians that are impractically large (as there are in principle an infinite number of vibrational levels and there could be a high number of relevant vibrations), we will merge this Task with 1.3, considering the vibration as a time-dependent term instead.
1.3	high	If solving the Master equation proves unmanageable, we will use TD-PT as backup and ultimately we can even focus all the efforts on calculating dimensionless decoherence rate.
1.4	low	This purely theoretical development poses no risk by itself, but it is possible that another group formulates this phenomenology before us. In that case, we will go forward and start with the design and implementation of pulse sequences to determine the newly-defined figures of merit.
1.5	low	If the compounds that are predicted to have optimal qubit properties are unstable or difficult to crystallize, we will focus on the most stable systems. For those compounds containing counterions with nuclear spins we will explore the possibility of changing those by spin-free counterions (for example substituting alkali ions by alkaline-earth ions in POM chemistry).
1.6	low	If the Landau-Zener description is not enough, as is often the case for slow sweep rates, we will check the assumptions of the theory using the tools developed in Tasks 1.1-1.3.
1.7	medium	If the interpretation or the implementation of a given EPR experiment is too challenging, we will seek collaborations with the physics labs of S. Hill and F. Luis. Additionally, if the theory is available sooner than expected (see Task 1.4) we will switch from quantum gates to the pulse sequences designed for an improved characterization of decoherence processes.
2.1	high	Consolidate any intermediate achievement, move focus to WP1.
3.1	medium	Although MOFs could in principle be optimal systems, if there are synthetic problems we can use the developed tools to systematically explore other chemical families.
3.2	high	If the experimental characterization of the samples is not satisfactory, we will resort to the DFT optimization of the lanthanoid-LBT structures and use SIMPRE 2.0 to predict their magnetic energy level structure. If there is no selectivity by nucleosome-positioning sequences, we will design use specially modified histones of larger size and DNA sequences designed for a wider histone wrapping. If this task is not producing the expected results in the medium term, we will consolidate any intermediate achievement, and focus on 3.1, exploring in particular the 1D and 2D MOFs.

Section c. Resources (including project costs)

Working environment

DECRESIM will be carried out at the Instituto de Ciencia Molecular (ICMol), a center of excellence in Molecular Nanoscience which is located at the *Parque Científico* of the the University of Valencia. The Director of this center is Prof. E. Coronado, who has an ERC Advanced Grant to work on Molecular Spintronics. This center will provide state-of-the-art facilities and also help attract researchers. ICMol hosts approximately 130 researchers with 30 staff members and internationally recognized groups of excellence in fields related to DECRESIM: Molecular Magnetism, Molecular Spintronics, Coordination Chemistry, Supramolecular Chemistry, Biomembranes and Quantum Chemistry. DECRESIM will benefit from this multidisciplinary environment. Specific equipment from the Biodiversity Institute Cavanilles which is also located at the *Parque Científico* will be used if needed for Task 3.2.

I believe that excellent science does not end with the peer-reviewed publication within a minimalistic open access model. On the contrary, open and dynamic relations with the scientific community and with society as a whole need to be established and maintained to obtain a wider scientific perspective. This means encouraging and supporting among the team actions and attitude such as:

- the release of the developed tools as free software
- working in an *open notebook science* environment
- not only dissemination, but active outreach efforts

Such openness, which enables external scrutiny of the scientific work, enhances research quality and integrity. The use of the arXiv and so-called Green Open Access will liberate funds that would otherwise be dedicated to the costly Golden Open Access.

