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QUANTUM PROPERTIES OF MOLECULAR NANOMAGNETS

Takeji Takui
OSAKA CITY UNIVERSITY

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14. ABSTRACT
The aim of this collaborative project is to explore fundamental quantum properties of molecular nanomagnets, more specifically spin entanglement and spin coherence at the molecular and supramolecular level. Ambitious targets are: the coherent manipulation of two (or more) entangled molecular spins, and the efficient coupling of molecular spins with microwave cavities with high quality factors such as superdonducting 2D resonators. These goals will also enable the definition of radically new paths for the development of molecular architectures of interest for Quantum Information Processing (QIP) (cited from Proposed Research Summary). The project will contribute to the implementation of emerging quantum spin technology applicable to QIP and quantum computing from both the experimental and theoretical sides

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AOARD Scientific Project on Novel Nanomagnetic and Multifunctional Materials

Title: *Quantum Properties of Molecular Nanomagnets (AOARD Project #134031)*

PI: Takeji Takui (Professor)
Department pf Chemistry and Molecular Materials Science, Graduate School of Science,
Osaka City University, Osaka 558-8585, Japan.
Tel: +81-(0)6-6605-2605 Fax: +81-(0)6-6605-2522
E-mail address: takui@sci.osaka-cu.ac.jp

***Collaborative Project with**:*
PI: Professor Marco Affronte
C.N.R.- Institute of nanoSciences S3 (http://www.nano.cnr.it/) and Dipartimento di Fisica,
Università di Modena e Reggio Emilia
via G. Campi 213/A, 41100 Modena, Italy
Tel: +39.059.205. 5327 // lab: .5271; skype: marcoaffronte
Fax: 0039.059.205.5651; mobile: 3389119869
email: marco.affronte@unimore.it

PI: Professor Stephen Hill
EMR Program Director
National High Magnetic Field Laboratory (NHMFL) & Department of Physics Florida State University
Tallahassee FL 32310-3706, USA
Tel: 850 644 0311 Fax: 850 644 4628
Office: C115 Lab: C101
www: http://fs.magnet.fsu.edu/~shill/
email: shill@magnet.fsu.edu

Objectives of AOARD Scientific Project:
The aim of this collaborative project is to explore fundamental quantum properties of molecular nanomagnets, more specifically spin entanglement and spin coherence at the molecular and supramolecular level. Ambitious targets are: the coherent manipulation of two (or more) entangled molecular spins, and the efficient coupling of molecular spins with microwave cavities with high quality factors such as superdonducting 2D resonators. These goals will also enable the definition of radically new paths for the development of molecular architectures of interest for Quantum Information Processing (QIP) (cited from "Proposed Research Summary"). The project will contribute to the implementation of emerging quantum spin technology applicable to QIP and quantum computing from both the experimental and theoretical sides.

Milestones of the Project:
(1) Identification of molecular systems with optimal performances as qubits. The design of organic spin clusters or heavy metallocomplexes with suitable magnetic features needs to be combined with the synthesis of molecules.
(1a) Syntheses and characterization of extremely stable triplet molecules with relatively large zero-field splittings in their ground states, which are capable of strongly coupling to the 2D microwave cavity resonator developed in Prof. M. Affronte's Group at low temperature (relevant to (2)).

(1b) Molecular optimization of prototypical molecular models for high spin quantum computers by utilizing genuinely organic high spin hydrocarbons or nitrenes.

(2) Identification of molecular spins coupled to one another or to other quantum systems. Control of spin entanglement at (supra-) molecular level is a fundamental step towards implementation of quantum gates.
(2a) The design of coupling experiments on the single-crystals of the triplet molecules (1a) and the 2D superconducting microwave cavity below 4 K. The experiments need extended coupling theories for triplet spins in ensemble coupled to multi-photon excitation modes.
(2b) "Quantum Control" challenges chemists/materials scientists to implement quantum-control mediated gate operations for realistic matter spin qubits. Any relevant prototypical experiments on molecular spins with one electron delocalized over at least two nuclear-spin client qubits have to be designed and executed with realistic spin qubits.

