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MAXIMUM ENTROPY RECONSTRUCTION OF SPIN DENSITIES INVOLVING NON UNIFORM PRIOR

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Diffraction experiments give microscopic information on structures in crystals. Such investigations correspond to Bragg intensity measurements. More and more accurate experiments are performed, which produce accurate maps of the scattering density itself: charge density in the case of X-ray, nuclear density in the case of unpolarized neutron and spin (magnetization) density in the case of polarized neutron experiments.

In crystals, the scattering densities are periodic and the Bragg amplitudes are the Fourier components of these periodic distributions. In principle, the scattering density $\rho(\vec{r})$ is given by the inverse Fourier series of the experimental structure factors. Such a series implies an infinite sum on the Miller indices h, k, l. Actually, what is performed is a truncated sum, where the indices are limited to those reflections really measured, and where all the structure factors are noisy, as a result of the uncertainty of the measurement. Given these error bars and the limited set of measured reflections, it exists a very large number of maps compatible with the data. Among those, the truncated Fourier inversion procedure selects one of them: the map whose Fourier coefficients are equal to zero for the unmeasured reflections and equal to the exact observed values otherwise. This is certainly an arbitrary choice.

An alternative method, which uses the concept of maximum of entropy (MaxEnt), appeared to be a formidable improvement in the treatment of diffraction data. This method is based on a bayesian approach: among all the maps compatible with the experimental data, it selects that one which has the highest prior (intrinsic) probability. Considering that all the points of the map are equally probable, this probability (flat prior) is expressed via the Boltzman entropy of the distribution, with the entropy defined as:

$$S[\rho(\vec{r})] = -\sum_i \rho_i \ln(\rho_i)$$

This method has been used for the reconstruction of charge densities from X-ray data (1-3), for maps of nuclear densities from unpolarized neutron data (4-6) as well as for distributions of spin (magnetization) density (7-9). The density maps obtained by this method, as compared to those resulting from the usual inverse Fourier transformation, are tremendously improved. In particular, any substantial deviation from the background is really contained in the data, as it costs entropy compared to a map that would ignore such features.

However, in most of the cases, before the measurements are performed, some knowledge exists about the distribution which is investigated. It can range from the simple information of the type of scattering electrons (electrons p, d or f) to an elaborate theoretical model. In these cases, the uniform prior which considers all the different pixels as equally likely, is too weak a requirement and has to be replaced. In a rigorous bayesian analysis, Skilling has shown (10) that prior knowledge can be encoded into the Maximum Entropy formalism through a model $m(\vec{r})$, via a new definition for the entropy

$$S[\rho(\vec{r})] = \sum_i \left(\rho_i - m_i - \rho_i \ln\left(\frac{\rho_i}{m_i}\right) \right)$$

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In the absence of any data, the maximum of the entropy functional is reached for $\rho(\vec{r}) = m(\vec{r})$. Any substantial departure from the model, observed in the final map, is really contained in the data as, with the new definition, it costs entropy. This paper presents illustrations of model testing in the case of intermetallic and molecular compounds.

An intermetallic compound: a model for the magnetization density in YCo_5

The magnetic properties of the YCo_5 intermetallic compound have been extensively investigated due to its ferromagnetism with a high Curie point and very high magnetocrystalline anisotropy which makes it a good representative of the RCo_5 permanent magnets. Its crystal structure is represented in figure 1. It includes one site of Y and two sites of Co: Co_I in the basal plane and Co_{II} in the intermediate plane. Both unpolarized neutron and polarized neutron experiments have been performed at room temperature, in the ferromagnetic state, in order to refine the nuclear structure and to determine the magnetization density.

