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Invited Review

Ab Initio Calculations Versus Polarized Neutron Diffraction for the Spin Density of Free Radicals

E. Ressouche* and **J. Schweizer**

CEA/Grenoble, DSM – DRFMC/SPSMS-MDN, 38054 Grenoble Cedex 9, France

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Summary. The determination of the magnetization distribution using polarized neutron diffraction has played a key role during the last twenty years in the field of molecular magnetism. This distribution can also be obtained by first principle *ab initio* calculations. Such calculations always rely on approximations and the question that arises is to know whether the obtained results are reliable enough to represent accurately the properties of these molecules. The comparison between polarized neutron experimental results and *ab initio* calculations has turned to provide stringent tests for these methods. In the present article a comparison between experimental and theoretical results is made and is illustrated by examples based on magnetic free radicals.

Keywords. Polarized neutron diffraction; Magnetization distribution; First principle *ab initio* calculations; *Hartree-Fock* approximation; Local density approximation; Magnetic molecular compounds; Free radicals.

Introduction

Molecular magnetism is a recently emerging field in science dealing with the conception, the design, the study, and the use of molecule based magnetic compounds with new but predictable properties. Such a class of compounds is supposed to fill a gap in the range of existing materials, and several new applications have already been invented. Due to the extraordinary flexible chemistry of organic and organometallic compounds, an infinite number of possibilities exists, and a goal for the future is to play with different molecules to finely tune the sought properties. But such a goal requires a perfect understanding of all the phenomena involved in these compounds.

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* Corresponding author. E-mail: ressouche@cea.fr

The molecular wave function is of fundamental importance, off course: if we were able to obtain an exact solution for the *Schrödinger* equation, then we would be able to predict any property for any system, and, as a result, experimentalists would loose their job. Unfortunately (not for experimentalists!), we are never able to obtain an exact solution, even in the simplest possible cases. In order to attempt a calculation of the wave function in a solid, some approximations must always be made. Once the idea to get an exact solution is abandoned, then the question to know whether the approximations made are valid or not remains. From an exact solution, any particular property could be predicted with confidence, but an approximate solution may predict the result of one type of experiment accurately whilst giving a widely incorrect result for another.

The charge density, as measured in an X-ray scattering experiment, or the spin density, as obtained from polarized neutron diffraction (PND) are two quantities closely related to the wave function. The charge density is the sum of the charge distribution of the two spin states $\rho^+(\mathrm{r})$ and $\rho^-(\mathrm{r})$, whereas the spin density simply corresponds to the difference between those two quantities. The charge density is nothing but the probability to find an electron in a volume element around one particular point, and is the integral of the squared wave function over all space coordinates. The spin density is just the probability to find an unpaired electron in the same volume. Techniques other than PND can be used as measures of spin densities, such as magnetization measurements, resonance technique (NMR, EPR or *Mössbauer* spectroscopy). But, with these techniques, the relationship between the quantities actually measured and the spin density is often indirect, or they represent only a small part of the information (e.g. density at the nuclei ...).

In this context, it is rather natural to use the comparison between the experimental densities maps obtained from X-ray or neutrons to first principle *ab initio* calculations as stringent tests for the validity of the approximations they imply. And because it involves only the highest lying molecular orbitals, the spin distribution, from the very first polarized neutron experiments performed on molecular systems, turned out to be much more a severe test than the charge density distribution, as we will see in the next sections.

Results and Discussion

UHF Versus Experiment on Isolated Molecules: A Failure of the Calculations

There are two main families of *ab initio* calculations. The first family, based on the *Hartree Fock* approximation, calculates the multicoordinate molecular wave functions, expressed as *Slater* determinants of single particle atomic wave functions. The Hamiltonian is a sum of single particle Hamiltonians including kinetic energy, *Coulomb* attraction by the nucleus and *Coulomb* repulsion by the other electrons. To express this last term, one assumes that the electrons are distributed over their wave function. This is in fact the main approximation. Such an assumption does not take into account the correlation between electrons, which results in an electron which does not stay unperturbed over his wave function when another one passes by. The calculation is processed self consistently. Each molecular wave function is occupied by two electrons, one with spin up (+) and one with spin down (−). The unpaired electron occupies the SOMO (Singly Occupied Molecular Orbital). In the Restricted *Hartree Fock* scheme (RHF), the orbital part of the wave functions of electrons of spin (+) and (−) are the same. Therefore, the spin density obtained by this method is automatically positive. As we will see, some regions of space may carry negative spin densities (spin polarization effect), and it is impossible for RHF methods to correctly account for this effect. Such methods are thus automatically discarded. In the Unrestricted *Hartree Fock* scheme (UHF), the spatial part of the wave functions of electrons of spin (+) and (−) may be different. The spin density thus obtained may be negative in some parts of the molecule.

To go beyond the *Hartree Fock* approximation, that is to take into account the correlation energy which exists between the electrons, one may admix excited states and optimize the mixing coefficients. The method is time consuming. According to the complexity of the development, one has the *Moller-Plesset* methods (MP2, MP3) [1] or the full Configuration Interaction (full CI) [2]. Another trick to reinject artificially the correlation term is the use of polarized basis sets. This approach consists in including in the calculations orbitals which are in principle empty, e.g. 2p/3d for an hydrogen or 3d/4f for an oxygen atom.

The first radical studied by polarized neutron diffraction was a nitroxide biradical, the tanol suberate [3], which was thought at the time to be the first ferromagnetic organic compound, with a very low T_C. Actually, this compound orders antiferromagnetically, but its behavior becomes ferromagnetic as soon as a small external field is applied [4]. The molecule consists in two rings $C_5H_5(CH_3)_4NO$, linked by a long chain $–OOC(CH_2)_6COO–$. Therefore, the two NO groups belonging to the same biradical are separated by more than 10 Å, and the shortest distance between two NO in the crystal is 6 Å. Each nitroxide group can therefore be considered as a well isolated radical. Polarized neutron experiments were made in the paramagnetic state at 4.2 K, with the magnetization aligned by an external magnetic field. The main results of these experiments were that the spin density in tanol suberate is mainly localized around the N and O atoms of the nitroxide groups, and that the spin is roughly equally shared by these two atoms [3]. This result strongly renewed the interest in the nature of the spin distribution in nitroxide free radicals. These radicals were extensively studied experimentally since they were synthesized, especially by ESR techniques, which give access to the spin density at nuclei positions. From the local values of the density at the nuclei semi-empirical relations exist that can be used to deduce more global information in terms of spin populations. However, such an estimation is indirect and rather ambiguous.