(3) Key pulse-based spin resonance experiments for molecular spin based qubits. Here, there are several technical challenges to be overcome in combining high power microwave pulses with low temperature and high sensitivity in detection.
(3a) NMR-paradigm ESR spin manipulation techniques to be implemented; particularly the techniques involve the design of microwave GRAPE (GRadient Ascent Pulse Engineering) pulses.
(3b) Relevant to the technological achievements (3a), adiabatic quantum computing (AQC) as a viable alternative to the standard quantum circuit approach for gate operations should be tested for the use of molecular spin qubits. Generally, the corresponding gate operations are carried out by means of designed sequences of microwave pulses, and thus order of magnitude faster CPU time is expected. Any relevant protocols, however, have never been tested yet from either the theoretical nor experimental side. Molecular spin qubits can afford a testing ground for this issue.

(4) From the theoretical side, a breakthrough in "practical" quantum algorithms for quantum chemistry (or quantum chemical calculations) is expected to be made. Apparently, the algorithm cannot be universal at the moment, and in our quest for implementing the practical quantum algorithm we carefully choose the subjects which are intractable by using classical computers.

1. Significant Achievements During 2015/2016 (- Oct., -Mar., 2017)

The aim of Collaborative Scientific Project is to identify molecular nanosystems/entities composed of molecular spins or any open shell molecular systems in 0-3 dimension and to optimize their molecular magnetic properties suitable for molecular spin qubits of quantum computers/simulators (QCs/QSs) and quantum information processing systems. Quantum control has been emerging in the field of QCs/QSs, and relevant molecular optimization challenges chemists/materials scientists to implement quantum control by the use of molecular spin qubits. We emphasize that the objectives are closely relevant to implementing highly sophisticated pulse-based microwave spin technology, which can afford "quantum control" among the qubits as the key spin technology. This quantum control is novel and generally termed "Molecular Spin Quantum Cybernetics", which is essential for spin-qubit based quantum computing and quantum information processing. Our theoretical basis for quantum control is underlain by Lie-group theory/Lie-algebra. In the context above, we have executed this collaborative project along the four main lines as follows:

(1) *Molecular Optimization for Matter Spin Qubits toward Molecular Spin Memories and High Spin Quantum Computers*

One is to optimize molecular spins for realistic matter spin qubits which are composed of electron bus-qubits and nuclear client-qubits in molecular frames. Thus, in this project our theoretical work has always included realistic molecular spins, with which we have implemented "Adiabatic Quantum Computing (AQC)", for example during the basic 2013/2014 (- Mar., 2015) years. We also have developed quantum chemical calculations to evaluate accurate spin-orbit interactions in

zero-field splitting (ZFS) tensors of both open shell metallic ion complexes and extremely stable organic spin-triplet molecular systems with sizable fine-structure constants/ZFS parameters. It has turned out that the introduction of bromine atoms in the π–electronic network enables us to tune the magnitude of the ZFS parameters of the organic triplet molecules. The tuning capability is useful to couple the triplet molecules in ensemble (quantum spin memory) with superconducting qubits or photons of planar microwave cavities during gate operations in the strong coupling scheme. This extremely stable ground-state triplet molecule survives in the crystal even at ambient temperature for years without any chemical reaction and the molecule itself is suitable for the two-qubit unit of high spin quantum computers as a counterpart of quadrupolar quantum computers. Molecular optimization affords eight electron spin qubits in a particular molecular scaffold. The molecular optimization and design utilize the topological symmetry of π–electron spin networks in the molecular scaffolds, and because of the nature of the symmetry there is no limitation to the number of high spin multiplicities for high spins in the ground state. The relevant protocols can afford two dimensional high spin arrays suitable for building up non-ensemble molecular spin qubit systems.