Timeline and task assignment

Personnel	Task	Postdoc profile	Year					
			1	2	3	4	5	
PostDoc1*	1.1	Theoretical chemist, Crystal Field						
PostDoc2	1.3	Theoretical / condensed matter physicist						
PostDoc3	1.4	Theoretical physicist						
PostDoc4	1.7	Experimental physicist, pulsed EPR						
PostDoc5*	3.x	Experimental chemist/biochemist						
		What will be done?						
PhD1	1.1	SIMPRES 2.0: CF method for lanthanoid complexes						
PhD2	1.2	Include coupling to spin bath, phonon bath						
PhD3	1.4	Develop phenomenology for decoherence in pulsed EPR						
PhD4	1.5+2.1	Synthesis and characterization of lanthanide complexes						
PhD5	3	Organisation of lanthanoid spin qubits						

PD1*: As part of the risk assessment / action plan, if the results on CF are not sufficiently accurate, PostDoc1 would be switched for PostDoc1a, with a background specialized in CASSCF-CASCI calculations.

PD5*: As part of the risk assessment / action plan, the five person-years of PostDoc5 might be divided into up to two researchers with backgrounds in either chromatin or coordination chemistry, depending on the results.

Project costs

After the period of intense investment in infrastructures, coinciding with the real state bubble that was dramatically important for Spain's economy, science in Spain is currently in a stage of austerity cuts, which are having dramatic effects on scientific research and education. Thus, the budget of research projects in Spain currently needs to focus on nurturing the human resources of R+D to avoid the waste of the already existing excellent infrastructures. Of course, this seems also the most efficient way to divide the resources in a project that is dominated by theory. This has been taken into account in the preparation of the budget, which focuses in personnel rather than in equipment. This is also the reason why I decided to drastically minimise the cost associated to my own salary as PI, allowing a large team of people. I was able to do this because I am already being paid by a Ramón y Cajal grant until the end of 2018, with a compromise of subsequent professional stabilization by the University of Valencia to every ERC grantee. Thus, the main costs will be in personnel: 17 person-years of postdocs (*32 000€) + 20 person-years of predocs (*22 000€) + 5 years of 1 technician (*47 000€). (XPS measurements, elemental analysis...), acquisition of books, etc. As stated in the "Guide for applicants", additional funding (109 000€) is requested for the purchase of major equipment. Despite the complete equipment available in the host institute, a Q-band extension for the existing pulsed EPR is essential for the success of the project. Frequencies higher than Q-band provide little additional benefit to the proposed experiments, thus this upgrade request is for a state-of-the-art Q-band pulsed EPR instrumentation. This facility is lacking not only at the University of Valencia but in the entire country, with only another group in Spain working with X-band pulsed experiments. This upgraded instrumentation capability will immediately and significantly advance the productivity of the projects outlined in this proposal and it will enhance the research environment of the surrounding community. Thus, there are 120 000€ in equipment cost, divided into:

(11 000 in hardware + software) + (109 000 = 218 000·0.5)⁴⁶; 110 000€ for consumables, 50 000€ for other costs and 100 000€ for travel expenses.

Cost Category		Total in Euro	
Direct Costs	Personnel	PI	60 000
		Postdocs	544 000
		Students	440 000
		Other (Technician)	235 000
	<i>i. Total Direct Costs for Personnel (in Euro)</i>		1 279 000
	Travel		100 000
	Equipment		120 000
	Other goods and services	Consumables	110 000
		Publications (Open Access fees, etc.)	20 000
		Other (measurements, books, inscription costs)	50 000
<i>ii. Total Other Direct Costs (in Euro)</i>		400 000	
A – Total Direct Costs (i + ii) (in Euro)		1 679 000	
B – Indirect Costs (overheads) 25% of Direct Costs (in Euro)		419 750	
C1 – Subcontracting Costs (no overheads) (in Euro)		5 500	
C2 – Other Direct Costs with no overheads (in Euro)		-	
Total Estimated Eligible Costs (A + B + C) (in Euro)		2 104 250	
Total Requested EU Contribution (in Euro)		2 104 250	

For the above cost table, please indicate the % of working time the PI dedicates to the project over the period of the grant:	85%
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⁴⁶ A 50% depreciation cost is taken into account for equipment with a useful life of 10 years.