From the theoretical point of view, a large number of calculations on nitroxide free radicals were already performed, prior to the neutron results, by using semi empirical methods. Mainly because of computational problems (the reader should not forget that the laptop (s)he is using now everyday is a few order of magnitudes more powerful than computers at this time), *ab initio* calculations were only performed on the simplest H_2NO model. Elaborate computations using double perturbation theory and configuration interaction, leading to a good matching with ESR results, indicated a strong localization of the unpaired electron around the oxygen atom [5]. And this qualitatively well established result turned out to be in

Table 1. Theoretical *Mulliken* spin populations for the tanol suberate; (a) UHF calculations performed in Ref. [6]; (b) LSD calculations of Ref. [15], polarized basis set; (c) from Ref. [16]

Molecule	Atoms	UHF (a)	LSD (b)	SDCI/6-31G (c)	Iterative CI/6-31G (c)
H_2NO	N	0.22	0.44	0.31	0.37
	O	0.82	0.57	0.72	0.66
$(CH_3)_2NO$	N	0.35	0.47	0.34	0.43
	O	0.71	0.46	0.66	0.56
$(C_2H_5)_2NO$	N	0.37	–	–	–
	O	0.69	–	–	–

contradiction with the almost equidistribution between nitrogen and oxygen found with neutrons. As a result, new calculations were performed by *Gillon et al.* [6], in particular to see whether it was meaningful to compare H_2NO and the true molecule. In other words, the question was to know if the difference between theory and experiment was only due to substitution of H by larger alkyl groups or not. *Ab initio* UHF calculations were then performed on a series of radicals ranging from H_2NO to $C_5H_{10}NO$. Comparison of spin populations and spin density maps in the series showed a net spin migration from oxygen to nitrogen when H was replaced by larger groups (Table 1). The predominant effect was the substitution of the first two methyl groups adjacent to the nitrogen. However, the final result on the most substituted model was a distribution of 35 %/65 % on N and O, compared to 21 %/79 % for H_2NO and 50 %/50 % experimentally. This result was important, since it showed the influence of the substitution, and that H_2NO was not a reference model for the theoretical spin density in nitroxides as it was considered so far. But only 50 % of the difference between experiment in tanol suberate and calculations in H_2NO was explained. 50 % was still to be explained.

DFT Versus Experiment on Isolated Molecules: A Relevant Comparison

The second family of electronic calculations, called the Density Functional Theory (DFT), is based on the *Hohenberg-Kohn* theorem [7], which states that the energy of an ensemble of electrons is a functional of the charge density only and that the fundamental state is the state which minimizes this functional. The method calculates directly the electron density instead of the wave functions, which simplifies the problem very much. The functional contains a kinematic term, a *Coulomb* term and an exchange-correlation term. However, the analytical expression of this last term cannot be derived in the general case, and approximations have to be made. A first approximation is the Local Density Approximation (LDA), which assumes that the exchange-correlation term for electrons in a crystal has the same expression as for an homogeneous interacting electron gas [8]. This approximation has been extended to magnetic systems (Local Spin Density Approximation or LSD) [9, 10] by introducing a functional of two electronic densities $\rho^{+}(\mathrm{r})$ and $\rho^{-}(\mathrm{r})$, where the exchange-correlation term is the same as for an homogeneous interacting and partly polarized electron gas (*Vosko-Wilk-Nusair* functional [11]).

Other approaches have been proposed to go beyond this local approximation. One of them is the gradient method [12] (sometimes also referred to as nonlocal).

A parenthesis should be opened here, concerning the basis sets used by the different DFT programs. There are two main programs for performing such calculations: DGAUSS [13] and DMOL [14]. Whereas DGAUSS uses gaussian basis sets, DMOL can also use atomic-like basis sets. This difference is of some importance, and will be discussed further in the text.

At the beginning of the eighties, LSD calculations were mainly applied to solid state electronic structure calculations, and very few to molecular systems. *Delley et al.* performed exactly the same calculations than *Gillon et al.* on the series of molecules H_2NO to $C_5H_{10}NO$ [15]. In marked contrast to what was found with UHF, that is a strong spin localization around the oxygen atom, LSD calculations yield a one to one distribution between N/O for $C_5H_{10}NO$, as found experimentally (Table 1). Another important result of this paper was a simulation of an hydrogen bond as it occurs in another nitroxide free radical: crystalline tanol. Hydrogen bridges provide another mechanism to affect the spin balance between nitrogen and oxygen, resulting in an additional transfer from O to N. This was, thus, the first time that the active role of an hydrogen bond in propagating magnetic exchange interactions was evidenced.

This result had a very strong impact on the community of theoreticians performing *ab initio* calculations, provoking in particular skepticism for scientists using UHF methods. Following these two pioneering results, and owing to the increase of power of computers, such calculations were repeated, to confirm these results. *Wang et al.* studied the same series of radicals using iterative CI methods [16]. Calculations at different geometries with various basis sets were performed. They confirmed the substitution effect, leading to the conclusion that H_2NO was not a suitable theoretical prototype for nitroxide radicals, and they observed further shifts from oxygen to nitrogen due to inclusion of higher excitations into the CI expansion and the use of better (*i.e.* much larger) basis sets. Those calculations, however, were not able to reproduce the observed spin balance, leading to a 43 %/57 % distribution in the most favorable case. Roughly at the same time, the same kind of comparison between polarized neutron experiment and *ab initio* calculations was repeated for another nitroxide derivative: the tano [17]. The influence of the alkyl substitution was studied for a series of molecules starting from H_2NO in the experimental geometry of tano up to the complete (real) molecule using UHF methods [17, 18]. The influence of the basis set was also checked. Here again, the conclusions were still the same: UHF was not able to reproduce the experimental equidistribution observed in tano (Table 2 and Fig. 1), even using large basis sets and the true molecule (which means very long calculations). On the contrary, LSD calculations performed by the same authors turned out to be very stable, with roughly no influence of the basis set used, and were able to give, in one order of magnitude less computing time, much more reliable (*i.e.* closer to the experiment) results than very sophisticated UHF calculations using large polarized basis sets.