A quest for a Lloyd model of electron spin qubits as scalable qubits is of extreme importance in terms of molecular spin qubit design and optimization. We have extended our helical symmetry approach to DNA-based double-stranded helical oligomers, whose specific sites are labeled with stable radical qubits (termed g-tensor engineering). Characterization/identification of the magnetic properties of the radical qubits embedded in the oligomer's helical structure is essential for the Lloyd model of the electron spin version. Thus, we have characterized the detailed magnetic properties of the four radical qubits embedded in a DNA oligomer (22-mer) by using PELDOR spectroscopy and MM calculations ([0-1] submitted to *Zeitschrift Fur Physikalische Chemie-International Journal of Research in Physical Chemistry & Chemical Physics* and under review: Later on accepted/published). Based on the acquired results, relevant synthetic work is in progress in collaboration with Prof. Schiemann's group, Univ. of Bonn. In 2016, further modifications have been required to complete the chemical reactions in good yield.

(2) *Quantum Control of Molecular Spin Qubits: Methodological Establishment*

The second is to implement quantum control technology applicable to few-qubit molecular spins in the solid state (single crystals) from both the theoretical and experimental side. We have applied a Lie-Algebra based control theory to realistic molecular spins and tested our quantum control approach, in which high fidelity and total computation time required to implement Controlled-NOT gates between the two client nuclear qubits by use of microwave GRAPE (Gradient Ascent Pulse Engineering) pulses are simulated. We have checked the anisotropic behavior of the quantum control occurring in the realistic molecular spins adopted in this project and found physical meanings behind the behavior, which serve for the molecular optimization. In this project, we have adopted the molecular spins of three-spin qubits, i.e., the systems with one electron bus-qubit and two nuclear client spin qubits which are indirectly connected through hyperfine couplings.

(3) *Pulse-Based Microwave Spin Control Technology: Establishment of NMR-paradigm Based ESR Spectroscopy*

In order to implement quantum control in the systems of molecular spin qubits from the experimental side, NMR-paradigm based electron spin resonance techniques as highly sophisticated electron magnetic resonance spin technology are required. We have designed and established such pulse-based microwave spin technology operating at X-band, in which an AWG (Arbitrary Wave Generator) is the heart of the setup. Quantum computing experiments for implementing Controlled-NOT gates by use of stable organic radicals in the solid state are underway. We have also implemented AWG based designs for X-band microwave GRAPE (chirp) pulses for adiabatic quantum computing by utilizing molecular spin qubits.

(4) *Quantum Chemical Calculations/Quantum Chemistry on Quantum Computers (QCC/QC-on-QCs) and Development of Adiabatic Quantum Computing (AQC) by the use of Molecular Spin Qubits.*

Since Shor's quantum algorithm appearing in 1993 for the factorization as an NP(Non-deterministic Polynomial)-complete problem, there has been no disruptive approach to the issues of the factorization from both the theoretical and experimental sides. Putatively, there are required a vast number of addressable qubits to tackle intractable subjects that modern "classical computers" cannot deal with. We note that there is another way to methodologically develop quantum computing besides the standard gate operation/circuit model approach. In this Project, we emphasize that Adiabatic Quantum Computing (AQC) is a promising counterpart, which can afford reduction of the number of the addressable qubits. We have shown for the first time that molecular spins are computing resources which can afford CPU 500-1000 times faster than NMR QC experiments for the factorization with three spin qubits.

Considerable advance in applications of QCs to quantum chemical calculations has been made from both the theoretical and experimental sides, until recently. We have implemented a quantum algorithm which enables us to construct configuration state functions (CSFs) for Full-CI (Configuration Interaction) calculations on QCs for vector space-demanding open shell molecular systems such as single molecule magnets, the first and typical example of nanomagnets. A notorious difficulty in QC applications to electronic structure theories in quantum chemistry has been relevant to the antisymmetrization of electronic wavefunctions. Full-CI for sizable molecules demands exponential CPU time, and it is intractable on any modern classical computers. A relevant paper is under review ([0-2] in **3. Publications**, submitted to *Journal of American Chemical Society*). One of the proposed quantum circuits enabling us to carry out the Full-CI calculations in realistic polynomial CPU time is displayed in Fig. 1.

