2.2.2 Report on Workshop Models and Theory for Molecular Magnetism

CECAM- Lyon

2006 July 18/21

We would like to thank CECAM, Psi-k and the Netwok of excellence MagmaNet for financial support, which made this workshop possible.

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`http://www.cecam.org/index.php?content=activities/pastWorkshops&action=details&wid=42`

Highlights and achievements of the workshop

One possible road to increase the capacity for information storage is decreasing the system size of the storage devices. This eventually suggests the need for a transition from bulk matter to nanoscale molecules and clusters. To achieve that goal one needs the ability to assemble these structures with the required electronic and magnetic properties in a controlled way. To a large extent, this explains the enduring interest in molecular magnetism. The progress in research on molecular magnetism is driven by advances in chemical synthesis of the materials and ingenious experiments. The advances in the capability to predict properties from first-principles calculations gives hope for an rational design of magnetic molecular materials. This workshop has been a focus point of the leading theoretical groups in order to define long term prospects and challenges for future research in the field of molecular magnetism.

The list of invited speakers contained a mix of the leading theoretical groups in the field together with world-wide regocnised leading experimentalists. Further the sessions were complemented by contributed talks from young scientists.

In the following we will only mentions a few highlights the workshop was focusing on.

Highlights day 1

The workshop started with a challenging talk by Roberta Sessoli discussing the emerging trends in molecular nanomagnetism form the point of view of an experimentalist, which was an important start for further discussion. The proper understanding of experimental techniques was another topic discussed by an very educational talk given by Hans-ulrich Güdel which explained how to measure magnetic properties of molecular materials. The morning sessions was then concluded by theoretical talks. Trond Saue and Martin Kaupp demonstrated that a proper theoretical description requires the correct treatment of relativistic effects. The accurate calculation of spin-orbit coupling is one of the major challenges and requirements. That this can be achieved by density-functional theory (DFT) calculations has been shown by several applications to estimate the zero field splitting parameters or the magnetic anisotropy.

The afternoon session started with with general discussion of stereochemistry and spin states of tetrahedral building blocks by Santiago Alvarez and a bottom-up approach for theoretical studies presented by Juan J. Novoa. The power of constrained DFT for the application of exchange parameters was shown by Troy Van Vooris and Coen de Graaf discussed the problems of calculation of magnetic interaction.

One of the main results of the lively discussion of the first day has been the importance of Non-Heisenberg Hamiltons. The Heisenberg-Modell may not be sufficient to describe some magnetic systems accurately enough. As a more general question it appeared the question if theory is indeed calculating the same parameters as experiments measure. The ambiguity appears because both experiment and theory normally map there result to some Hamiltonian. However, the approximations involved in both cases may be different.

Highlights day 2

The interesting discussion from day one on the validity of the Heisenberg Hamiltonian continued. Frederico Totti posed this question directly for multi-nuclear paramagnetic clusters and Jürgen Schnack demonstrated for a Ni_4Mo_{12}-System that the Heisenberg Hamiltonian with constant exchange parameters in indeed unable to explain the observed magnetic field dependence. A possible explanation was found in the suggestion of magnetostriction at the molecular level. Natalie Guihery continued the discussion in the afternoon in mixed valence systems.

John McGrady explored the interface between antiferromagnetism and metal-metal bonding, whereas Mark Cassida introduced the rich phenomena of spin crossover in the discussion. Another new class of materials was discussed by Vincent Robert, which focused on the theoretical aspects of non-innocent ligands in organnometallic chemistry.

Highlights day 3

The third day started with an excellent educational talk by Stephen Blundell on muon studies applied to molecular magnets. The application of limitations of DFT has been shown by Furio Cora in case of some examples form solid state systems. Illaria Ciofini modelled photo-magnetic molecular devices. Andrei Postnikov discussed non-collinear states and frustration, a topic very important for molecular magnetism but other fields of magnetism as well. Sergei Borshch was talking on energetics of spin transition complexes.

Kyangwha Park demonstrated the power of DFT to calculate exchange coupling and magnetic anisotropy for manganese based single molecules. This talked made clear that one needs a proper understanding of both these magnetic properties, if one attempts to optimize molecular magnetic materials. Valerio Bellini focused on ab-initio studies of Cr-based single molecule materials, which have been also of interest by a contribution of Daria Tomecka.

Highlights day 4

The last day contained only invited talks. The importance of synthesis was nicely shown by Hiroki Oshio. Carlo Canali discussed Cern-Number spin Hamiltonians which may become important for the proper choice of Hamiltonian. Alexander Lichtenstein as a well known expert on techniques beyond DFT showed the imporatance of these extension for the calculation of exchange parameters. The final talk was given by Mark Pederson by a nice review of application of DFT to molecular magnetism.

Main conclusions

1. The Heisenberg Hamiltonian may not be always adequate for a proper description of magnetic properties of molecular materials.
2. In comparison experiment and theory one has to be very cautious, if one is comparing indeed the same.
3. DFT is can be accurate enough to calculate magnetic anisotropy in molecular magnetic materials. However, there are exceptions which require to go beyond standard DFT.
4. The calculation of magnetic exchange coupling for multi-nuclear systems is possible within DFT, but requires a proper chosen Hamiltonian.
5. Experimentalists are producing continously new exciting systems which poses new theoretical challenges for theory.
6. There is still a long way to go for a rational design of molecular materials with predetermined magnetic properties from first-principles.

Program

Day 1: July 18 2006

Session : 0 Welcome-Opening

08:50 to 09:00 : Welcome

Session : 1 Experiment & Theory I

09:00 to 09:45 : Presentation

Emerging trends in Molecular Nanomagnetism: The point of view of an experimentalist

Roberta Sessoli

09:45 to 10:30 : Presentation

Inelastic neutron scattering on Single Molecule Magnets and antiferromagnetic wheels

Hans-Ulrich Güdel

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation

Magnetism in a relativistic perspective

Trond Saue

11:45 to 12:30 : Presentation

Computation of magnetic parameters by density functional theory: One-component perturbational vs. two-component variational inclusion of spin-orbit coupling.

Martin Kaupp

12:30 to 12:45 : Presentation

Calculation of Zero Field Splitting Parameters from First Principles

Jordi Cirera

12:45 to 13:00 : Presentation

A DFT study of the magnetic anisotropy of FeII cubes

Jordi Ribas

13:00 to 14:30 : Lunch Break

Session : 2 Session II

14:30 to 15:15 : Presentation

Stereochemistry and Spin Sates of Tetrahedral Building Blocks Revisited

Santiago Alvarez

15:15 to 16:00 : Presentation

Magnetism in low-dimensional systems: theoretical studies using a first-principles bottom-up methodology

Juan J. Novoa

16:00 to 16:30 : Coffee Break

16:30 to 17:15 : Presentation

Computing Exchange Couplings with Constrained Density Functional Theory

Troy Van Voorhis

17:15 to 18:00 : Presentation

Toward a variational treatment of the magnetic coupling between centers with elevated spin moments

Coen de Graaf

18:00 to 18:15 : Presentation

Contrasting direct versus mediated through-space magnetic interactions in pyridyl-verdazyl : hidroquinone molecular co-crystal

Joaquim Jornet

18:15 to 18:30 : Presentation

Magneto-structural correlations in polynuclear complexes: The Fe4 butterflies.