A few years later, the radical-based cyano-acceptor tetracyanoethylene $(TCNE)^{\bullet -}$ received considerable interest when the compound $[\mathrm{Fe}(\mathrm{C}_5Me_5)_2]^{\bullet +}(TCNE)^{\bullet -}$ was discovered to be a ferromagnet with $T_C = 4.8\,\mathrm{K}$ [19]. Another successful synthesis involving $(TCNE)^{\bullet -}$ was that of $\mathrm{V}(TCNE)_x{\bullet}y\mathrm{CH_2Cl_2}$ [20], which magnetically order

Table 2. Theoretical *Mulliken* spin populations for the tano [17, 18]; UHF calculations have been performed using the basis set of Ref. [6], LSD calculations according to [15]

Molecule	Atoms	UHF	LSD
H_2NO	N	0.24	–
	O	0.80	–
$(CH_3)_2NO$	N	0.38	–
	O	0.69	–
$(C_2H_5)_2NO$	N	0.41	–
	O	0.66	–
$(C_3H_7)_2NO$	N	0.43	–
	O	0.64	–
Tano: $C_9H_{16}NO_2$	N	0.42	0.48
	O	0.65	0.48

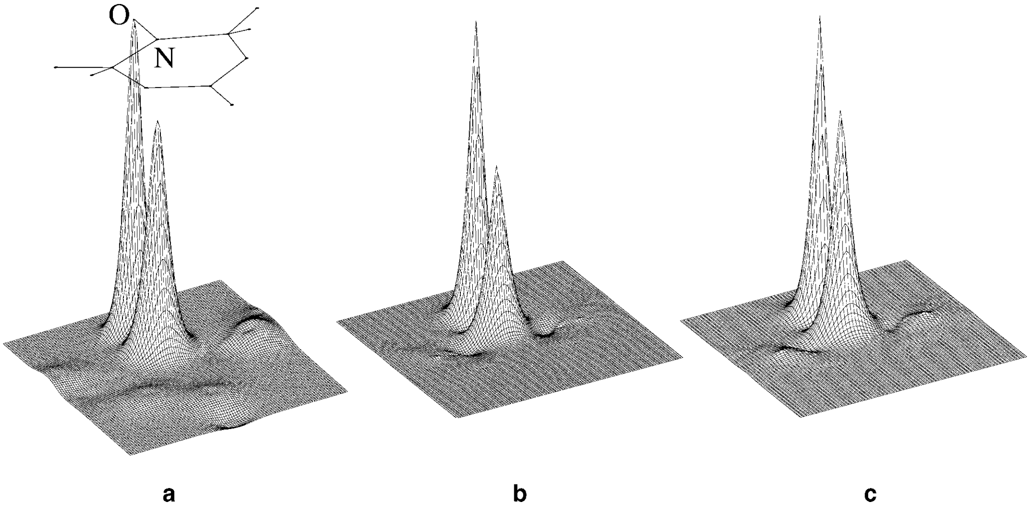

Fig. 1. Spin density projections along the π-direction for the free radical tano; (a) Experimental map; (b) UHF calculation, performed using the polarized basis set of Ref. [6]; (c) LSD calculation, using the polarized basis set described in Ref. [15]

above room temperature. The spin density in $(TCNE)^{\bullet -}$ has been determined with polarized neutrons, and compared with *ab initio* calculations (Table 3) [21]. The singly occupied orbital of $(TCNE)^{\bullet -}$ is the π^* antibonding molecular orbital consistent with molecular orbital predictions. The main part of the density is localized on the central sp^2 carbon atoms, but a combination of both the spin delocalization effect and the spin polarization effect yields a distribution of 33 %, -5 % and 13 % of the total spin on the sp^2 carbons, the sp carbons and nitrogen atoms, respectively (Fig. 2). In Table 3 are also presented the different results of *ab initio* calculations. As it can be clearly seen, none of the UHF methods is able to reproduce the experimental distribution, since these methods overestimate the negative contribution on the intermediate sp carbon atoms. On the contrary, LSD based methods predict with a rather good accuracy what has been found experimentally.

Table 3. Experimental and theoretical atomic spin populations for the radical $(TCNE)^{\bullet -}$; UHF calculations were performed using GAUSSIAN 92 [22], DFT calculations using DGAUSS [13]

Atoms	UHF 3-21G	MP2 3-21G	UHF 6-311G*	LDFT TZVP	NLDFT TZVP	Experiment
C_1 (sp^2)	0.51	0.52	0.48	0.28	0.30	0.33
C_2 (sp^2)	0.56	0.55	0.50	0.28	0.29	0.33
C_3 (sp)	− 0.50	− 0.62	− 0.40	− 0.02	− 0.04	− 0.05
C_4 (sp)	− 0.70	− 0.67	− 0.60	− 0.03	− 0.05	− 0.04
C_5 (sp)	− 0.55	− 0.53	− 0.46	− 0.03	− 0.04	− 0.03
C_6 (sp)	− 0.61	− 0.63	− 0.54	− 0.03	− 0.05	− 0.08
N_3	0.49	0.50	0.42	0.13	0.14	0.12
N_4	0.69	0.70	0.60	0.15	0.16	0.12
N_5	0.53	0.52	0.44	0.14	0.14	0.13
N_6	0.60	0.51	0.53	0.13	0.15	0.16

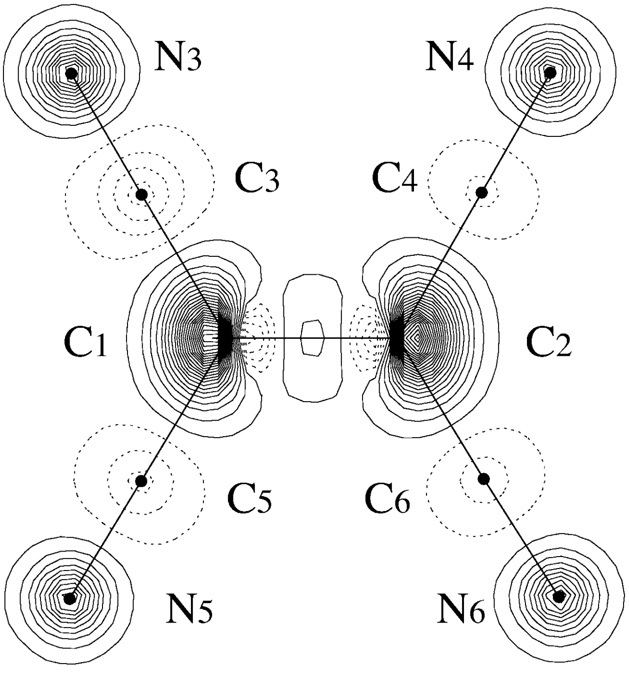

Fig. 2. Experimental spin density in the tetracyanoethylene $(TCNE)^{\bullet -}$ anion-radical, determined by PND