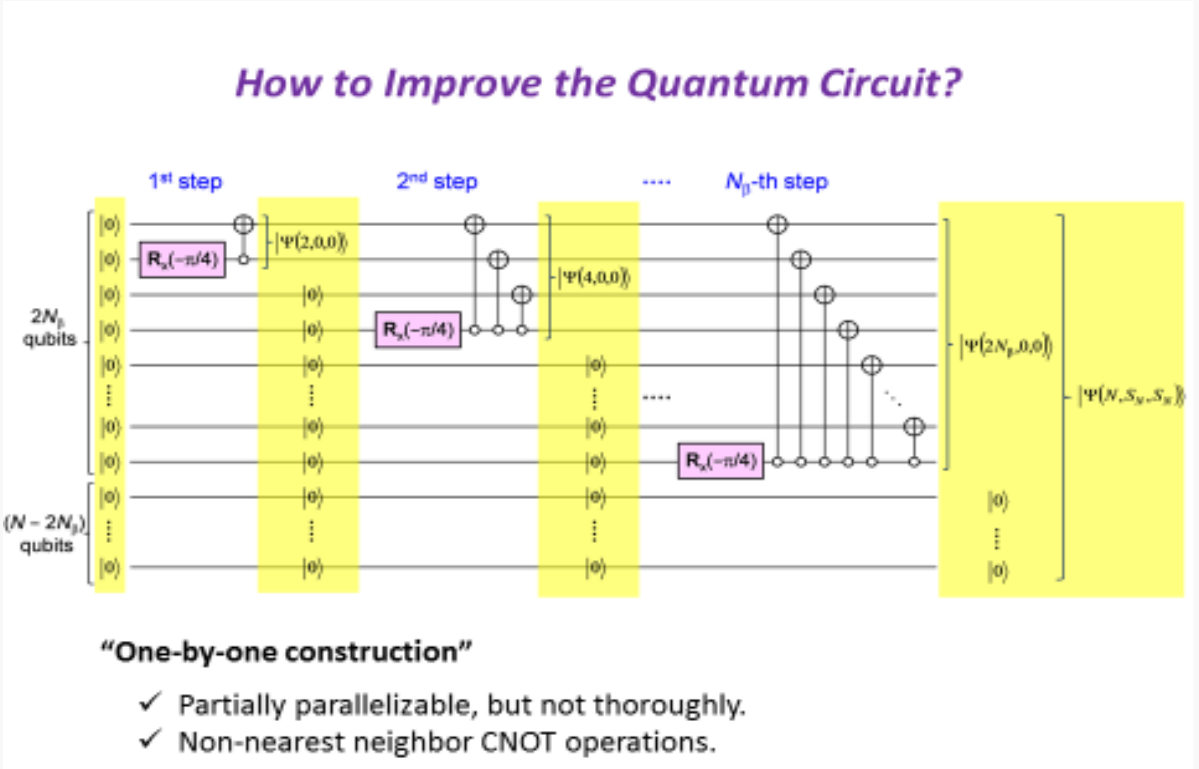

Figure 1. One of the proposed quantum circuits enabling us to construct configuration state functions (CSFs) for Full-CI (Configuration Interaction) calculations on QCs for vector space-demanding open shell molecular systems such as single molecule magnets.

2. Significant Activities of Collaboration with the Other PIs

In the following are exchange meetings to initiate collaborative researches, noting that in order to conduct AOARD Scientific Collaborative Project a university-level cooperative agreement between Osaka City University and Florida State University was executed in November, 2014. Prior to the formal conclusion, mutual understanding of terms and conditions in detail was made in every level for five months after July, 2014. A similar agreement between Graduate School of Science, Osaka City University and Department of Physics, University of Modena and Reggio Emilia was concluded in Aug., 2014.