Thomas Cauchy

Day 2: July 19 2006

Session : 3 Session III

09:00 to 09:45 : Presentation

Is still the Heisenberg Spin Hamiltonian reliable for multi-nuclear paramagnetic clusters?

Federico Totti

09:45 to 10:30 : Presentation

Field-dependent magnetic parameters in Ni4Mo12: Magnetostriction at the molecular level?

Juergen Schnack

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation

Exploring the interface between antiferromagnetism and metal-metal bonding

John McGrady

11:45 to 12:30 : Presentation

Theoretical studies of spin-crossover compounds

Mark Casida

12:30 to 12:45 : Presentation

Modeling of non-Heisenberg exchange interactions in tetrameric Ni(II) clusters of S4 symmetry
Nadeschda Kirchner

12:45 to 13:00 : Presentation
Cu-based metalorganic systems: an ab-initio study of the electronic structure
Andrea Salguero

13:00 to 14:30 : Lunch Break

Session : 4 Session IV
14:30 to 15:15 : Presentation
The magnetic properties of polyoxovanadates
Carmen Calzado

15:15 to 16:00 : Presentation
Modeling of the Magnetic Behavior of Low Dimensional Magnetic Systems
Marc Drillon

16:00 to 16:30 : Coffee Break

16:30 to 17:15 : Presentation
Competition between double exchange and purely magnetic Heisenberg models in mixed valence systems : application to half doped manganites
Nathalie Guihery

17:15 to 18:00 : Presentation
Non-Innocent Ligands in Organometallic Chemistry : Theoretical Aspects
Vincent Robert

18:00 to 18:15 : Presentation
Ab-inition study on a chain model of the Cr8 molecular magnet
Daria Tomecka

18:15 to 18:30 : Presentation
A first principles bottom-up theoretical study of the bis(2,3-dimethylpyridinium) tetrabromocuprate spin-ladder
Merce Deumal

Day 3: July 20 2006

Session : 5 Session V

09:00 to 09:45 : Presentation

Muon studies of molecular magnets

Stephen Blundell

09:45 to 10:30 : Presentation

Hybrid DFT functionals in the solid state

Furio Cora

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation

DFT for the modeling of Photo-Magnetic Molecular Devices (PMMDs)

Ilaria Ciofini

11:45 to 12:30 : Presentation

Magnetic frustration, resolved by non-collinearity, in a Co-trinuclear triazin-based system

Andrei Postnikov

12:30 to 12:45 : Presentation

Molecular Dynamics of Antiferromagentically Spin-Coupled Systems

Nisanth Narayanan Nair

12:45 to 13:00 : Presentation

Energetics of binuclear spin transition complexes

Sergei Borshch

13:00 to 14:30 : Lunch Break

Session : 6 Session VI

14:30 to 15:15 : Presentation

Magnetic anisotropy and exchange coupling for manganese-based single molecule magnets

Kyungwha Park

15:15 to 16:00 : Presentation

Calculation and madel of the electronic g-matrix of transition metal and actinide ions.

Hé lène BOLVIN

16:00 to 16:30 : Coffee Break

16:30 to 17:15 : Presentation

An ab-initio study of Cr-based single molecule magnets
Valerio Bellini

17:15 to 17:30 : Presentation
Strong antiferromagnetic coupling between orthogonal orbitals: an ab initio study of non-innocent ligand-based complex
Maria Carvajal

20:00 to : Dinner

Day 4: July 21 2006

Session : 0 Sesion VII
09:00 to 09:45 : Presentation
Facile syntheses of homo- and hetero-metal single molecule magnets
Hiroki Oshio

09:45 to 10:30 : Presentation
Chern-number spin Hamiltonians for magnetic clusters by ab-initio methods
Carlo M. Canali

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Exchange calculations in molecular magnets beyond standard DFT
Alexander Lichtenstein

11:45 to 12:30 : Presentation
Applications of Density Functional Theory to Molecular Magnets
Mark Pederson

12:30 to 12:35 : Closing word

Abstracts

Facile syntheses of homo- and hetero-metal single molecule magnets

Hiroki Oshio
University of Tsukuba, Japan

Abstract

Single molecule magnets (SMMs) have attached an intense research interest due to their char-

acteristic quantum phenomena and possible applications to quantum devices. There have been many homo-metal SMMs reported since the discovery of the first SMM, but the number of hetero-metal systems were still limited. Syntheses of hetero-metal complexes are not simple, and ligands with different coordination sits suitable for different metal ions are sometimes indispensable to prepare hetero-metal systems. During the course of synthetic effort, we found that simple Schiff bases with alkoxo-group assemble hetero-metal ions and form multi-nuclear complexes. We report here syntheses, structures, and magnetic properties of homo- and mixed-metal clusters, some of which were recognized as single molecule magnets.

Inelastic neutron scattering on Single Molecule Magnets and antiferromagnetic wheels

Hans-Ulrich Güdel
University of Bern, Switzerland

Abstract

Exchange and anisotropy interactions split the ground state of polynuclear molecular complexes of transition metal ions. The magnetic properties of such materials are governed by these splittings. Inelastic neutron scattering (INS) is a powerful tool for the direct spectroscopic determination of such splittings. Besides the energies, INS also provides important information about the wavefunctions. The principles shall be briefly explained and examples from recent research in our group used for illustration. Single Molecule Magnets(SMM), in particular the prototype SMM Mn12-acetate, shall be covered as well as antiferromagnetically coupled wheels.

References

G. Chaboussant, A. Sieber, S. Ochsenbein, H.-U. Güdel, M. Murrie, A. Honecker, N. Fukushima and B. Normand
Exchange interactions and high-energy spin states in Mn12-acetate
Phys. Rev. B 70, 104422/1-16 (2004)

O. Waldmann, C. Dobe, H. Mutka, A. Furrer and H. U. Güdel
Né el-Vector Tunneling in Antiferromagnetic Molecular Clusters
Phys. Rev. Lett. 95, 057202/1-4 (2005)

O. Waldmann, C. Dobe, S. T. Ochsenbein, H. U. Güdel and I. Sheikin
Field-Induced Magnetoelastic Instabilities in Antiferromagnetic Molecular Wheels
Phys. Rev. Lett. 96, 027206/1-4 (2006)

O. Waldmann, G. Carver, C. Dobe, D. Biner, A. Sieber, H. U. Güdel, H. Mutka, J. Ollivier and N. E. Chakov
Magnetic relaxation studies on a single-molecule magnet by time-resolved inelastic neutron scattering
Appl. Phys. Lett. 88, 042507/1-3 (2006)

Roland Bircher, Gré gory Chaboussant, Chris Dobe, Hans U. Güdel, Stefan T. Ochsenbein, Andreas Sieber and Oliver Waldmann
Single-Molecule Magnets Under Pressure
Adv. Funct. Mater. 16, 209-220 (2006)

Field-dependent magnetic parameters in Ni4Mo12: Magnetostriction at the molecular level?