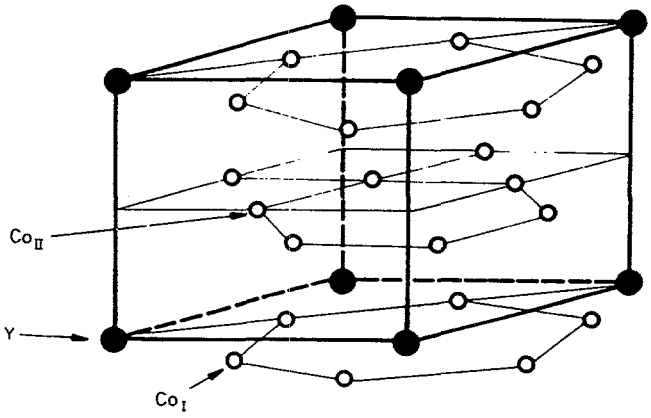

Fig.1: The unit cell of YCo_5

As at room temperature Bragg reflections contain both nuclear and magnetic structure factors, the nuclear structure was refined from a combination of polarized and unpolarized neutron data. Contrarily to the ideal structure where only 3 atomic sites are present, it has been shown (11-12) that some Y atoms were substituted by pairs of cobalt. These pairs, parallel to the c axis are responsible for a structure deformation which shrinks the cobalt hexagons surrounding the substitutions.The amount of these substituted Y was refined to be 0.046±0.008. Furthermore the thermal vibration parameter of Co_I site appeared to be very anisotropic. The nuclear structure factors F_N were calculated from this refined structure and were introduced in the polarized neutron data to get the magnetic structure factors F_M.

The reconstruction of the magnetization density was done by the Maximum Entropy method with a uniform prior. The projection on the basal plane is shown in figure 2. Besides a small contribution at the origin due to the Y substituted by cobalt pairs, the magnetization is well localized on the 5 atoms of the 2 cobalt sites.

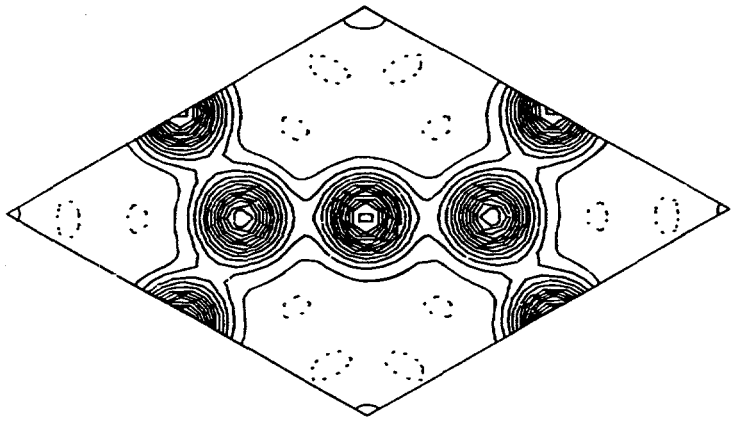

Fig.2: YCo_5: MaxEnt reconstruction with a uniform prior

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Therefore an atomic model, made of a superposition of independent densities centered at the magnetic atoms, was built. The magnetic structure factor can be written:

$$F_M(\vec{K}) = \sum_j m_j f_j(K) \exp(i\vec{K}\vec{r}) \exp(-W_j)$$

where f_j is the magnetic form factor and m_j the moment of the jth atom. The magnetic form factors are the sum of two contributions: orbital and spin: $f(K) = lf_l(K) + sf_s(K)$. Assuming that the 3d orbital is almost quenched, the orbital form factor was taken as isotropic and equal to $f_l(K) = < j_0(K) > + < j_2(K) >$. For the spin part one took into account the anisotropy of the spin density around each magnetic atom: Co_I with one singlet (dz^2) and two doublet (dxy and dyz) Co_{II} with the five-fold degeneracy completely removed. Altogether 10 parameters were refined from the experimental F_M to determine the atomic magnetic model: the localized moments m_I and m_{II}, the orbital contributions l_I and l_{II} and the occupation numbers: 2 for the site Co_I and 4 for the site Co_{II}. The agreement between observed and calculated F_M is very good; the parameters are displayed in table I. The magnetization density corresponding to the atomic model and projected on the basal plane is represented in figure 3. Comparing with the MaxEnt projection (fig. 2) one sees that the distributions are not far one from the other, but with more asphericities on the atoms of site Co_I for the refined model.

