Density Functional Response Theory with Applications to Electron and Nuclear Magnetic Resonance

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Abstract

This thesis presents quantum chemical calculations, applications of the response function formalism recently implemented within the framework of density functional theory by our research group. The purpose of the calculations is to assess the performance of this perturbative approach to determining heavy atom effects on magnetic resonance parameters. Relativistic corrections can be generated by spin-orbit interactions or by scalar relativistic effects due to high velocity electrons in the atomic core region of heavy atoms. In this work, the evaluation of nuclear magnetic resonance parameters is considered, the nuclear shielding tensor and the indirect nuclear spin-spin coupling tensor. For series of homologous compounds, it is found that both types of corrections to these parameters are increasing in size upon substitution of a constituent atom by a heavier element, but that their relative importance is system dependent. The obtained results are compatible with the ones provided by electron correlated ab initio methods, and a qualitative agreement with experimentally determined parameters is overall achieved. The methodology presented in this thesis aims to be a practical approach which can be applied in the study of molecular properties of large systems.

This thesis also addresses the calculation of hyperfine coupling constants, and evaluates a novel approach to the treatment of spin-polarization in spin restricted calculations without the spin contamination associated with spin unrestricted calculations.
List of publications


My contribution

- I performed all calculations in papers I, II, and IV.
- I performed a part of calculations in papers III, V, and VI.
- I participated in the code implementation in paper V.
- I participated in the analysis of results and preparation of manuscript for all papers.
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Chapter 1

Introduction

A wide range of complex biochemical processes including metabolism, enzymatic catalysis, electron transport, photosynthesis, and bioelectrocatalysis, are guided by the physical and chemical properties of participant molecular compounds as derived from their electronic structure. A thorough investigation of the electronic structure may be carried out by means of different spectroscopic techniques. The spectroscopic analysis allows one to establish relationships between structure and spectral features of well-defined chemical systems, and to transfer these results to the characterization of complicated natural systems. In most cases a single technique alone is not enough to obtain all necessary information and one has to combine and analyse results from several techniques. In this thesis are presented studies employing electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) spectroscopies.

Techniques pertaining to EPR spectroscopy are widely utilized in chemistry, biomedical research, and solid state physics. In the former it deals with open-shell molecules, which include transition metal complexes and organic radicals among other compounds. In addition to the capability of paramagnetic molecules to participate in various chemical processes, their unpaired electron spins confer the possibility of controlling the process by means of an applied magnetic field [1]. Also, special magnetic properties turn open-shell compounds into candidates as building blocks of molecular magnets [2, 3, 4]. EPR can provide fairly detailed chemical and structural information about trapping centers for charge carriers, and the densities of paramagnetic centers [5]. All these are reasons for an extensive use of EPR spectroscopy in investigations of paramagnetic compounds in biochemistry and materials science, as it provides insights on electronic structure, interaction of unpaired electrons, and electron density distribution in molecules [6, 7].

The behavior of nuclear spin in the case of nuclei possessing magnetic properties is studied with the help of NMR spectroscopy. A successful application of this method is the determination of geometrical structure of biomolecules by analysis of dipolar shifts [8]. However, the analysis of experimental results is difficult to accomplish in most cases where EPR and NMR spectra have very
CHAPTER 1. INTRODUCTION

complicated structure. The evaluation of magnetic resonance parameters by quantum chemistry methods offers the possibility to reliably connect the EPR and NMR spectra to the geometrical and electronic molecular structure, with the help of spectral parameters [9]. The combined development of theoretical methods and experimental technology for high resolution EPR and NMR leads to an increasing importance of this research area.

Past decades have witnessed important steps in the development of methods to provide accurate wave function and accurate molecular properties. The treatment of heavy element compounds or compounds with large number of atoms is often hampered by the present computing capabilities. Density functional-based methods offer the possibility to explore sensibly larger systems than it was previously possible at Hartree-Fock (HF) or semiempirical levels, and with a substantially increased accuracy. A large variety of exchange-correlation functionals to be combined with proper basis sets allows one to perform calculations of magnetic properties of high quality at low cost. This advantage of density functional theory (DFT) comes particularly at hand for systems containing large mass atoms that experience important relativistic effects [10], where the treatment of these effects requires more computationally demanding algorithms. A way to approach this problem is to introduce physically justified approximations to the full treatment. Already existing implementations of density functional response theory (DFRT) are capable to handle within a single formalism general perturbations and a wide range of molecular properties of closed shell systems. Part of the work presented in this thesis contributes to this area of quantum chemistry and consists of development, implementation and applications of DFRT methods for calculation of NMR parameters including heavy atom effects up to third order in the perturbation theory sense. A spin-restricted DFRT formalism capable of computing arbitrary quadratic response functions in molecules with a high spin ground state was developed and applied in the evaluation of relativistic effects on electronic $g$-tensors. The challenge in the development of DFRT of unpaired electron molecules came from the complex nature of their electronic structure, the description of molecular properties requiring an account of e.g. single and double excitations mixing, spin-flip excitations, absent in the closed shell case.