Juergen Schnack
Uni Osnabrueck, Germany

Abstract

We investigate the bulk magnetic, electron paramagnetic resonance, and magneto-optical properties of Ni4Mo12, a magnetic molecule with antiferromagnetically coupled tetrahedral Ni ions of spin s=1 in a diamagnetic molybdenum matrix. The low-temperature magnetization exhibits steps at irregular field intervals, a result that cannot be explained using a Heisenberg model even if it is augmented by magnetic anisotropy and biquadratic terms. Allowing the exchange and anisotropy parameters to depend on the magnetic field provides the best fit to our data, suggesting that the molecular structure (and thus the interactions between spins) may be changing with applied magnetic field. Such a behavior could be denoted as Magnetostriction at the molecular level.

The presentation will focus on existing experimental and theoretical results as well as on forthcoming investigations.

Calculation and madel of the electronic g-matrix of transition metal and actinide ions.

Hé lène BOLVIN
CNRS, France

Abstract

Starting from the formula proposed by Gerloch and McMeeking in 1975, the electronic g-matrix is expressed as a sum of two matrices called Lambda and Sigma describing the orbital and spin contributions respectively. This approach is applied on benchmark diatomic and triatomic molecules and on TiF3 and [Cu(NH3)4]2+ using either CASPT2 or CCSD(T) methods to calculate the spin-free states and SO-RASSI to calculate spin-orbit coupling. Results compare very well to experimental data and to previous theoretical works and for each molecule, the anisotropy of the g-matrix is modelled by the mean of few parameters. This approach is then applied to a mixed valence compound, the Creutz-Taube molecule: numerical results are in good agreement with experiment and are fully interpreted in the frame of a model that shows that the g-matrix is independent of the electronic coupling between the two metallic atoms. Finally, the method is applied to two actinide complexes: [NpO2]2+ with equatorials ligands and NpF6 where again, our results are in accordance with experimental data and permits the full interpretation of the anisotropy.

Calculation of Zero Field Splitting Parameters from First Principles

Jordi Cirera

Universitat de Barcelona, Spain

Abstract

We have performed first-principles density functional calculations on some simple molecules with one metal center and different oxidation states and molecular environments, using the NRLMol code, which has been used succesfully to study several Single Moleculer Magnets, in order to calculate the second order magnetic anisotropy parameters. The theoretical results will be compared with the available experimental information from HF-EPR. The dependence of this method on different basis sets and DFT functionals will be discused. Using simple models we have studied the variation of the magnetic anisotropy with some typical strucutral distortion pathways for four-, five- and six coordinate complexes. The ability to predict computationally the magnetic anisotropy barrier should allow us to understand which factors modify the zero field splitting values, which is crucial for a rational design of single molecule magnets

AB-INITIO STUDY ON A CHAIN MODEL OF THE Cr8 MOLECULAR MAGNET

Daria M. Tomecka

Adam Mickiewicz University, Poznan, Poland

Abstract

In that contribution we present an ab-initio investigation by means of density functional theory (DFT) simulation techniques of the electronic and magnetic properties of the antiferromagnetic Cr8 molecular ring (i.e. [Cr8F8Piv16], where HPiv - pivalic acid, trimethyl acetic acid). Here the linearized augmented plane wave method (LAPW) (in the Wien2k package [1]) is used to calculate the electronic density of states, band structures and exchange couplings J of Cr8 [2] and that of a chain model system, which aim to represent the magnetic interactions in the Cr8 ring. The smaller size of the simulation cell of the model, as compared to the one of the original ring-like molecule, enables us to calculate the above mentioned properties more efficiently and systematically. By the thorough comparison between the model complex and the Cr8 ring, we prove that the chain model is reliable and mimics with good approximation the electronic and magnetic properties of Cr8. Moreover the model can be easily extended to systems like 'Ni doped' Cr rings or broken Cr segments, which have recently attracted much attention for their application in the field of quantum computing.

References

[1] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, (Karl-heinz Schwarz, Techn. Universitaet Wien, Austria) (1999), ISBN 3-9501031-1-2.

[2] V. Bellini, A. Olivieri and F. Manghi; Phys. Rev. B 73, 184431 (2006).

DFT for the modeling of Photo-Magnetic Molecular Devices (PMMDs)

Ilaria Ciofini
ENSCP Paris, France

Abstract

With the aim of designing new Photo-Magnetic Molecular Devices (PMMDs), able to display a target magnetic behavior at the ground and at the excited state, a series of systems containing transition metal ions (Os(II) and Ru(II)) have been investigated. To form target magnetic excited states we rely on photoinduced intramolecular electron transfers (ET) within covalently linked assemblies of active components usually referred to as polyad systems. Basically, the topology adopted for the novel photo-magnetic molecular devices derives from that of acceptor dyads (P− A) devised to produce charge separated states (CS) upon light excitation in the framework of researches devoted to artificial photosynthesis. These supermolecules are comprising the following functional elements: -P: the photosensitizer unit; here a Ru(II) or Os(II) complex. -A: an electron(s)-accepting unit which traps the electron promoted from *P -Spin carriers (Sc) surrounding A. The basic working principles of such devices are the following: upon light excitation, an electron will be promoted from P to A to form the target charge separated excited state [P+-A-]*. As a consequence the coupling between the Sc surrounding A will be modified inducing a different magnetic coupling at the excited state. In this contribution, we propose an analysis, based on DFT and TD-DFT, of the properties of existing dyads (P-A) as well as of new acceptor units specifically designed to obtain efficient PMMDs. Various mechanisms of coupling, as a function of the topology of the acceptor units, are also discussed

Magnetic frustration, resolved by non-collinearity, in a Co-trinuclear triazin-based system

Andrei Postnikov
Paul Verlaine University, Institute de Physique Electronique et Chimie, Laboratoire de Physique des Milieux Denses, France

Abstract

The electronic structure of [Co3(L)3(H2O)(OH)]HNEt3, where L stands for a dianion of the 2,6-bis(5-hydroxy-6-phenyl-1,2,4-triazin-3-yl)pyridine, is analyzed on the basis of first-principles calculations within the density functional theory (DFT), applying the computer code SIESTA [1]. The calculations are done for an isolated molecular fragment (147 atoms), using the generalized gradient approximation after Perdew-Burke-Ernzerhof for the exchange-correlation. Due to a predominantly antiferromagnetic interaction between Co ions, which are all connected to the central hydroxyl ion, the system is magnetically frustrated. The DFT calculation finds the ground state with two high-spin (s=3/2) Co ions set antiparallel and the third Co ion being in the low-spin state (s=1/2), yielding the net spin S=1/2. This finding was further refined by taking into account non-collinear (i.e. smoothly changing its direction in space from one point to another) variations of the magnetic density, which yielded all three Co local magnetic moments

of about 2.6 956;B, with different spatial orientation.

From considering different trial orientations of Co magnetic moments, the values of interatomic interaction parameters are estimated.