Another very important result on the ability of these two kinds of methods to account for the spin polarization effect was met during the experimental study of the phenyl nitronyl nitroxide by *Zheludev et al.* [23]. In recent years, nitronyl nitroxide free radicals have played a key role in the engineering of molecule-based magnetic materials: they are stable, capable of being handled under ordinary conditions, and they carry a spin $1/2$. The phenyl derivative (*NitPh*) crystallizes in the monoclinic space group $P2_1/c$ with two molecules per asymmetric unit, and remains paramagnetic down to very low temperature, with very little interactions between neighboring molecules. It was, thus, a good example of a well isolated member of the nitronyl nitroxide family. Polarized neutron experiments were performed on this compound in the paramagnetic state, with the magnetization aligned by an external magnetic field. The experimental spin density map is represented in Fig. 3 as a projection onto the O–N–C–N–O plane. As expected from simple molecular orbital arguments, the unpaired electron occupies a π^* antibonding molecular

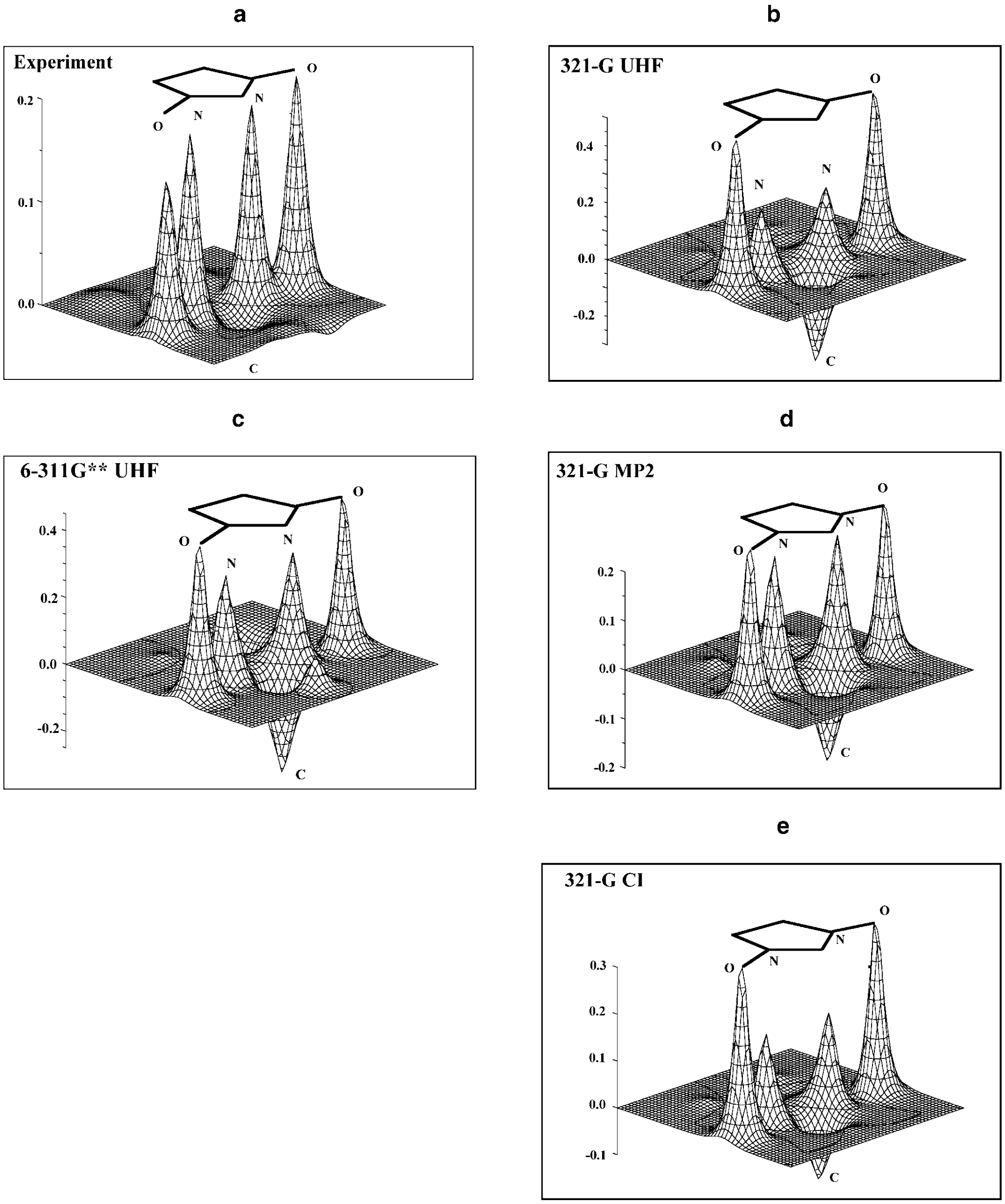

Fig. 3. Spin density projections along the π-direction for the phenyl nitronyl nitroxide free radical; (a) Experimental map; (b) UHF calculation using the small 3-21G basis set; (c) UHF calculation using the large 6-311G** basis set; (d) MP2 calculation in 3-21G; (e) Full CI in 3-21G

orbital mainly built from the $2p_z$ atomic orbitals of the two oxygen and the two nitrogen atoms. The spin density is equally shared between these four atoms. The fraction of spin delocalized on the rest of the molecule is rather small. One particular feature deserves a special attention: there is a large negative contribution (roughly $1/3$ of the other contributions) on the sp^2 bridging carbon atom. Such an effect, or spin polarization effect, is conveniently explained in terms of a triplet HOMO–LUMO excitation induced by the unpaired spin of the SOMO. These frontier orbitals have a large contribution from the atomic orbital $2p_z$ on this carbon, which becomes polarized. The resulting density is negative, as pointed out by *Anderson* [24], since the positive spins on the frontier molecular orbitals are attracted by the positive spin on the SOMO, leaving behind the negative spins on the node of the SOMO, that is on the carbon site. The sign alternating spin densities found on the carbon atoms of the phenyl ring are also manifestations of this spin polarization effect.

