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Charge, Spin and Momentum Densities simultaneous refinement. From the method to the code. Jean-Michel Gillet[a], Yurii Ciumacov[a], Pietro Cortona[a], Pierre Becker[a], Mohamed Souhassou[b], Nicolas Claiser[b], Maxime Deutsch[b], Sebastien Pillet[b], Claude Lecomte[b], Beatrice Gillon[c], Dominique Luneau[d], Ana Borta[d], Olga Iasco[d]. *[a]Laboratoire de Cristallographie, Résonance Magnétique et Modélisations, Institut Jean Barriol, Université des Sciences et Techniques, BP 70239, boulevard des Aiguillettes, Vandoeuvre-lès-Nancy, France[c]. [b]Laboratoire Structures et Propriétés des Matériaux Solides, UMR CNRS 8580, Ecole Centrale Paris, Grande Voie des Vignes, 92290 Châtenay-Malabry, France. [c]Laboratoire Leon Brillouin, CEA-Saclay, 91191 Gif sur Yvette, France. [d]Laboratoire Multimatériaux et Interfaces, Université Claude Bernard, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France.*
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We present the latest progress of the Convergence of spin, charge and momentum Electron Density Analysis project.
In the last decade, few methods have been proposed to build a quantum model with the goal to refine some of its important features using a set of different experiments. Among these experiments, high resolution x-rays and polarized neutrons diffraction, convergent beam electron diffraction, magnetic and non magnetic X-rays Compton scattering are the most popular.
The joint refinement of charge and spin electron densities in position and momentum spaces from a set of different experiments, as those previously mentioned, requires the use of a common quantity known as the "one particle reduced density matrix" (1-RDM). Its role will be briefly presented.
We will then explain the model(s), the method and the strategies that were adopted in constructing a general joint refinement computer code.
Results from preliminary tests will be described as well as possible future joint studies.

Keywords: electron density, spin density, charge density, momentum density, density matrix, refinement.

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Spin density distributions in molecular magnetic materials. Javier Campo. *Materials Science Institute of Aragón, (CISC-University of Zaragoza), C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain.*
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A good understanding of the magnetic interaction mechanisms, which are strongly influenced by the spin density distribution on the molecules, has a great importance in the design of new molecular magnets with high ordering temperatures. Moreover, we will show how spin density investigations can seed light to fundamental problems in molecular magnetism, such as the anisotropy in molecular clusters.
The aim of this contribution is to understand the particular magnetic behavior, through the analysis of the experimental

and computational determination of the spin density distribution and the magnetic coupling constants of different magnetic molecular materials; the family $A_2FeX_5 \cdot H_2O$ (A=alkali, X=Cl, Br), the thiazyl-based magnets p-X-$C_6F_4CNSSN \cdot$ (X=Br, NO_2, CN) and the Mn-based molecular cluster $Mn_3L_4(ClO_4)_2(H_2O)_2$, (HL=2-methoxy-6-(pyridine-2-hydrazonomethyl)phenol).
Although the family $A_2FeX_5 \cdot H_2O$ had been extensively studied we were interested in these 3D low anisotropy antiferromagnetic series because still remained an interesting open question: why are their transition temperatures relatively high considering that in these compounds there are no μ-bridging groups between the iron ions, such as Fe-O-Fe or Fe-X-Fe linkages, but all the super-exchange pathways are of the type Fe-X···X-Fe or Fe-O···X-Fe? Our results shown a high spin density delocalization (20 %) to the halogen atoms being the more important at the X_4-halogen belonging to the H bond [1].
On the other hand the sulphur based free-radical family represents an alternative to the classical nitrogen-oxygen one for the design of purely organic magnets. In fact, the dithiadiazolyl radical family includes the organic material with the highest known transition temperature into a phase showing spontaneous magnetization and the organic magnet with the second highest transition temperature into a ferromagnetic phase. The subject addressed in our studies was to explore and understand the magnetic interaction mechanisms, via the spin density determination and *ab initio* modelizations, in this free-radical family and to investigate its suitability for achieving ferromagnetic interactions [2].
The Mn3 cluster has been described as an almost lineal trimer of Mn(II) in a high spin configuration with two isotropic magnetic interactions. One striking fact is the experimental EPR g factor of 2.14 for such an isotropic system. Due to its isotropic and not degenerate nature, the system is an ideal benchmark to investigate the interplay of the magnetic interactions in systems with several magnetic centers and more than one electron per magnetic center. An in deep study of the system through the combination of several experimental and theoretical methods has allowed us to demonstrate the isotropic nature of the system and the ferromagnetic character of the intra-molecular magnetic interactions.