(1) In January 8, 2015, Dr. Stefano Pittalis and Dr. Carlo Rozzi (CNR-Modena) of the Modena team were invited to OCU and gave their lectures at the departmental seminar, hosted by PI of OCU.
(2) In January 12-15, 2015, the Modena, Florida and Osaka teams met at Workshop on Molecular Electron Spin Qubits at the University of Manchester, UK. Multiple members of each team were present at the WS, allowing us to have extensive discussions of the scientific results and outlining of manuscripts. In addition, several other researchers who have collaborated on this project and co-authored joint publications with Prof. S, Hill, PI of the Florida team were at the meeting (Freedman, Carretta, Timco and Winpenny).
(3) Several members of the collaboration met and discuss the latest results and further collaborative plans in September 15-18, 2015, Warsaw at the European Materials Research Symposium on Molecular Materials for Quantum Computing: Hill (Florida); Ghirri and Troiani (Modena); Takui (Osaka); Ruben (Karlsruhe); Freedman and Graham (Northwestern); and Santini (Parma).
(4) Prof. Freedman, a collaborator of the Florida team was invited to AWEST 2015, an intn'l WS on Electron Spin Science and Technology: Biological and Materials Science Oriented Applications, held from June 14-17, 2015, Awaji Island, Japan, organized by PI, Takeji Takui, and discussed future collaboration in view of theoretical calculations of zero-field tensors with him.
(5) In July 4-8, the Modena, Florida and Osaka teams met at the 4th International Workshop on Magnetic and Multifunctional Materials organized jointly with French-Korean Meeting on Functional Materials for Organic Optics, Electronics, and Devices at Universite Pierre et Marie Curie, Paris. The three PIs presented their latest results at the WS, allowing us to have extensive discussions of the scientific results and further collaborative schemes in detail.

3. Publications

Publications during the academic year of 2015 (until Oct., 2016/Mar., 2017) relevant to the objectives of AOARD Scientific Project are listed in the following: The publications cite the financial support from AOARD Scientific Project.

The following are book chapters (reviewed and written in English, ones in Japanese not included) relevant to the objectives of the Project. The first publication of the book chapters is an account article (reviewed), and the rest is all original and reviewed.

"Electron Spin Resonance (ESR) Based Quantum Computing", Biological Magnetic Resonance Vol. 31 has been edited by PI, Takeji Takui with Lawrence Berliner and Graeme Hanson.

(1) "Molecular spin qubits: Molecular optimization of synthetic spin qubits, molecular spin AQC and ensemble spin manipulation technology", ed. by Y. Yamamoto, K. Semba, Chapter 28, *Principles and Methods of Quantum Information Technologies*, Lecture Notes in Physics 911, DOI 10.1007/978-4-431-55756-2_28, 2016.
(2) "Exploiting quantum effects in electron-nuclear coupled molecular spin systems" in *Electron Spin Quantum Computing: Electron Spin-Qubit Based Quantum Computing and Quantum Information Processing*, Robabeh Rahimi Darabad, Kazunobu Sato, Patrick Carl, Peter Höfer,

Raymond Laflamme, Takeji Takui, Chapter 2, Biological Magnetic Resonance, Vol. 31, Pages 25-50 (2016).

(3) "Adiabatic quantum computing on molecular spin quantum computers", in *Electron Spin Quantum Computing: Electron Spin-Qubit Based Quantum Computing and Quantum Information Processing*, Satoru Yamamoto, Shigeaki Nakazawa, Kenji Sugisaki, Kazunobu Sato, Kazuo Toyota, Daisuke Shiomi and Takeji Takui, Chapter 4, Biological Magnetic Resonance, Vol. 31, Pages 79-118 (2016).

The following are article papers under review (accepted/published):

0-1. "Behaviour of DFT-based approaches to the spin–orbit term of zero-field splitting tensors: A case study of metallocomplexes, $M^{III}(acac)_3$ (M = V, Cr, Mn, Fe and Mo)",
Kenji Sugisaki, Kazuo Toyota, Kazunobu Sato, Daisuke Shiomi and Takeji Takui
Physical Chemistry Chemical Physics (under review).

0-2. "Molecular Optimization for Nuclear Spin State Control via A Single Electron Spin Qubit by Optimal Microwave Pulses: Quantum Control of Molecular Spin Qubits",
Taiki Shibata, Satoru Yamamoto, Shigeaki Nakazawa, Elham Hosseini Lapasar, Kenji Sugisaki, Koji Maruyama, Kazuo Toyota, Daisuke Shiomi, Kazunobu Sato and Takeji Takui
Physical Chemistry Chemical Physics (under review).