A comparison between these experimental results and the spin densities calculated by the different *ab initio* methods has been made in Ref. [23]. The theoretical spin populations on the oxygen, nitrogen and central carbon are reported in Table 4, together with the experimental values averaged and normalized to $1\mu_B/NitPh$ molecule. We report here UHF results with two basis sets: the rather small 3–21G and the huge polarized 6–311G**, the results of the MP2 method and the full CI. The resulting theoretical spin density maps from UHF methods are also presented in Fig. 3, where they are compared with the experimental map. Due to the large computing time, those UHF calculations have been done for an optimized, planar and truncated molecule, where the phenyl and methyl groups were replaced by hydrogen atoms. As it is clear from the maps and from Table 4, all these methods overestimate considerably the spin polarization effect, that is the negative spin density on the central carbon. Another discrepancy, for all but MP2, is the ratio O/N. Surprisingly, full CI, which in principle is more elaborate than MP2, is farther from reality. We can then conclude that the methods based on *Hartree Fock* approximation not only are unable to account correctly for the spin density in nitronyl nitroxides, but also that they are unstable: the results depend very much on which method is used and which basis set has been taken for the calculation. Such a conclusion could also be drawn from the studies on simple nitroxides and on the $(TCNE)^{\bullet -}$ anion radical previously described.

In Table 4 are also displayed the results obtained by the LSD family calculations: at the local approximation level (VWN functional), with DZVP (double zeta) and TZVP (triple zeta) basis sets, and at the non local level referred as B88VWN. Those calculations were performed on the real molecule, in its experimental

Table 4. Experimental and theoretical atomic spin populations for the ONCNO fragment of *NitPh*; DFT calculations were performed using (a) the DGAUSS [13] and (b) the DMOL [14] programs

Atoms	UHF 3-21G	UHF 6-311G**	MP2 3-21G	CI 3-21G	VWN$^{(a)}$ DZVP	VWN$^{(a)}$ TZVP	VWN$^{(b)}$ DNPP	B88VWN$^{(b)}$ DNPP	Experiment
O	0.50	0.40	0.32	0.39	0.32	0.30	0.29	0.29	0.27
N	0.27	0.36	0.34	0.23	0.21	0.22	0.20	0.21	0.27
C(sp^2)	– 0.55	– 0.52	– 0.31	– 0.24	– 0.08	– 0.07	– 0.02	– 0.04	– 0.11

Table 5. Theoretical atomic spin populations calculated by DGAUSS (TZVP) for one of the two *NitPh* molecules and compared to experimental PND populations

Atoms	Experiment	DGAUSS (TZVP)
O_4	0.277 (13)	0.319
N_4	0.278 (15)	0.238
C_{20}	– 0.121 (17)	– 0.065
N_3	0.278 (16)	0.210
O_3	0.247 (13)	0.288
C_{14}	0.024 (16)	0.004
C_{15}	0.000 (13)	– 0.009
C_{16}	0.025 (13)	0.002
C_{17}	– 0.016 (12)	– 0.009
C_{18}	0.011 (12)	0.002
C_{19}	– 0.037 (13)	– 0.009
C_{21}	– 0.025 (16)	– 0.004
C_{22}	0.009 (13)	– 0.005
C_{23}	0.055 (12)	0.021
C_{24}	0.009 (13)	0.000
C_{25}	– 0.008 (12)	0.001
C_{26}	– 0.005 (13)	0.023

geometry. Two points must be emphasized: on the one hand these calculations are stable: changing approximation or basis set changes very little the calculated spin populations. On the other hand, even if the observed ratio O/N is not exactly reproduced, the theoretical results are not very far from the experimental ones.

As the DFT calculations have been made on the complete *NitPh* molecule, we can look at the amount of spin which is localized on the ONCNO fragment. PND has found 0.97 for the first molecule and 0.96 for the second one. The DFT predictions vary a little (Table 4): 0.98 and 0.97 with the program DGAUSS and the basis set DZVP and TZVP, respectively, and 0.96 with the program DMOL.

Table 5 compares more closely the spin density found by DGAUSS to the experimental one for one of the two molecules (Fig. 4). On the phenyl rings, DGAUSS reproduces very well the spin alternation which has been found experimentally, but it reduces the values of the positive and negative spin populations. If one compares the sum of the absolute values of the populations on the carbon atoms, DGAUSS puts forward 0.035 while it was found experimentally 0.113. It is the same for the sum of the absolute values on the $C(CH_3)_2$ groups: 0.054 for DFT and 0.112 found experimentally.

To conclude this paragraph, we can say that DFT methods account rather well for the spin densities of the central part of the free radical, but we can already anticipate that there will be problems to predict the delocalized part of the spin density.

DFT Versus Experiment on Interacting Molecules: A Difficult Challenge

When molecules are interacting, the pathways of the exchange interactions imply, most of the times, atoms which do not belong to the localized part of the spin

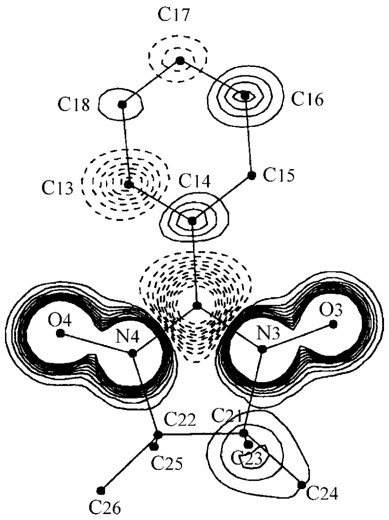

Fig. 4. Experimental spin density (low contours) of one of the two *NitPh* molecules of the asymmetric unit, determined by PND

density distribution. These trails are generally revealed in PND experiments by a wake of spin density on the concerned atoms. As first principle calculations are not so reliable to account for the delocalized spin distribution, we can expect that DFT will have some difficulties in visualizing such effects.

The effects of an hydrogen bond mediating the magnetic exchange interactions on the spin density have been evidenced in the *NitPy* radical (6-HC$\equiv$C*Py*NN). In this compound the molecules form ferromagnetic chains, the pyridine of one molecule being connected to the oxygen of the next molecule by a weak $C\equiv C{-}H\cdots O$ hydrogen bond. The spin density determined by PND [25] is represented in Fig. 5 and the corresponding spin populations are reported in Table 6 and Table 7. Several points deserve attention in this distribution:

- on the one hand, the part of the spin population localized on the ONCNO fragment is 0.877 only, compared to 0.971 and 0.959 for the two "isolated" molecules of the *NitPh* radical. This reflects that in *NitPy* the exchange interactions between molecules imply a delocalization of the spin.
- the spin population on oxygen O_1, the oxygen atom which participates to the hydrogen bond, is depleted compared to that of O_2, the other oxygen atom of the group ONCNO.
- carbon C_6 and hydrogen H_{16}, on the $C\equiv C{-}H\cdots O$ hydrogen bond, carry a substantial spin population: 0.030 and 0.045.