Further on, we considered the effect of the spin-orbit interaction (SOI), recently implemented in SIESTA in the on-site approximation [2]. In this approach the SOI and the non-collinearity of magnetic density are treated in a natural way on equal footing. According to our preliminary results, the high-spin configuration on all three Co atoms survives also in the presence of SOI.

AP gratefully acknowledges the cooperations within the priority program SPP 1137 by the Deutsche Forschungsgemeinschaft (DFG), discussions with S. Blü gel and J. Schnack, and the use of computational facilities provided by the DFG.

References

1. http://www.uam.es/siesta ; José M Soler et al., J.Phys.:Condens.Matter 14, 2745 (2002).
2.cond-mat/0601093, L. Ferná ndez-Seivane et al.

Computing Exchange Couplings with Constrained Density Functional Theory

Troy Van Voorhis
MIT Boston, United States

Abstract

We demonstrate an accurate method for extracting Heisenberg exchange coupling constants from constrained DFT calculations. We note that the true Ising-like low-spin state of a given molecule can be identified with the ground state of the system subject to a constraint on the spin density of the atoms. Using an efficient optimization strategy for constrained DFT we obtain these states directly, leading to a simple, physically motivated formula for the exchange coupling. Preliminary applications to bi- and poly-nuclear transition metal complexes show that this C-DFT approach is competitive with, if not more accurate than, the best broken symmetry (BS) DFT techniques. In particular, we find that C-DFT gives a robust treatment of frustrated magnetic molecules, which have heretofore been problematic for DFT. Time permitting, we will also discuss how the exchange couplings obtained from either BS- or C-DFT can be incorporated into a simple model Hamiltonian that accounts for magnetic anisotropy.

An ab-initio study of Cr-based single molecule magnets

Valerio Bellini
CNR-INFM-S3, Modena, Italy

Abstract

Molecular nanomagnets, which show intriguing quantum and critical phenomena, like quantum tunneling of magnetization, have recently attracted much interest as next-generation nanoscale, monodisperse magnets for specialized applications. We are interested in molecular rings, a subclass of molecular magnets, composed of heterometallic nanostructures with a cyclic shape and an antiferromagnetic exchange coupling between nearest neighbouring magnetic ions. We have

characterized the electronic and magnetic properties of the ground state of Cr8 molecule, as well as investigated the role of doping, by substituting Cr(III) ions with divalent Ni(II) atoms in changing the ground state of such molecules. The tailoring of the ground and excited states of such substituted Cr rings has been pointed out to carry important applications in the field of quantum computing. The calculations have been performed by density functional theory, by means of the Wien2K package [1]. The exchange interaction constants J's, which have been extracted by mapping the ab-initio total energies onto an effective localized spin classical Hamiltonian, compare well with the values extracted by the experiments, on condition that the electronic correlations in the transition metal d orbitals is taken into account beyond the standard LDA or GGA approximations [2], e.g. by the LDA(GGA) +U method [3].

References

[1] P. Blaha et al., WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Techn. Universitaet Wien, Austria), 1999. ISBN 3-9501031-1-2.
[2] V. Bellini, A. Olivieri and F. Manghi, to appear in Phys. Rev. B (2006).
[3] See for instance the pioneering work of A. I. Liechtenstein et al., J. Magn. Magn. Materials 67, 65 (1987).

Magnetism in a relativistic perspective

Trond Saue
CNRS UMR7177, France

Abstract

My talk will be divided in two parts:

1. In the first part I will discuss magnetism in a relativistic perspective. I will discuss the strict non-relativistic limit of electrodynamics and what can be learned from my conclusion. I will also discuss the separation of paramagnetic and diamagnetic contributions at the 4-component relativistic level, that is starting from the Dirac equation. It should be noted that when a magnetic field is introduced at this level only a linear and no quadratic term in the field appear in the Hamiltonian.

2. In the second part I will discuss more general aspects of 4-component relativistic molecular calculations and possible savings when going to the 2-component level. I will furthermore discuss the difference between the introduction of spin-orbit coupling in a perturbational and variational manner.

Some real applications will be shown for illustration.

Competition between double exchange and purely magnetic Heisenberg models in mixed valence systems : application to half doped manganites

Nathalie Guihery
Toulouse, France

Abstract

The low-energy spectrum of the Zener polaron in half-doped manganites studied by means of explicitely correlated ab initio calculations has been confronted to the spectrum of different model Hamiltonians. It will be shown that the electronic structure of the low-enery states results from a subtle interplay between double exchange configurations and Oxygen $2p_\sigma$ to Mn 3d charge transfer configurations that obey a Heisenberg logic. The purely magnetic Heisenberg model is analytically solved in the general case of two metals (having N magnetic orbitals) bridged by a magnetic oxygen. Unexpectedly the confrontation of the Heisenberg energies to those of the double exchange model reveals that the two spectra are analytically identical except for one state which does not belong to the model space of the double exchange Hamiltonian. Since the ab initio energy of this state fits perfectly with the predicted energy of the Heisenberg model, the comparison of the spectra does not provide any arguments to discriminate between the two models. In order to settle the question, a model which combines different antiferromagnetic contributions to the Zener Hamiltonian is used. It leads to a significant improvment in the reproduction of the low energy spectrum showing that the Zener polaron is ruled by a refined double exchange model in which the local excited non-Hund states play a non negligible role.

Chern-number spin Hamiltonians for magnetic clusters by ab-initio methods

Carlo M. Canali
Kalmar University – Sweden, Sweden

Abstract

Combining field-theory methods and ab-initio calculations, we construct an effective Hamiltonian with a single giant-spin degree of freedom, capable of describing the low-energy spin dynamics of ferromagnetic metal nanoclusters consisting of up to a few tens of atoms. In our procedure, the magnetic moment direction of the Kohn-Sham spin-density functional theory wave-function is constrained by means of a penalty functional, allowing us to explore the entire parameter space of directions, and extract the magnetic anisotropy energy and the Berry curvature functionals. The average of the Berry curvature over all magnetization directions is a so-called Chern number, a topological invariant that can only take on values equal to multiples of half-integers, which represents the dimension of the Hilbert space of the effective spin system[1]. The spin Hamiltonian is obtained by quantizing the classical anisotropy-energy functional, after a change of variables to a constant Berry-curvature space. We illustrate this procedure by explicitly constructing the Hamiltonian for dimers and trimers of transition-metal atoms, whose spin dynamics has been recently investigated experimentally by STM methods[2].

References

[1] C.M. Canali, A. Cehovin and A.H. MacDonald,
Phys. Rev. Lett. volume 91, 046805 (2003).

[2] C.F. Hirjibehedin et al., Science volume 312, 1021 (2006).