Table I: YCo_5: Refined parameters for the atomic magnetic model

Site	Localised moment	Spin proportion	Occupation parameter	
Co_I	1·77 (2) μ_B	0·74 (5)	dz^2	0·23 (3)
			dxz, dyz	0·18 (12)
			$dx^2 - y^2$, dxy	0·58
Co_{II}	1·72 (2) μ_B	0·84 (4)	dz^2	0·15 (2)
			dxz	0·24 (4)
			dyz	0·19 (3)
			$dx^2 - y^2$	0·22 (3)
			dxy	0·20
Sum of the localised moments in one cell				8·90 (10) μ_B
Magnetisation measured for one cell				7·99 (2) μ_B

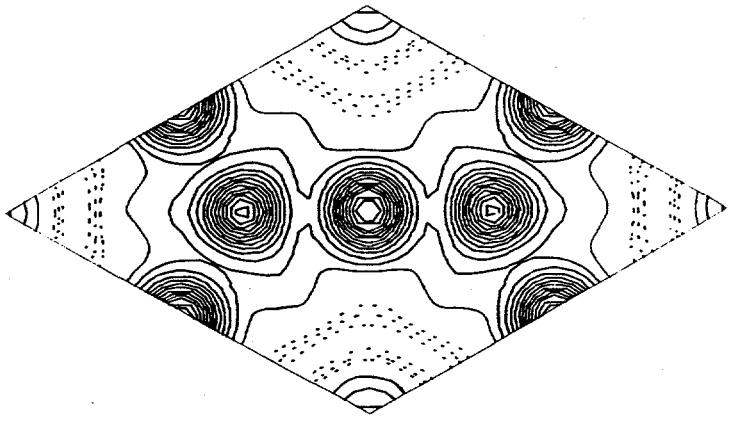

Fig 3: YCo_5: Magnetization density of the magnetic atomic model

How to judge the relevance of these asphericities? Are they really compatible with the data or are they simply the biased result of an ill-adapted model? The best way to answer this question is to use this result as a prior probability for a new MaxEnt reconstruction. The map thus obtained, which is given in figure 4, is striking: the new reconstruction is very similar to that obtained with the uniform prior. All the asphericities which were present in the model have been rubbed out, in spite of the fact that, with the new definition of entropy, it costs entropy. We can conclude that

the distribution of the magnetization density which is contained in the data is spherical and that the magnetic model has to be revisited, which is currently being done.

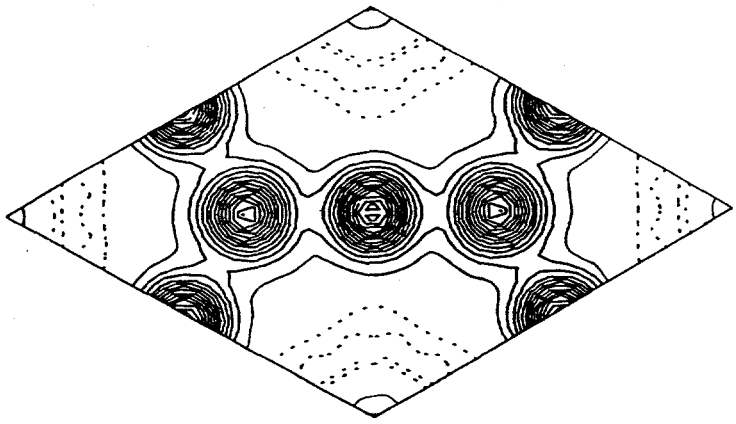

Fig. 4: YCo_5: MaxEnt reconstruction with a non uniform prior

A molecular compound: the antibonding wave function in an imino nitroxide free radical