DFT calculations are presented in Tables 6 and 7. For an isolated molecule (Table 6), two calculations have been performed with the program DGAUSS with different basis sets, and one with DMOL. Molecules interacting in the crystal have been studied with DMOL [26]. As expected, the main features of the spin distribution on the central fragment ONCNO, particularly the negative value on the

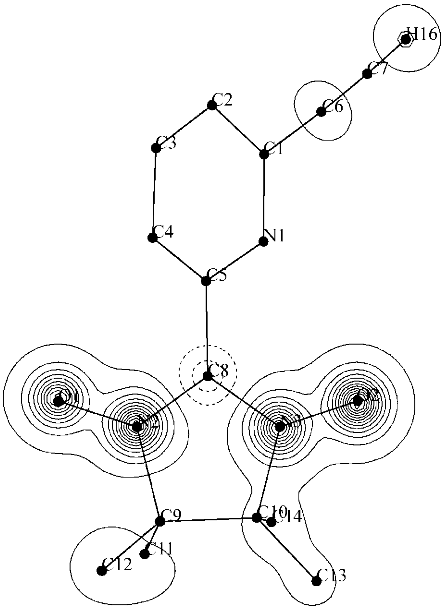

Fig. 5. Experimental spin density of the *NitPy* radical, determined by PND

Table 6. Theoretical atomic spin populations calculated by DGAUSS (DZVP), DGAUSS (TZVP) and DMOL for one isolated molecule of the *NitPy* radical and compared to experimental PND populations

Atoms	Experiment	Isolated molecule DGAUSS (DZVP)	Isolated molecule DGAUSS (TZVP)	Isolated molecule DMOL
O_1	0.203 (10)	0.292	0.270	0.274
N_2	0.242 (12)	0.208	0.212	0.187
C_8	– 0.071 (11)	– 0.069	– 0.086	– 0.076
N_3	0.225 (12)	0.217	0.230	0.198
O_2	0.278 (7)	0.335	0.312	0.312
Sum ONCNO	0.877 (24)	0.983	0.938	0.895
H_{16}	0.045 (10)	0.000	0.000	0.000

Table 7. Theoretical atomic spin populations calculated by DGAUSS (DZVP), DGAUSS (TZVP) and DMOL for interacting *NitPy* molecules and compared to experimental PND populations

Atoms	Experiment	Two interacting molecules DGAUSS (DZVP)	Two interacting molecules DGAUSS (TZVP)	Crystal DMOL
O_1	0.203 (10)	0.273	0.243	0.239
N_2	0.242 (12)	0.216	0.224	0.188
C_8	– 0.071 (11)	– 0.066	– 0.084	– 0.075
N_3	0.225 (12)	0.216	0.230	0.212
O_2	0.278 (7)	0.341	0.318	0.299
Sum ONCNO	0.877 (24)	0.980	0.931	0.863
H_{16}	0.045 (10)	0.001	0.002	0.004

central carbon, are encountered. However, if we refer to the points underlined above:

- the total amount of spin population localized on the central fragment is not stable: DMOL and DGAUSS programs do not give the same localized/delocalized partition of the spin density. For the isolated molecule, this part varies from 0.983 for DGAUSS (DZVP) to 0.938 for DGAUSS (TZVP) and 0.895 for DMOL. Compared to experiment, DGAUSS localizes too much. Program DMOL has the possibility to make also spin density calculations when the molecule is inserted in the crystal. With the same computational conditions, this sum decreases only from 0.895 for the isolated molecule to 0.863 for the molecules interacting in the crystal.
- the effect of the hydrogen bond has been looked at with DGAUSS by calculations on two interacting molecules, having the geometry of the crystal, and with DMOL on the whole crystal. The results are reported in Table 7. As expected, the spin population on O_1, the oxygen atom connected to the hydrogen bond, decreases, compared to isolated molecules, for molecules in interaction. This reduction is 0.019 for DGAUSS (DZVP), 0.027 for DGAUSS (TZVP) and 0.035 for DMOL. However, even in the isolated molecule, the spin population is smaller on O_1 than on O_2, the atom which does not participate to the bond. It has been shown that this difference in the isolated molecule comes from the presence of the nitrogen atom which dissymetrizes the piperidine ring [27].
- the spin population on H_{16} was zero for all calculations of the isolated molecules. For molecules in interaction DFT found some spin density on the hydrogen atom of the bond: 0.001 for DGAUSS (DZVP), 0.002 for DGAUSS (TZVP), and 0.004 for DMOL in the crystal. These values are one order of magnitude less than that observed with the neutrons (0.045). However, all these calculations underline the pathway of the magnetic exchange interactions which goes through the hydrogen bond. DFT sees the magnetic interactions but underevaluates their influence on the spin density and, as expected, DGAUSS produces effects which are weaker than DMOL.

Another example of perturbation of the spin density due to magnetic exchange interaction and revealed by PND in nitronyl nitroxide free radicals has been encountered in *Nit*(S*Me*)*Ph*. This compound is also ferromagnetic ($T_C = 0.2\,\mathrm{K}$) and the packing of molecules in the crystal reveals a weak intermolecular contact (3.72 Å) between oxygen O_2 of the nitronyl nitroxide and carbon C_{14} of the methylthio group of the next molecule. The experimental spin density is reported in Table 8 and displayed in Fig. 6. The striking point in this figure is the presence of some spin density on the atom C_{14}, which supports the existence of a magnetic pathway along the molecule and through the C_{14}–O_2 contact [28].