Hybrid DFT functionals in the solid state

Furio Cora

Department of Chemistry, University College London, United Kingdom

Abstract

The focus of this talk is the computational study of crystalline inorganic materials, and the accuracy with which their structural and electronic properties can be predicted. In particular, we shall examine functional materials, which are characterised by the presence of competing structural and electronic states, and/or of long-range ordered magnetic states separated by very small energy differences. Determining the details of the electronic and magnetic properties requires the application of techniques with sufficient accuracy and resolution. The computational characterisation of magnetic oxides requires the application of quantum mechanical (QM) techniques that consider explicitly the unpaired electrons at the origin of magnetism. The method of choice for electronic structure calculations on solids is Density Functional Theory (DFT); however, the standard formulations of DFT based on local and gradient-corrected functionals (LDA, GGA) fail in describing well localised electronic states, such as those of the d (f) electrons responsible for magnetism. This failure is related to the selfinteraction error, so called because the DFT Hamiltonian contains a spurious interaction of each electron with its own electronic density. The computational study of magnetic solids requires techniques that go beyond local DFT. One possible approach is represented by the hybrid exchange functionals, and consists in mixing the DFT exchange with the corresponding definition in the Hartree-Fock (HF) theory. The HF exchange corrects for the self-interaction error of the local DFT functionals; however, the amount of HF exchange to include in the hybrid functional should be treated as parametric, and determined by comparison to known experimental observables. We have recently investigated systematically the accuracy that is obtained in describing the electronic properties of transition metal oxides, including rocksalt-structured materials, ferroelectric and ferromagnetic perovskites, and other ternary and more complex compounds. By analysing results, we shall show that not only the localisation of the electronic states, and hence the magnetic coupling in the solid, is very sensitive to the amount of HF exchange employed in hybrid DFT studies, but also that the equilibrium structures depend on the functional. In ternary and more complex materials, the self-interaction influences to a different extent bonds with a different ionicity, resulting in non-uniform structural errors that may hide important structural and electronic distortions. The availability of reliable solid-state functionals, able to reproduce at the same time the electronic and structural properties of solids is an important result, because it makes the computational work independent from knowledge a priori of experimental geometries. This feature is particularly desirable for cases in which modelling has to be employed predictively, for instance in the design of new compositions, or in the investigation of defect chemistry, and how this modifies the electronic properties. Examples taken from recent works will include magnetic oxides, but also a number of non magnetic compounds, added to illustrate important structural trends. Finally, hybrid functionals will be compared with the results of GGA+U calculations, now commonly used in solid-state physics.

References

[1] F. Corà et al. 'The performance of hybrid density functionals in solid state chemistry',

Structure and Bonding 113 (2004) 171.
[2] F. Corà , ' The performance of hybrid density functionals in solid state chemistry − the case of BaTiO3', Mol. Phys. 103 (2005) 2483.
[3] R. Grau-Crespo, F. Cora, A.A. Sokol, N.H. de Leeuw and C.R.A. Catlow, 'Electronic structure and magnetic coupling in FeSbO4: A DFT study using hybrid functionals and GGA+U methods', Phys Rev. B 73 (2006) 035116

Emerging trends in Molecular Nanomagnetism: The point of view of an experimentalist

Roberta Sessoli

Uni Florence, Italy

Abstract

In the field of molecular magnetism theory has kept pace with experiments, sometime anticipating them as in the case of the phase interference in the tunnel pathways for the reversal of the magnetization. Novel materials comprising lanthanide metal ions or linear arrays of slow relaxing units appear as promising candidate to increase the blocking temperature. Moreover , in the generalized trend towards nanoscale enegineered structures, synthetic chemists and experimentalists in molecular magnetism have started to address the individual molecules by organizing them on surfaces or putting them between electrodes. This new research field, undoubtfully promising for applications like spintronics, requires however a synergic effort between experimentalists and theoreticians in order to understand how the interaction with the substrate affects the magnetic properties and vice versa. Preliminary results and open questions we have encountered in our recent research in this field will be discussed.

Stereochemistry and Spin Sates of Tetrahedral Building Blocks Revisited

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Abstract

Now that a great deal of control can be exerted on the exchange interaction between paramagnetic centers in large polynuclear systems, it is timely to look back at the stereochemical and spin state preferences of the basic building blocks.[1] We have done that for the case of tetrahedral transition metal complexes with a qualitative theoretical perspective supported by extensive shape analysis of experimental structural data and density functional calculations on thoughtfully designed model complexes covering all the dn electron configurations (0 8804; n 8804; 10). The results to be presented show an excellent match between the calculated potential energy surfaces and the frequency of experimental structures, when both are plotted as a function of the generalized minimum distortion interconversion coordinate between the tetrahedral and square planar geometries.[2] The importance of several factors in determining the stereochemistry and ground spin state in each particular case will be evaluated, including the number of valence d electrons, the presence of 960;-donor ligands, the metal oxidation state and the row of the periodic table to which the metal belongs.

References

[1] S. Alvarez, J. Cirera, Angew. Chem., Int. Ed. 2006, 45, 3012.
[2] J. Cirera, E. Ruiz, S. Alvarez, Chem. Eur. J. 2006, 12, 3162.

Computation of magnetic parameters by density functional theory: One-component perturbational vs. two-component variational inclusion of spin-orbit coupling.

Martin Kaupp
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Abstract

Computation of magnetic parameters by density functional theory: One-component perturbational vs. two-component variational inclusion of spin-orbit coupling.

Martin Kaupp

Universitä t Wü rzburg

Spin-orbit coupling is frequently of substantial importance for magnetic properties of molecules, sometimes the by far dominant contribution, as for g-tensors or zero-field splittings. When using quantum chemical calculations to compute these or related magnetic resonance parameters, one has in principle two choices when treating spin-orbit coupling: One may introduce it as a perturbation (typically in leading order, for example within the framework of the Breit-Pauli Hamiltonian) on top of a one-component nonrelativistic or scalar relativistic wavefunction. Or one may introduce it variationally into the wavefunction within a relativistic framework (four- or two-component). Within the ReSpect code developed jointly in Wü rzburg and Bratislava, this is done in a non-collinear spin-density two-component Douglas-Kroll-Hess DFT approach. In this talk, the insight provided by comparing these treatments is discussed for a variety of magnetic parameters, including zero-field splittings and g-tensors. Recent developments of computing NMR chemical shifts for paramagnetic systems will also be reported. Here a combination of NMR experiment and theory offers substantial potential to map spin-density distributions of building blocks in magnetic materials, e.g. of prussian blue type.

References

References: S. Komorovsk, M. Repisk, O. L. Malkina, V. G. Malkin, I. Malkin, M. Kaupp J. Chem. Phys. 2006, 124, 084108. I. Malkin, O. L. Malkina, V. G. Malkin, M. Kaupp J. Chem. Phys. 2005, 123, 244103. I. Malkin, O. L. Malkina, V. G. Malkin, M. Kaupp Chem. Phys. Lett. 2004, 396, 268-276. R. Reviakine, A. V. Arbuznikov, J.-C. Tremblay, C. Remenyi, O. L. Malkina, V. G. Malkin, M. Kaupp J. Chem. Phys., submitted.

Non-Innocent Ligands in Organometallic Chemistry : Theoretical Aspects

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Abstract

A variety of intriguing ligands which may display different oxidation states when coordinated to metallic centers has been under intense investigation over the last decade. The possibility to generate radical ligands in coordination compounds has given rise to intense investigation since interesting magnetic materials can be anticipated. Magnetic properties are split between a metallic center and a so-called non-innocent ligand . In particular, excited state coordination chemistry (K. Wieghardt et al.) has become a tremendously important field of research. Correlated ab initio calculations have been performed to look into the low-energy spectrum of one particular system. The electronic structure of different systems will be discussed and compared to available experimental data and previous DFT calculations. Such approaches are very powerful to elucidate the actual charge organization and to detail spectrum characteristics.