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On the *ab-initio* calculation of all-atom ADPs for molecules in crystal structures. Birger Dittrich[a].
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Thermal motion and electron density are convoluted, and one can not distinguish between them from X-ray diffraction data alone [1]. The ability to calculate atomic displacement parameters (ADPs) for molecules in crystal structures would allow application of charge-density methodology to datasets of 'normal resolution' (fulfilling the Acta C limit), since a

considerable number of least-squares parameters could be omitted. Recent efforts have shown that this could indeed be a feasible approach [2]. We are currently investigating how ADPs can be calculated efficiently *via* cluster calculations. A suitable approach appears to be the ONIOM method [3], where a quantum chemical calculation is split into a high-level and a low-level part. ONIOM calculations allow geometry optimizations of a central molecule in a cluster of surrounding molecules as found in the crystal lattice. A C-program to generate input clusters for use with the GAUSSIAN program [4] was coded. We have performed a series of calculations treating a central molecule of interest with various high-level basis sets, and the surrounding layer of molecules with the UFF force field or various other lower-level quantum chemical approximations. Input geometries from invariom refinement [5] are suitably accurate to grant successful optimizations, and we find that accurate H-atom positions are crucial for convergence. It has already been shown that the 'internal' modes of hydrogen-atom vibrations can indeed be predicted from such calculations [6]. The next step, obtaining all-atom vibrational frequencies that can be converted to ADPs, requires a realistic description of the interaction between central and surrounding molecules in the cluster. To benchmark the calculated ADPs we attempt to predict the temperature dependence of ADPs. A number of amino-acid structures are studied where both high-quality low- or multi-temperature X-ray data, but also room-temperature ADPs from neutron diffraction are available. A by-product of these efforts are *temperature-dependent* ratios between the Uiso of riding H- and the respective parent atom. Their inclusion would be beneficial for crystallographic refinements with constrained hydrogen atoms based on low-temperature data. Despite the fact that the R-factor is rather insensitive to H-atom scattering in general, these ratios are more realistic than the fixed values for room temperature data currently in use.

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Keywords: *ab-initio* calculations, charge density, atomic displacement parameters

FA3-MS20-T04

Spin and magnetization density in the kagome staircase system $Co_3V_2O_8$. N. Qureshi[a], M. Zbiri[b], H. Fuess[c], H. Ehrenberg[d], Y. Sakurai[e], M. Itou[e]. [a]*University of Cologne, Institute of Physics II, Germany.* [b]*Institut Laue Langevin, Grenoble, France.* [c]*Materials Science, Technical University Darmstadt, Germany.* [d]*Institute for Complex Materials, IFW Dresden, Germany.* [e]*Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Japan.*
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$Co_3V_2O_8$ represents the $3d$ transition metal ortho-oxo vanadates labeled as kagome staircase structures and crystallizes in the orthorhombic space group Cmca [1]. Its crystal structure is characterized by edge-sharing CoO_6 octahedra forming buckled layers of corner-sharing triangles, the kagome staircases, which are separated along the b axis by VO_4 tetrahedra. In contrast to the ideal kagome net the geometric frustration is relieved due to two inequivalent Co sites (Co_c *cross-tie* on 4a sites, Co_s *spine* on 8e sites) and slightly different Co-Co bond lengths. The magnetic coupling is effectuated via a 90° Co-O-Co superexchange pathway. The ferromagnetic ground state reveals two strongly different magnetic moments for the Co_c and Co_s of 1.54 μ_B and 2.73 μ_B, respectively [2], despite the fact that both Co^{2+} ions apparently present high-spin configurations as macroscopic measurements exhibit saturation of the *cross-tie* moments [3]. Investigating the magnetization density may reveal preferred superexchange pathways with the presence of magnetization on the involved O sites. Eventual induced magnetization on the empty d-shell of V sites would allow interlayer coupling by super-superexchange. Therefore, magnetic Compton scattering and polarized neutron diffraction experiments have been carried out leading to the spin density in momentum space and the magnetization density in real space, respectively. *Ab initio* wave functions have been derived by hybrid DFT-based quantum chemical cluster calculations for the two different CoO_6 clusters. The resulting molecular orbitals have been used to build up a theoretical model able to be refined to the real and momentum space quantities at the same time.

Our results give the first reasonable explanation for the strongly reduced Co_c moment in this system, which is not due to competing magnetic interactions, but a consequence of the covalent character of the Co_c ion.

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Keywords: spin density, momentum density, *ab-initio* calculations

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Time-resolved X-ray diffraction study of the piezoelectric response of single crystals. Raphael Grifone[a], Oleg Schmidt[a], Semen Gorfman[b], Ullrich Pietsch[a]. [a]*Solide State Physics, University of Siegen, Siegen, Germany.* [b]*Department of Physics, University of Warwick, Coventry, UK.*
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The atomistic origin of the physical properties of solids such as dielectricity and piezoelectricity can be understood on the basis of precise investigations of the atomic movements induced by an applied electric field. In our previous studies we investigated the bond-selective response of $Li_2SO_4 \cdot H_2O$ [1] and GaAs [2] single crystals to a quasi-static external electric field. In order to generate dynamical processes in a crystal we developed special electronic circuits allowing for fast (down to 200 ns) switching of electric, between four states of high voltage (HV), U_+, U_0, U_+, U_0, applied periodically to thin plane-parallel crystal plates. The frequency of the applied HV can be adjusted between 1Hz and 10 kHz, so that we were able to perform the experiment at a resonance frequency of the crystal plate. The time-dependent dynamical crystal response was studied by measuring the ω-rocking curves of a few Bragg reflections. Minimum time resolution of 20ns was achieved