The spin density has been calculated by the DGAUSS program, with a DZVP basis set for an isolated molecule and for two molecules in interaction, with a geometry corresponding to the crystal packing [26, 27]. The results of this calculation are also presented in Table 8. As expected, the localization of the spin density on ONCNO is much too strong. Nevertheless, for the bond DGAUSS finds a depletion of spin density on the oxygen atom concerned by the contact, but this depletion has not been detected by the neutrons. Furthermore, on C_{14} the magnetic

Table 8. Theoretical atomic spin populations calculated by DGAUSS (DZVP) for one isolated *Nit*(S*Me*)*Ph* molecule and for two interacting molecules, compared to experimental PND populations

Atoms	Experiment	One isolated molecule DGAUSS (DZVP)	Two molecules DGAUSS (DZVP)
O_1	0.226 (7)	0.304	0.307
N_1	0.272 (9)	0.221	0.221
C_1	– 0.099 (8)	– 0.063	– 0.063
N_2	0.247 (9)	0.225	0.229
O_2	0.226 (8)	0.308	0.298
Sum ONCNO	0.872 (18)	0.995	0.992
C_{14}	0.031 (7)	0.000	0.001

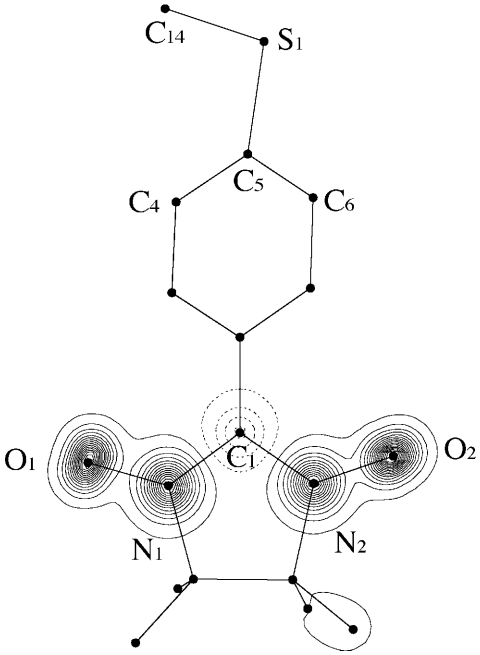

Fig. 6. Experimental spin density of the *Nit*(S*Me*)*Ph* radical, determined by PND

exchange interaction induces some spin density, only 0.001 according to DFT, when 0.031 were found by PND. Here again, *ab initio* calculations see qualitative effects, but quantitatively, these effects are much too small compared with the experimental ones.

Comparative DFT Calculations: A Possible Way to Trace the Magnetic Interactions

DFT calculations are reliable to describe the main part of the spin density in free radicals, but underestimate enormously the effects of small perturbations. However, it is possible to use such calculations in a comparative way. Having in parallel, with the same program and the same basis set, two computations differing

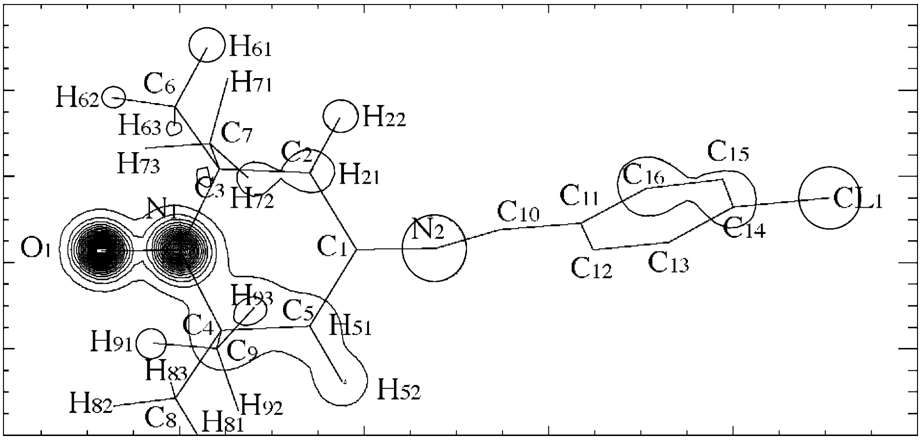

Fig. 7. Experimental spin density of the Cl-*TEMPO* radical, determined by PND

Table 9. Theoretical atomic spin populations calculated by DGAUSS for one isolated Cl-*TEMPO* molecule and for two interacting molecules, compared to experimental PND populations

Atoms	Experiment	One isolated molecule	Two interacting molecules	
			molecule 5	molecule 1
O_1	0.401 (14)	0.490	0.477	0.489
N_1	0.393 (19)	0.444	0.451	0.445
Sum NO	0.794 (24)	0.934	0.928	0.934
C_2	0.006 (16)	0.007	0.006	0.011
H_{22}	− 0.032 (13)	0.000	0.000	0.000
C_6	− 0.055 (16)	0.003	0.004	0.004
H_{61}	0.038 (12)	− 0.001	− 0.001	− 0.002

only by one given perturbation, it is possible to obtain not quantitative results, but, at least, a qualitative information concerning this perturbation.

The search of the magnetic pathways in the ferromagnetic ($T_C = 0.28$ K) compound Cl–*TEMPO* is an illustration of this approach [29]. The spin density, as determined by PND is represented in Fig. 7. Almost 80% of the spin is localized on the NO group, the rest being diluted on different atoms of the other parts of the molecule (Table 9). In particular, the presence of a significant spin density on H_{22} (− 0.032) and on H_{61} (0.038) suggests that along the *c* axis of the monoclinic cell (Fig. 8) the contacts between adjacent molecules (2.73 Å for O_1–H_{22} and 2.37 Å for O_1–H_{61}) propagate the ferromagnetic interaction.

This hypothesis has been put to the test by comparing DFT spin densities on one isolated molecule and on two interacting molecules: molecule 1 and molecule 5, in the geometry of the crystal packing. The spin populations, obtained with the DGAUSS program, are reported in Table 9. As expected, the localization obtained by DGAUSS on the NO group is much too strong. However, when molecule 5 interacts with molecule 1 through the two contacts explicited above, on the one hand, on molecule 5, this concentration of spin on the oxygen atom of the NO