The spin polarization takes into account the fact that the unpaired electron interacts differently with the two electrons of a spin-paired bond or inner shell, since the exchange interaction is operative only for the electrons with parallel spins. The evaluation of EPR parameters is generally burdened by the poor description of spin polarization in open-shell molecules, which is over-estimated by spin-unrestricted methods and neglected by spin-restricted methods. We seek to address this issue by employing a version of the so-called restricted-unrestricted (RU) approach [11], which relies on a restricted wave function treatment of the unperturbed molecular system and a spin-relaxed wave function in the presence of specific magnetic interactions. The thesis contains a gen-
eralization of the implementation of RU method at DFT level of theory [12] which accounts for the full unrestricted response of the system to hyperfine perturbations.

A topic of increasing interest in bio-sciences is the investigation of transition metal centers in proteins. The blue copper site in mononuclear copper proteins (plastocyanins, azurins, stellacyanin, etc.) plays an important role in inter-protein electron transfer. DFT is the proper tool to use in the prediction of accurate results for relatively large models of transition metal centers, our study of EPR parameters aiming to clear aspects such as oxidation state of the metal center, the geometry of its coordination sphere and the type of ligand atoms involved in metal bonding. In summary, the thesis presents applications of recently developed and implemented DFRT methods for evaluation of spin Hamiltonian parameters in closed shell and paramagnetic molecules, with an extention to EPR parameters of biological relevant molecular systems.
Chapter 2

Magnetic Resonance Spectroscopy

In magnetic resonance spectroscopy transitions between states are studied that result from magnetic interactions in molecules. The data this method provides may be used in describing physical and chemical properties of molecules [13, 14, 15, 16, 17]. A simple picture of a magnetic resonance experiment consists of the splitting of molecular energy spin levels due to magnetic interactions, followed by transitions between these levels induced by a resonant electromagnetic field. The sources of the interacting magnetic fields can be electronic spins, nuclear magnetic momenta or an applied magnetic field, and relative to them one defines the magnetic resonance spectroscopies and parameters. The transitions can be observed either for electrons (electron spin resonance, ESR) or nuclei (nuclear magnetic resonance, NMR), with transition frequencies of the order of GHz and MHz, respectively.

The spectral lines are to be assigned to molecular spin levels employing the spin Hamiltonian approach. With this approach, the molecular interactions are correlated to the experimental measurements through a set of phenomenological parameters relevant for the system investigated. In the case of molecules with non-zero electronic spin the parameters of ESR may describe the coupling of unpaired electronic spins to each other, their coupling to an external magnetic field, or to nuclear magnetic momenta. The technique is also known in the literature as electron paramagnetic resonance (EPR) spectroscopy. Nuclear magnetic resonance (NMR) spectroscopy applies to molecules possessing non-zero nuclear spins. Its parameters describe the coupling of nuclear spins to each other, either directly as nuclear magnetic dipoles or indirectly via interactions with system’s electrons, or the coupling of nuclear spins to an external magnetic field.

The experimental data obtained in magnetic resonance spectroscopy contains information on the observed transition energies, transition intensities, line shapes and widths, information which carries insights on the physical properties of the studied systems. However, it is difficult to extract molecular structural details because of the complex nature of the relationships between magnetic momenta and the molecular environment. One approach to obtain struc-
tural information from magnetic resonance spectra, is to evaluate spin Hamiltonian parameters of the initial molecular structure by accurate quantum chemistry methods, and match them with the ones obtained from fitting of experimental data. This approach allows one to obtain reliable relationships between the spin Hamiltonian parameters and the molecular structure in a self-consistent manner by varying the molecular structure used in the theoretical evaluation of spin Hamiltonian parameters [9].