Is still the Heisenberg Spin Hamiltonian reliable for multi-nuclear paramagnetic clusters?

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Uni Florence, Italy

Abstract

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Attempts to prove the validity or not of the Heisenberg Spin Hamiltonian when two or more paramagnetic spin centers are considered have been recently done. Here we want to report a detailed study on model systems with paramagnetic centers with a local spin ⟩ and with nuclearity ranging from 2 to 4. The role played by spin delocatisation will be also discussed. Moreover, the advantages and the drawbacks of the use of the Broken Symmetry approach in multi-centered paramagnetic clusters will be covered.

Toward a variational treatment of the magnetic coupling between centers with elevated spin moments

Coen de Graaf
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Abstract

A multireference configuration interaction scheme is presented to calculate electronic structure parameters for systems with an elevated number of unpaired electrons. The presentation concentrates on the magnetic coupling but the method will also be applied to other parameters such as the on-site repulsion energy and hopping parameters. The reference wave function contains not only the usual configurations contained in the Anderson model but is extended with ligand-to-metal charge transfer configurations. Subsequently a small subset of the complete difference dedicated configuration interaction space is included in the calculation. Different strategies to introduce the charge transfer configurations in the reference wave function are compared. Projected model ligand vectors ensure the optimal inclusion of the charge transfer effects and good agreement with more extensive calculations is obtained at a more reduced computational cost.

Energetics of binuclear spin transition complexes

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Theoretical studies of spin-crossover compounds

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Abstract

A knowledge of the spin state of a molecule is often of fundamental importance for understanding its physical properties and chemical reactivity. This is certainly the case for 3d transition spin crossover complexes. We are primarily interested in the spin states of Fe(II) complexes where the size of the compounds of experimental interest and the presence of a transition metal makes densityfunctional theory (DFT) the most promising method for the quantitative description of differences between the high spin (HS) and low spin (LS) states. Our comparison of functionals with ab initio calculations on small complexes [1,2] and with experiment [3,4] show that the ability of DFT to correctly describe the spin pairing energy is very much functionaldependent but that the right generalized gradient approximation (GGA) can give results, which still imperfect, compare favorably with what can be expected from ab initio calculations on small Fe(II) clusters.

References

(1) Fouqueau, A.; Mer, S.; Casida, M.E.; Lawson Daku, L.M.; Hauser, A.; Mineva, T.; Neese, F. J. Chem. Phys. 2004, 120, 9473.
(2) Fouqueau, A.; Casida, M.E.; Lawson Daku, L.M.; Hauser, A.; Neese, F. J. Chem. Phys. 2005, 122, 044110.
(3) Ganzenmü ller, G.; Berkae, N.; Fouqueau, A.; Casida, M.E.; Reiher, M. J. Chem. Phys. 2005, 122, 234321.
(4) Lawson Daku, L.M.; Vargas, A.; Hauser, A.; Fouqueau, A.; Casida, M.E. ChemPhysChem 2005, 6, 1.

Exploring the interface between antiferromagnetism and metal-metal bonding

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Abstract

Metal clusters are traditionally divided into two distinct categories, one where direct covalent

bonds link the metal centres, and the other where indirect exchange interactions dominate. In this presentation, I will describe the remarkable electronic structure of the linear tricobalt chain compound, Co3(dpa)4Cl2, which spans these two extreme limits. The cluster exists into two distinct forms, one symmetric, the other with very different Co-Co bond lengths.1 The structural and magnetic properties can only be fully rationalised using 3 distinct electronic states, two doublets and a quartet, all of which are populated under different conditions (temperature, solvent of crystallisation). One of the two doublet states is an 'open-shell' species containing a high-spin (S = 3/2) CoII centre, antiferromagnetically coupled to a Co-Co dimer unit in a locally excited triplet state. The relaxation of this unusual electron distribution occurs along a very flat potential energy surface gives rise to the remarkable temperature dependence of the unsymmetric form of Co3(dpa)4Cl2.2

References

1 (a) Yang, E.-C.; Cheng, M.-C.; Tsai, M.-S.; Peng, S.-M. J. Chem. Soc., Chem. Commun. 1994, 2377. (b) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV. J. Chem. Soc., Chem.Commun. 1997, 421.
2 D.A. Pantazis and J.E. McGrady, J. Am. Chem. Soc., 2006, 128, 4128.

Magnetic anisotropy and exchange coupling for manganese-based single molecule magnets

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Abstract

Molecular magnets are large, well-defined, discrete molecules consisting of several transition metal ions interacting through organic and/or inorganic ligands. Among thousands of synthesized molecular magnets, there is a class of molecular magnets known as single-molecule magnets (SMMs) which have large effective energy barriers between different directions of the magnetic moment and behave as single-domain magnetic nanoparticles in an external magnetic field. They are particularly interesting because of observed quantum tunneling of magnetization and their possible applications in magnetic recording and molecular electronics. In this talk, I will present density-functional calculations of the electronic, vibrational, and magnetic properties of selected manganese-based SMMs, such as the total magnetic moment, electronic energy gaps, Raman scattering spectra, exchange constants, spin excitation energetics, and magnetic anisotropy barriers. I will also discuss what types of molecular environmental changes can significantly influence the exchange interaction, magnetic anisotropy, and observed quantum tunneling in the SMMs. [This work has been done in collaboration with Mark Pederson, Tunna Baruah, Noam Bernstein, Stephen Hellberg, Steven Richardson, N. Aliaga-Alcalde, and George Christou.]

Muon studies of molecular magnets

Stephen Blundell

Oxford, United Kingdom

Abstract

I will describe recent results on molecular magnets studied using the technique of muon-spin rotation. These studies include work on Cu-chain systems, single molecule magnets and other low-dimensional molecular magnets.

Modeling of non-Heisenberg exchange interactions in tetrameric Ni(II) clusters of S4 symmetry

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Abstract

A new developement of the generalized effective spin hamiltonian formalism will be presented: antisymmetric exchange interactions and local crystal fields were introduced into the Hamiltonian for the first time as non-collinear tensors. Application of the model for simulation of the temperature dependence of dc susceptibility, magnetization and INS-measurements on Ni(II)tetrameric cluster of S4 symmetry will be shown.

The magnetic properties of polyoxovanadates

Carmen Calzado
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Abstract

Polyoxovanadates containing quasi spherical $V_{18}O_{42}$ shells present an interesting magnetic behaviour: the antiferromagnetic coupling increases with the oxidation degree of the shell (1). While structural effects induced by the change on the electronic populations have been discarded, it is not clear the role that electronic effects could play on their magnetic properties.

We have studied the dependence of the magnetic properties of these systems on their oxidation state by means of a computational strategy combining ab initio calculations and the diagonalization of a model t-J-V Hamiltonian. From ab initio quantum chemistry calculations we have estimated the amplitudes of the nearest-neighbour (NN) and next-nearest-neighbour (NNN) magnetic coupling constants and hopping integrals. These values have been injected onto a t-J-V model Hamiltonian to evaluate the susceptibility at different temperatures.