Conjugated nitroxides free radicals are among the most widely used spin carriers in the design of molecular compounds. As their unpaired electron is delocalized over the different atoms of the molecule, they are convenient building blocks and ideal magnetic bridges between magnetic metals to achieve new compounds with particular magnetic properties. In the case of nitronyl nitroxides, the unpaired electron is supposed to be, in a first approximation, equally shared by the four atoms O, N, N and O, and the single occupied molecular orbital (SOMO) is supposed to exhibit a node on the C atom in between the two NO's (fig 5a). In the case of imino nitroxides, the unpaired electron is mainly carried by the three atoms N, N and O, but, as the symmetry is broken, no node is expected on the central C atom for the SOMO (fig. 5b). Several studies of spin densities have been performed on nitronyl nitroxides (13). We demonstrate here the use of MaxEnt reconstruction with a non uniform prior for 2-(3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (p-NPIN), an imino nitroxide with two non equivalent molecules in the asymmetric unit cell : molecule A and molecule B.

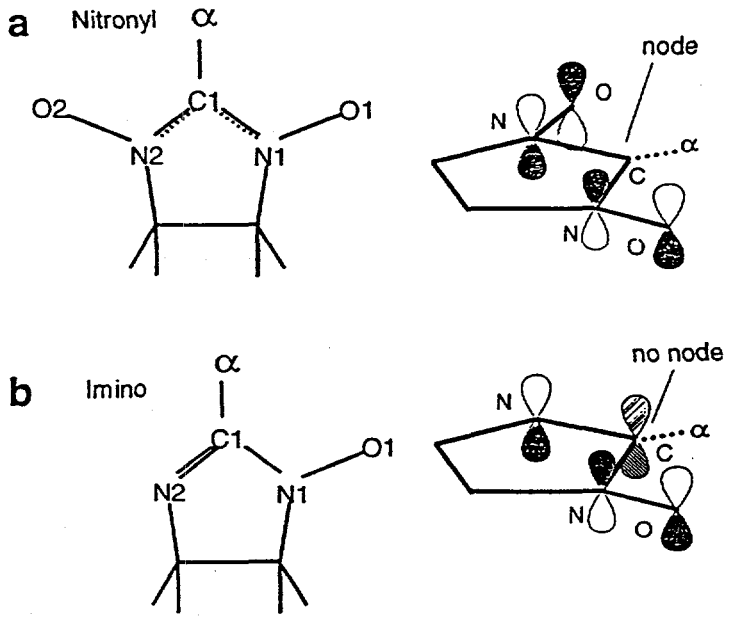

Fig. 5: Nitroxide radicals and their SOMO
(a) nitronyl nitroxide
(b) imino nitroxide

In order to figure out the F_N 's, the nuclear structure was refined from unpolarized neutron data taken at 30K, in the paramagnetic state, on a 4 circle diffractometer. Furthermore a set of 248 flipping ratios was measured with polarized neutrons at 1.6K, with the spin density long range ordered by a 4.65 T applied magnetic field. An approach to solving the inverse Fourier problem is, to reconstruct a parametrized spin density based on axially symmetrical p orbitals (pz orbitals) centered on all the atoms of the molecule (wave function modeling). In the model which was actually used, the spin populations of corresponding atoms of A and B were constrained to be equal. The "averaged" populations thus refined are displayed in table II. Most of the spin density lies on the O1, N1 and N2 atoms. However, the agreement obtained between observed and calculated data (χ^2=2.1) indicates that this model is not completely satisfactory.

Table II: p-NPIN: spin populations in the wave function modeling

Site	Wave function modeling
O1	0.322(9)
N1	0.258(9)
C1	-0.042(7)
N2	0.193(7)

The spin density reconstructed from MaxEnt with a uniform prior, and projected on the plane of the molecule, is represented with its low contours and with its high contours, for molecules A and B in figure 6. The majority of the spin resides on the N1, N2 and O1 atoms, equally shared between those sites. On the N1 and O1 sites of both molecules the density is not centered on the nuclei but is slightly shifted away from the center of the N1-O1 bond. The effect is more pronounced on the N1 site. On the central C1 carbon atoms, the spin density is negative. Moreover it is off-centered, shifted in the N1-N2 direction.