2.1 The EPR spin Hamiltonian

The EPR spin Hamiltonian defines a Hermitian operator containing only effective spin operators and parameters quantifying the magnetic interactions. This type of operator facilitates the computation of molecular properties from energy expressions containing products of electronic or nuclear spin operators. Terms that contribute to the splitting of energy spin levels are gathered in the following form of the EPR spin Hamiltonian

$$\hat{H}_{\text{ESR}} = \mu_B S^T \cdot g \cdot B + \sum_N S^T \cdot A_N \cdot I_N + S^T \cdot D \cdot S$$

(2.1)

where $S$ is the effective electronic spin operator, $\mu_B$ is the Bohr magneton, $B$ is the applied homogeneous magnetic field and $I_N$ is the spin operator of nucleus $N$. The first term in Eq. 2.1 describes the coupling of the effective electronic spin to the applied field, or the electronic Zeeman effect. The changes the local chemical environment induces in the unpaired electronic spin density are quantified by deviations of electronic $g$-tensor from the free-electron $g$-factor $g_e$. The second term arises from the interaction between the spin density and a specific magnetic nucleus $N$, parameterized by the hyperfine coupling tensor $A_N$. The third term in Eq. 2.1 measures the interaction of effective electronic spins, occurring in systems with at least two unpaired electrons, and the corresponding parameter is called the zero-field splitting tensor $D$.

As an example of electronic spin level splitting, let us study the simple case of molecules possessing one magnetic nucleus of spin $I = \frac{1}{2}$, and only one unpaired electron [13]. The zero-field splitting term (third term in Eq. 2.1) has then to be discarded from the expression of EPR spin Hamiltonian. Assuming that the experiment is carried out in gas phase or solution, the molecules rotate freely and orientation-dependent components of the interaction tensors will vanish upon averaging. The splitting of spin levels is then sufficiently described by isotropic tensor components, and the EPR spin Hamiltonian of such system, placed in a magnetic field $B$ which defines $z$-axis of the laboratory frame, reads

$$\hat{H}_{\text{EPR}}^{\text{iso}} = g \mu_B B S_z + A \cdot S \cdot I.$$

(2.2)

In the expression above, $g$ denotes the isotropic $g$-tensor of the unpaired electron, $A$ is the isotropic hyperfine coupling constant, and $S_z$ is the electronic spin...
projected along the direction of applied field. The degeneracy of doublet electronic states, which differ by their magnetic quantum numbers $m_S = \pm \frac{1}{2}$, is removed by the Zeeman effect represented by first term in Eq. 2.2. The second term describes the hyperfine coupling between the electronic $S$ and nuclear $I$ spin operators.

In order to obtain expressions for the relative energies of states split by the interactions present in $\hat{H}_{\text{EPR}}^{\text{iso}}$, one represents the Hamiltonian in the basis of electronic and nuclear spin functions defined as the product $|m_S, m_I\rangle = |S, m_S\rangle |I, m_I\rangle$, where electronic and nuclear spin quantum numbers have same values $S = I = \frac{1}{2}$, resulting in half-integer electronic and nuclear magnetic quantum numbers: $m_S = \pm \frac{1}{2} = m_I$. The four linearly independent spin states in this basis are denoted as

$$ \left\{ |m_S, m_I\rangle \right\}_{m_S, m_I = \pm \frac{1}{2}} = \left\{ |\uparrow, \uparrow\rangle; |\uparrow, \downarrow\rangle; |\downarrow, \uparrow\rangle; |\downarrow, \downarrow\rangle \right\}. \quad (2.3) $$

To evaluate the $\hat{H}_{\text{EPR}}^{\text{iso}}$ operator in the basis of the spin functions of Eq. 2.3, we rewrite the scalar product of electronic and nuclear vectorial spin operators with the help of raising and lowering operators,

$$ S_\pm = S_x \pm i S_y \quad (2.4) $$

$$ I_\pm = I_x \pm i I_y. \quad (2.5) $$

When acting on one of the spin states, these operators raise or lower by one unit the corresponding magnetic quantum number of respective state. The EPR spin Hamiltonian takes the following form:

$$ \hat{H}_{\text{EPR}}^{\text{iso}} = g \mu_B B S_z + A \left[ \frac{1}{2} (S_+ I_- + S_- I_+) + S_z I_z \right] \quad (2.6) $$