0-3. "Analyses of Sizable ZFS and Magnetic Tensors of High Spin Metallo-porphyrins, Fe^{III}(Cl)OEP and Co^{II}OEP and A Pseudo-Octahedral $Re^{III,IV}$ Dinuclear Complex by X-Band CW/Pulsed ESR and Electron Spin Nutation Spectroscopy: Exact Analytical and Zeeman Perturbation Treatments, and Quantum Chemical Calculations",
Takeshi Yamane, Kenji Sugisaki, Tomoki Nakagawa, Hideto Matsuoka, Takahisa Nishio, Shigemori Kinjyo, Nobuyuki Mori, Satoshi Yokoyama, Chika Kawashima, Naoki Yokokura, Kazunobu Sato, Yuki Kanzaki, Daisuke Shiomi, Kazuo Toyota, David H. Dolphin, Wei-Ching Lin, the late Charles A. McDowell, Makoto Tadokoro, and Takeji Takui
Physical Chemistry Chemical Physics (under review, and later on accepted), in press.
DOI: 10.1039/c7cp03850j

The reviewed published papers are listed below:

1. "Structural determination of a DNA duplex oligomer/oligonucleotide with double pair-wise molecular spins by MM calculations and PELDOR spectroscopy: toward a DNA-based Lloyd model of electron spin qubits for QC/QIP",
Satoru Yamamoto, Shigeaki Nakazawa, Kenji Sugisaki, Kensuke Maekawa, Kazunobu Sato, Kazuo Toyota, Daisuke Shiomi, Takeji Takui
Zeitschrift Fur Physikalische Chemie- International Journal of Research in Physical Chemistry & Chemical Physics.
Published in Feb., 2017: Vol. 231 (Issue 2; Special Issue), Pages 439-458 (2017).
DOI: 10.1515/zpch-2016-0799
2. "Quantum Chemistry on Quantum Computers: A Polynomial-Time Quantum Algorithm for Constructing the Wave Functions of Open Shell Molecules",
Kenji Sugisaki, Satoru Yamamoto, Shigeaki Nakazawa, Kazuo Toyota, Kazunobu Sato, Daisuke Shiomi, Takeji Takui
Journal of Physical Chemistry A.
Published in Aug. 26, 2016: Vol. 120, Issue 32, Pages 6459-6466 (2016).
DOI: 10.1021/acs.jpca.6b04932
3. "Quasi-Restricted Orbital Treatment for the Density Functional Theory Calculations of the Spin-Orbit Term of Zero-Field Splitting Tensors",
Journal of Physical Chemistry A.
Published in Dec. 15, 2016: Vol. 120, Issue 49, Pages 9857-9866 (2016).
DOI: 10.1021/acs.jpca.6b04932

4. "Hyperfine spin qubits in irradiated malonic acid: heat-bath algorithmic cooling",
Daniel K. Park, Guanru Feng, Guanru, Robabeh D. Rahimi, Stephane Labruyere, Taiki Shibata, Shigeaki Nakazawa, Kazunobu Sato, Takeji Takui, Raymond Laflamme, Jonathan Baugh,
Quantum Information Processing, Volume 14, Issue 7, Pages 2435-2461 (2015).
Published: JUL 2015. DOI: 10.1007/s11128-015-0985-1
5. "Probing an untouchable environment for its identification and control",
Masaki Owari, Koji Maruyama, Takeji Takui, Go Kato,
Physical Review A. Volume 91, Issue 1, Article Number 012343 (2015). Published: JAN 30 2015. DOI: 10.1103/PhysRevA.91.012343
6. "Adiabatic quantum computing with spin qubits hosted by molecules",
Satoru Yamamoto, Shigeaki Nakazawa, Kenji Sugisaki, Kazunobu Sato, Kazuo Toyota, Daisuke Shiomi, Takeji Takui,
Physical Chemistry Chemical Physics, Volume 17, Issue 4, Pages 2742-2749 (2015).
Published: JAN 28 2015. DOI: 10.1039/c4cp04744c