The results to be presented show that (i) the NN and NNN coupling constants have similar values, despite larger V-V distances (ii) the hole doping induces a general increase of the AF coupling, which could be related to the observed magnetic behaviour, (iii) the interaction betweeen magnetic coupling and electron delocalization seems to be in the origin of the enhancement of the antiferromagnetic coupling.

References

(1) A. Mü ller et al. Inorg. Chem. 1997, 36, 5239-5250.

Magnetism in low-dimensional systems: theoretical studies using a first-principles bottom-up methodology

Juan J. Novoa

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Abstract

The nature of the magnetic interactions are evaluated and the macroscopic magnetic properties are computed for a series of 1D and 2D low-dimensional crystals using a recently introduced first-principles bottom-up methodology. This methodology uses first-principles methods to compute the microscopic JAB radical-radical interactions. Then, using these JAB values the macroscopic magnetic properties are computed by diagonalization of the matriz representation of the Heisenberg Hamiltonian (in a finite space that properly reproduces the magnetic topology of the infinite crystal). The procedure allows to connect the computed macroscopic results with their microscopic origins. We have used this procedure in the study of isolated chains, spin-ladders, and 2D-planes, to test the quality of the first-principles bottom-up procedure on these systems. An excellent agreement is found between the computed and experimental results.

Magneto-structural correlations in polynuclear complexes: The Fe4 butterflies.

Thomas Cauchy

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A first principles bottom-up theoretical study of the bis(2,3-dimethylpyridinium) tetrabromocuprate spin-ladder

Merce Deumal

Universitat de Barcelona, Spain

Abstract

The bis(2,3-dimethylpyridinium) tetrabromocuprate (2,3dmpyH)2CuBr4 spin-ladder has been studied using a first principles bottom-up theoretical procedure [1], which rigorously computes the macroscopic magnetic properties from the only knowledge of the JAB microscopic magnetic interactions. Spin-ladders have been a special topic of interest due to the presence of an energy gap in their spin excitation spectrum. Moreover, under certain conditions, ladders have been shown to undergo a transition to a superconducting phase. The JAB magnetic interactions responsible for the magnetism of (2,3dmpyH)2CuBr4 have been analyzed and evaluated. The magnetic topology of (2,3dmpyH)2CuBr4 results to be a set of strong-rail exchange spin-ladders (Jrail = − 7.8 cm-1, Jrung = − 3.5 cm-1). The 2,3dmpyH+ (2,3-dimethylpyridinium) counterions are shown to be important when computing the value of the JAB microscopic magnetic interactions. The singlet-triplet spin-gap has been computed, and agrees with the available experimental data. Two crystal structures of (2,3dmpyH)2CuBr4 determined at 88K and 273K have been used to show the effect of the temperature on the magnetic topology and susceptibil-

ity data. It will be shown that at 88K the numerically computed magnetic susceptibility data properly reproduces the experimental magnetic curve for (2,3dmpyH)2CuBr4 magnet.

References

[1] M. Deumal, M.J. Bearpark, J.J. Novoa, M.A. Robb, J. Phys. Chem. A 106, 1299 (2002).

Contrasting direct versus mediated through-space magnetic interactions in pyridyl-verdazyl : hidroquinone molecular co-crystal;

Joaquim Jornet
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Abstract

The magnetism in non-purely organic molecule-based magnets is mostly explained in terms of through-bond metalligandmetal superexchange interactions, where two spin-containing metals are connected by means of the orbitals of a diamagnetic ligand. Similarly, the mechanism of the magnetic interactions in the pyridyl-verdazyl:hidroquinone (pyvd:hq) molecular co-crystal was suggested to originate by a unique "mediated through-space" magnetic interaction. This interaction was proposed to magnetically connect two non-adjacent pyvd radicals within a p stack, where adjacent radicals pile up in a head-over-tail orientation, through a third radical sitting between the previous two mediated radicals. Given the relevance of this proposal, the magnetic properties of pyvd:hq co-crystal were reinvestigated using a first-principles bottom-up theoretical procedure [1,2]. The microscopic JAB values for all direct through-space magnetic interactions between nearby pyvd radicals were computed. There are two non-negligible magnetic interactions of similar strength (– 56 and – 54 cm-1) corresponding to the direct through-space interactions between two adjacent radicals of a p stack. The co-crystal also exhibits a radical-mediated through-space interaction of – 0.31 cm-1 between two non-adjacent radicals of a p stack. Direct through-space magnetic interactions are two orders of magnitude larger than the mediated through-space interaction. Thus, first-principles calculations do not support a mediated through-space mechanism to explain the magnetism of the pyvd:hq co-crystal. The magnetic topology generated by the two dominant antiferromagnetic interactions in pyvd:hq consists of one-dimensional alternating chains (interacting very weakly along the b and c axes). By using this topology, the computed macroscopic magnetic susceptibility values properly reproduce the experimental data. ;

Magneto-structural correlations in the [Mn(porphyrin)][TCNE] family of molecule-based magnets;

Jordi Ribas
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Abstract

The dependence of the JAB interaction with the geometry in the meso-tetraphenylporphyrinato-manganese(III) tetracyanoethenide family of molecule-based magnets has been re-evaluated by performing B3LYP calculations. The calibration of the B3LYP results with the experimental data of seven [Mn(porphyrin)][TCNE] representative systems and with CASSCF and CASPT2 calculations, shows that the B3LYP method is the most cost/quality efficient form of evaluating the magneto-structural correlations in these systems. After this calibration, the JAB was systematically evaluated as a function of the intermolecular coordinates that define the position and orientation of [TCNE].- relative to the [Mn(porphyrin)]+. The JAB have been found to be antiferromagnetic in all regions, with the largest values being associated to the smallest angles between the [Mn(porphyrin)]+ and the TCNE planes. On the other hand, the B3LYP results have been compared to those obtained using the three spin exchange me chanisms applicable to these systems (i.e. orthogonality, spin coupling, and CI mechanisms). None of these three mechanisms gives trends in fully agreement with the B3LYP results. Therefore, one has to resort to results from first principles methods. ;

Applications of Density Functional Theory to Molecular Magnets

Mark Pederson
NRL, United States

Abstract

In addition to summarizing some of the density-functional theory and methods that are now widely used for calculations on molecular magnets, I will summarize the results of DFT-based applications to anisotropic molecular magnets (AMM) and to molecular spin-systems (MSS). The idealization of the former class of molecules, exemplified by Mn12-Acetate, is that the exchange interactions are very large. Within this idealization the lowest-energy excitations and consequently resonant tunneling of magnetization are due to second-order spin-orbit effects which can be calculated using perturbation theory on a single configuration of the system. Even within the ansatz of a density-functional-theory or single-configuration picture, additional effects due to self-consistency exist. Recent work aimed at further justifying a second-order approach and in identifying additional corrections will be presented. At the opposite extreme of AMM are the MSS. For these systems, such as the V15 cluster, the low energy excitations are due to many-spin excitations that can be extracted from density-functional-based determination of Heisenberg Hamiltonians followed by exact diagonalization. DFT-based calculations can be used to determine whether a given molecule containing transition-metal ions fits within one of these idealizations and for determining the magnetic excitations for either idealized case. A discussion of the challenges for understanding intermediate cases within DFT will be presented. I will also discuss how magnetic anisotropy barriers or a spin excitation depend upon environmental factors such as addition of charges, electric fields, or vibrational excitation and show that these factors can be accounted for within a density functional framework.