and employing the orthonormality property of the basis of spin functions one obtains the matrix-form of $\hat{H}_{\text{EPR}}^{\text{iso}}$ operator as:

$$ \begin{pmatrix}
\frac{1}{2}g \mu_B B + \frac{1}{4}A & 0 & 0 & 0 \\
0 & \frac{1}{4} A & \frac{1}{2}g \mu_B B - \frac{1}{4} A & 0 \\
0 & \frac{1}{4} A & -\frac{1}{2}g \mu_B B - \frac{1}{4} A & 0 \\
0 & 0 & 0 & -\frac{1}{2}g \mu_B B + \frac{1}{4} A
\end{pmatrix}. \quad (2.7) $$

We notice here that the hyperfine coupling mixes the $|\uparrow, \downarrow\rangle$ and $|\downarrow, \uparrow\rangle$ states, thus the EPR Hamiltonian is non-diagonal in spin function basis. Defining

$$ \tan(2\theta) = \frac{|A|}{g \mu_B B} $$

the eigenstates can be expressed as the following linear combinations of spin functions:
CHAPTER 2. MAGNETIC RESONANCE SPECTROSCOPY

Figure 2.1: Magnetic energy levels and allowed transitions in a system with one unpaired electron and one nucleus with \( I = \frac{1}{2} \).

\[
\begin{align*}
\text{Zeeman, } B &> 0 \quad \text{hyperfine, } A > 0 \\
E_1 &
\end{align*}
\]

\[
\begin{align*}
|1\rangle & = | \uparrow, \uparrow \rangle \quad (2.8) \\
|2\rangle & = \cos \theta | \uparrow, \downarrow \rangle + \sin \theta | \downarrow, \uparrow \rangle \quad (2.9) \\
|3\rangle & = -\sin \theta | \uparrow, \downarrow \rangle + \cos \theta | \downarrow, \uparrow \rangle \quad (2.10) \\
|4\rangle & = | \downarrow, \downarrow \rangle \quad (2.11)
\end{align*}
\]

The energy levels are obtained as eigenvalues of Hamiltonian operator Eq. 2.7:

\[
\begin{align*}
E_1 & = \frac{1}{2} g \mu_B B + \frac{1}{4} A \quad (2.12) \\
E_2 & = \frac{1}{2} g \mu_B B \sqrt{1 + \tan^2(2\theta)} - \frac{1}{4} A \quad (2.13) \\
E_3 & = -\frac{1}{2} g \mu_B B \sqrt{1 + \tan^2(2\theta)} - \frac{1}{4} A \quad (2.14) \\
E_4 & = -\frac{1}{2} g \mu_B B + \frac{1}{4} A \quad (2.15)
\end{align*}
\]

From these expressions one notices that the levels which are initially degenerate states with \( m_S = \pm 1 \) are split by the Zeeman effect into two levels, which are further split into sub-levels of different \( m_I \) by the hyperfine interaction, as in the example in Fig. 2.1.
2.1. THE EPR SPIN HAMILTONIAN

Figure 2.2: EPR spectrum recorded for the system with one unpaired electron and one nucleus with $I = \frac{1}{2}$.

The observed transitions in conventional EPR spectroscopy are those between states with different $m_S$, obeying the selection rule $\Delta m_S = \pm 1$. Consequently, in the strong field limit $A^{\text{iso}} << g^{\text{iso}} \mu_B B$, the allowed EPR transitions of this system are between states $|1\rangle \leftrightarrow |3\rangle$ and states $|2\rangle \leftrightarrow |4\rangle$ (see Fig. 2.1). The frequencies of these transitions can be computed from Eqs. 2.12-2.15 as:

\[ E_1 - E_3 \approx g\mu_B B + \frac{1}{2}A \quad (2.16) \]
\[ E_2 - E_4 \approx g\mu_B B - \frac{1}{2}A \quad (2.17) \]

yielding that the separation between the two transitions equals the hyperfine coupling constant $A$. The EPR spectrum of this system consists out of two peaks are observed at different frequencies separated by $A$, as shown in Fig. 2.2.

Moreover, in this approximation the size of the splitting does not depend on the strength of applied magnetic field, and EPR spectroscopy determines directly the absolute value of electronic spin density on the site of magnetic nucleus.