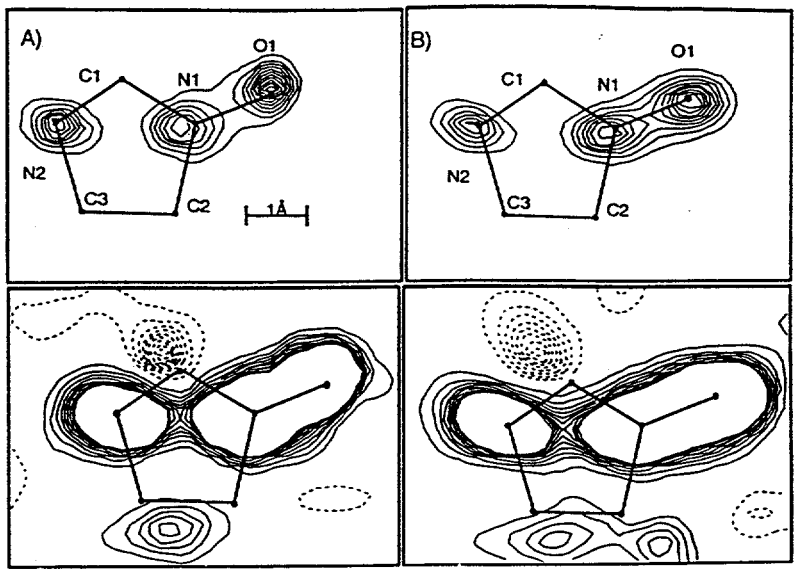

Fig 6: p-NPIN: MaxEnt reconstruction for molecules A and B with a flat prior

Are these off-centering real or due to an artefact of the reconstruction? The fact that they occur the same way on two unequivalent molecules is already an indication. The best way to completely answer the question is to reconstruct the spin density with a MaxEnt method and a non uniform prior, prior in which the density is centered on the nuclei. We have done this reconstruction, taking as a prior for the two molecules the "averaged" parametrized spin density refined above. The result is shown in figure 7. The off-centering of the N1-O1 density and of the negative C1 density is still there, even at the price of a lost of entropy, as it departs from the model.

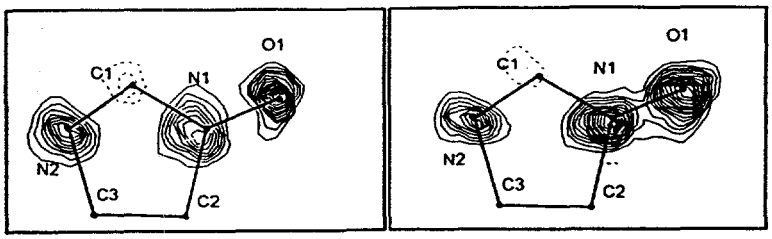

Fig 7: p-NPIN: MaxEnt reconstruction for molecules A and B with a non uniform prior

On the one hand, the antibonding character of the SOMO appears clearly on the N-O bond: the 2p orbitals are slightly bent and pushed away from the center of the bond. On the other hand the observed negative and off-centered density from the carbon nucleus is the result of a competition between spin polarization and spin delocalization. Both are of the same order of magnitude, the spin polarization being slightly larger, providing a negative density and a shift from the central position.

Through these examples we see that we have with the non uniform prior MaxEnt reconstruction, not only a method which takes advantage of all the knowledge to get the best possible map, but also a very powerful way to tell to what extend a proposed model is compatible with experimental data. Work at Brookhaven was carried out under contract No. DE-AC02-CH00016, Division of Materials Science, U.S. Department of Energy.

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