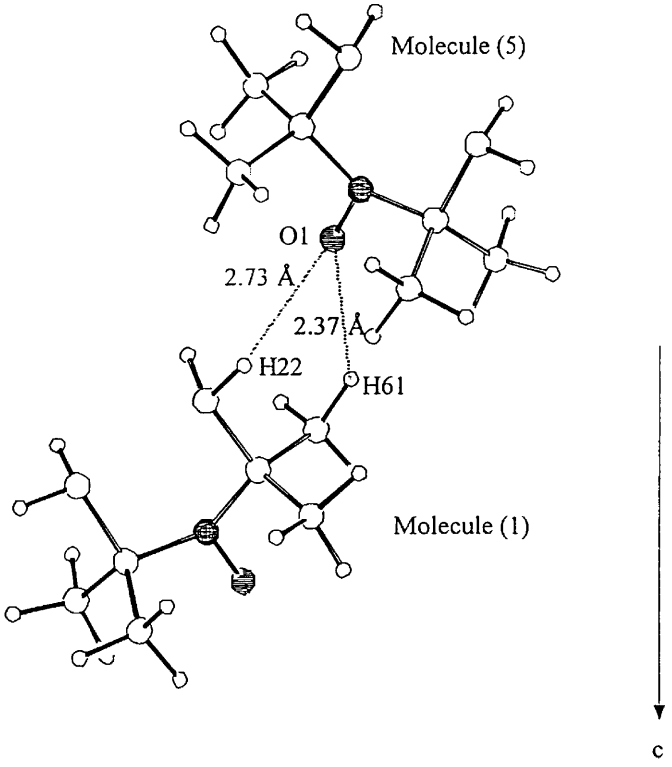

Fig. 8. Hydrogen bonds contacts between two molecules of Cl-*TEMPO*

group is reduced, and the balance between oxygen and nitrogen is modified in favour of nitrogen. On the other hand, on molecule 1, the spin density on the methylene atom H_{22} has not been modified, but the carbon atom C_2, which is attached to it, has now a spin population which is increased by 0.004. Furthermore, the negative spin on the methyl atom H_{61} changes from -0.001 to -0.002. From this comparison, we cannot conclude anything about the strength of the exchange interactions, but we can confirm that magnetic interactions propagate through such contacts.

Another example concerns the hydrogen bonds in the *PNNB* complex [30]. This complex consists of chains where *NitPh* radicals alternate with phenylboronic acid $B(OH)_2$*Ph* molecules. Along these chains, the ONCNO groups of the *NitPh* are connected together via the HOBOH atoms of the phenylboronic acid through hydrogen bonds NO $\cdots$ HOB. At room temperature the structure is monoclinic, but on cooling, due to the ordering of the methyl groups, the symmetry is reduced and the structure becomes triclinic. Therefore, at low temperature, there exist two crystallographically non equivalent *NitPh* molecules. The hydrogen bond distances, which were almost equivalent at room temperature, are now quite different: 1.96, 1.84, 1.96, and 1.91 Å for $H_{24} \cdots O_2$, $H_3 \cdots O_1$, $H_4 \cdots O_{21}$ and $H_{23} \cdots O_{22}$, respectively, each *NitPh* molecule being connected to two phenylboronic acids through a long and a short hydrogen bond. The spin density, determined by PND at low temperature, shows for each of the two *NitPh* radicals a strong asymmetry between the two NO groups, as shown in Fig. 9. For the two molecules the

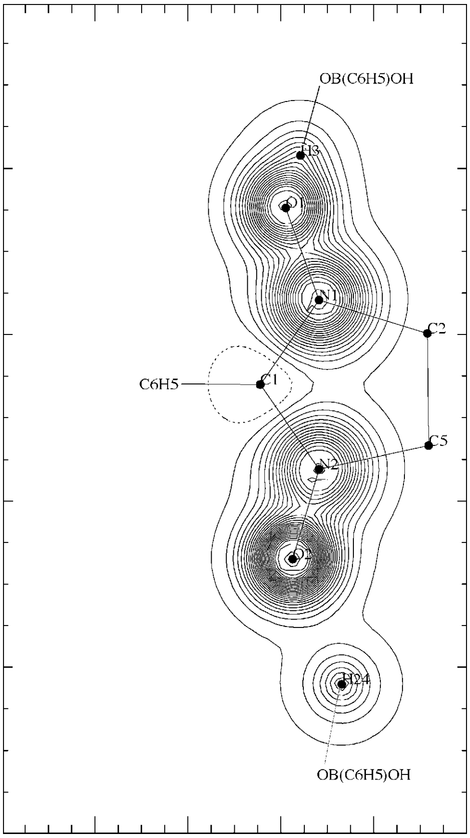

Fig. 9. Experimental spin density of the *PNNB* complex, determined by PND

Table 10. Theoretical atomic spin populations calculated by DGAUSS for one isolated *NitPh* molecule and for one *NitPh* radical connected to two phenylboronic acids, compared to experimental PND populations

Atoms	Experiment	Isolated *NitPh*	Connected molecules
H_3	0.024 (36)	0.000	− 0.001
O_1	0.227 (25)	0.290	0.253
N_1	0.307 (25)	0.220	0.233
C_1	− 0.025 (20)	− 0.089	− 0.101
N_2	0.246 (25)	0.224	0.252
O_2	0.328 (25)	0.285	0.268
H_{24}	0.056 (25)	0.000	0.002

spin density on oxygen is the weaker for the shorter length of the hydrogen bond, which is in accordance with former results.

To confirm this view, a DFT calculation (DGAUSS) was carried out for the geometry of one of the two *NitPh* molecules, first isolated and then surrounded by the two phenylboronic acids. The results are presented in Table 10. A bond distance of 1.96 Å ($H_{24} \cdots O_2$) induces a depletion of the spin population of 0.017 on the oxygen atom, while a bond distance of 1.84 Å ($H_3 \cdots O_1$) induces a depletion of 0.037. The shorter the distance is, the stronger the oxygen depletion is; the effect of the hydrogen bond length is firmly established by this comparative calculation.

Conclusions

The comparison of first principle predictions with the results of polarized neutron diffraction, experiments which measure the spin density everywhere in the molecules, has been and still is a very selective test to judge which approximation and which method is most reliable to account for spin densities in free radicals.

If it was obvious, as soon as negative spin densities appeared in some parts of the experimental distributions, that RHF was unable to yield a complete view of such maps, it took more time to convince people that UHF methods must be discarded as they are unstable and unable to account for the reality of the spin density.

Now, the superiority of DFT calculations to describe the spin density in free radicals is clear. On the one hand they are stable: calculations made with different programs give roughly the same results. On the other hand, they compare rather well with the spin densities measured by PND, at least for the parts of the molecules where the main part of the density is localized. For the delocalized part of the molecules for which the comparison with experiment is poor, DFT calculations produce results which depend on program and basis set. DGAUSS, with its gaussian basis sets, emphazises the localized part of the spin density much more than DMOL with an atomic like basis set. Both programs reduce enormously the influence on the spin density of the magnetic interactions between adjacent molecules, but DGAUSS does it more than DMOL. Nevertheless these programs may be useful in the investigation of magnetic exchange interactions, as long as one considers their predictions as qualitative and not quantitative.

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