I thank S.N. Khanna, J. Kortus, T. Baruah, K. Park, N. Bernstein, S. Hellberg, and S. Richardson for interesting discussions and collaborations on many different aspects of molecular magnets during the last decade.

Modeling of the Magnetic Behavior of Low Dimensional Magnetic Systems

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Abstract

The use of adapted theoretical tools for modeling the thermodynamical functions of magnetic solids is of prime importance for an accurate analysis of their experimental behaviors allowing the establishment of detailed structure-properties relationships. A model of "hierarchical superparamagnetism" was developed recently which generalizes the idea of scaling by taking advantage of the non-singular solutions that are introduced, together with the singular ones, when the hypotheses of "critical scaling" are formulated. These non-singular solutions, although they have the same legitimacy, have simply been set aside when the goal was to describe the singularities of phase transitions. They happen to be very useful when correlations exist, but which are not sufficient to trigger a long range order at a finite TC, either because frustration is strong, near e.g. an antiferromagnetic (AF) order, or because we sit at, or below, a lower critical dimensionality. Model systems, such as the 1D or 2D-Heisenberg systems of spin S=1/2, 1,…8734; display such behaviors. For this reason, much effort has been devoted in performing exact calculations on such finite systems of increasing size, and in trying to infer which type of limit is reached when the size diverges. On another hand, the progresses of chemistry have made it possible to design organometallic clusters, chains or planes, of axial, planar or isotropic spins, which are close approximants of the above mentioned systems, and are well appropriate to investigate the properties of interest. We will show on a few examples, that the model of hierarchical superparamagnetism provides the right framework to approach these problems and suggests a strategy adapted to each case.

References

[1] M. Drillon et al., Phys. Rev. – B 65, 104404(1-8) (2002).
[2] J. Souletie et al., Phys. Rev. B 70, 054410(1-6) (2004).
[3] J. Souletie et al., Phys. Rev. B 72, 214427(1-4) (2005).
[4] J. Souletie et al., in Magnetism : Molecules to Materials V, Ed. by J.S. Miller and M.Drillon (Wiley-VCH, Weinheim, Germany), 347-377 (2005).

Molecular Dynamics of Antiferromagentically Spin-Coupled Systems

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Abstract

Proteins with iron-sulfur clusters of the type Fe1-4S08722;4(SR)2-4 are important electron transfer agents in living cells from bacteria to higher animals. These clusters are characterized by complex spin coupling between the iron atoms.

The exact electronic groundstate of such iron-sulfur clusters cannot be accessed from conventional single determinant density functional theory. We propose a generalized approach for determining the electronic ground state structure of binuclear spin-coupled systems. A Car-Parrinello Lagrangian is then formulated in this frame work for studying their dynamics. Further, this method is extended to a mixed QM-MM coupled scheme, which allows the treatment of [2Fe-2S]

proteins fully in our calculations, including the effect of its environment. Initial results from our ab initio molecular dynamics simulations are presented.

Cu-based metalorganic systems: an ab-initio study of the electronic structure

Andrea Salguero
Frankfurt University, Germany

Abstract

Within a first principles framework, we study the electronic structure of the recently synthesized polymeric coordination compound Cu(II)-2,5-bis(pyrazol-1-yl)-1,4-dihydroxybenzene (CuCCP), which has been suggested to be a good realization of an antiferromagnetic Heisenberg spin-1/2 chain. By using a combination of classical with ab-initio quantum mechanical methods, we design on the computer reliable modified structures of CuCCP aimed at studying effects of Cu-Cu coupling strength variations and dimensional crossover on this spin-1/2 system. For this purpose, we performed two types of modifications on CuCCP. In one case, we replaced H in the linker by i) an electron donating group (NH_2) and ii) an electron withdrawing group (CN), while the other modification consisted on adding H_2O and NH_3 molecules in the structure which change the local coordination of the Cu(II) ions. With the downfolding method within the framework of N-th order muffin-tin orbital technique (NMTO-downfolding) we provide a quantitative analysis of the modified electronic structure and the nature of the Cu-Cu interaction paths in these new structures and discuss implications for the underlying microscopic model.

Strong antiferromagnetic coupling between orthogonal orbitals: an ab initio study of non-innocent ligand-based complex

Maria Carvajal
ENS Lyon, France

Abstract

Structural magnetic information upon Fe(bpb)(CN)2, bpb- = 1,2-bis(pyridine-2-carboxamido) benzoate complex is obtained by means of density functional theory and correlated ab initio calculations. It is shown that strong antiferromagnetism is achieved between an iron(III) ion and a flat non-innocent bpb2- ligand, the singlet state lying 600cm-1 lower in energy than the triplet. Even thought magnetic orbitals are orthogonal, antiferromagnetism goes through the dynamical polarization of the ionic valence bond forms between metallic center and organic ligand part. The intrinsically delocalized nature of the magnetic orbital of the bpb ligand and its redox versatile character clearly enhance antiferromagnetism.

References

(1) Dutta, S. K.; Beckmann, U.; Eckhardt, B.; Weyhermü ller, T.; Wieghardt, K. Inorg. Chem. 2000, 39, 3355.
(2) Patra, A. K.; Ray, M.; Mukherjee, R. Inorg. Chem. 2000, 39, 652.

Exchange calculations in molecular magnets beyond standard DFT

Alexander Lichtenstein

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Abstract

I will present calculations of exchange parameters in molecular magnets using methody beyond standard DFT in order to treat correlations more accurate (LDA+U, DMFT).

Contribution of correlated ab initio calculations to the description of magnetic behaviors in Prussian blue analogues;

Boris Le Guennic

Ecole Normale Superieure de Lyon, France

Exchange calculations in molecular magnets beyond standard DFT

Alexander Lichtenstein

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Abstract

Realistic approach to the electronic structure of complex oxides which contains correlated d-electrons will be discussed. The density functional theory within the local spin density approximation have been highly successful for electronic structure calculations and zero temperature magnetic properties of non-correlated systems. We investigate some failures of the LDA-scheme for the charge, spin and orbital ordering in transition metal compounds. General formulation of the LDA+U method which takes into account local Coulomb correlations for the d-shell of transition metals ions in the crystal within the mean-field approximation will be presented. The LDA+U scheme describe well the antiferromagnetic Mott insulators and gives reasonable values of superexchange interactions. Electronic structure, spin and orbital moments and lattice distortions of transition-metal compounds can be analyzed in the framework of rotationally invariant LDA+U method. We discuss the result of LDA+U investigations of electronic structure and exchange interactions of different molecular magnets.

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