Transitions are triggered by a resonant electromagnetic field applied perpendicularly to $B$, e.g. along $x$-axis. One can estimate the transition intensities from the matrix elements of $S_x$ component of spin operator, between corresponding states. In general, for any strength of the static field, the intensities of the two transitions are found to be equal:

\[ |\langle 1|S_x|3\rangle|^2 = |\langle 2|S_x|4\rangle|^2 = \cos^2 \theta . \quad (2.18) \]

Thus, with the help of spin Hamiltonian approach one finds that EPR spectra for this particular molecule having one unpaired electron and one nuclear magnetic momentum reduces to two identical peaks split by the hyperfine coupling.
CHAPTER 2. MAGNETIC RESONANCE SPECTROSCOPY

2.2 The NMR spin Hamiltonian of diamagnetics

To a great extent, nuclear magnetic resonance (NMR) spectroscopy shares many similarities with EPR spectroscopy, in both experimental and theoretical methods employed in the determination and the analysis of molecular spectra. The analogy between the two magnetic resonance spectroscopies is based on the utilization of Zeeman effect, the lifting of degeneracy of nuclear or electronic spin levels under the influence of an applied static magnetic field. Moreover, both NMR and EPR spectroscopies provide information about a set of properties, including the molecular structure.

The most common terms that enter the NMR spin Hamiltonian are

\[ \hat{H}_{\text{NMR}} = - \sum_N g_N \mu_p I_N^T \cdot (1 - \sigma_N) \cdot B + \sum_{M>N} I_M^T \cdot (D_{MN} + K_{MN}) \cdot I_N \]  

(2.19)

where \( B \) is the applied homogeneous magnetic field, \( I_N \) is the spin operator of nucleus \( N \), \( g_N \) is the nuclear \( g \)-factor, and \( \mu_p \) is the proton magneton. The first term accounts for the nuclear Zeeman interaction, the splitting of spin levels of a magnetic nucleus which is subject to an applied field. The influence the electron distribution has on the field experienced by the nucleus is expressed through the nuclear shielding tensor \( \sigma_N \). The second term originates in the following nuclear spin-spin interactions: the classical magnetic dipole-dipole interaction and the nuclear spin-spin interaction mediated by the molecular electronic density. Corresponding parameters are the direct nuclear spin-spin coupling tensor \( D_{MN} \) and the indirect nuclear spin-spin coupling tensor \( K_{MN} \).

In order to depict the differences between the descriptions of EPR and NMR spectra, and to introduce physical grounds of the NMR spin Hamiltonian, we treat in this section the simple case of a closed-shell molecule with two magnetic nuclei of identical spins \( I_1 = I_2 = \frac{1}{2} \). The treatment follows the general steps as the one applied to the ESR Hamiltonian in the previous section. In addition to the nuclear Zeeman effect the two magnetic nuclei experience the spin-spin interaction as introduced by the last term in the spin Hamiltonian of Eq. (2.19), from which we consider only the indirect nuclear spin-spin coupling. For simplicity, we assume the two nuclei to be equivalent, possessing equal \( g \)-factors \( g_{n1} = g_{n2} = g_n \), and that their electronic environments are similar, i.e. their isotropic nuclear shielding constants are equal \( \sigma_1 = \sigma_2 = \sigma \). The isotropic NMR spin Hamiltonian of studied system reduces to the simple form:

\[ \hat{H}_{\text{NMR}}^{\text{iso}} = -\mu_p g_n (1 - \sigma)(I_{z1} + I_{z2})B + K I_1 \cdot I_2 \]  

(2.20)

where, for simplicity, the indirect nuclear spin-spin coupling tensor \( K \) is assumed to be isotropic, \( I_1 \) and \( I_2 \) are the nuclear spin operators of the two magnetic nuclei, having \( I_{z1} \) and \( I_{z2} \) projections on the direction of the applied field \( B \).
Nuclear spin operators are represented in the basis by direct products of nuclear spin states $|m_{I_1}, m_{I_2}\rangle = |I_1, m_{I_1}\rangle|I_2, m_{I_2}\rangle$, where the nuclear spin projections on $z$-axis take half-integer values $m_{I_1}, m_{I_2} = \pm \frac{1}{2}$.

With the help of raising and lowering nuclear spin operators defined similarly to Eq. 2.4, we re-write the NMR spin Hamiltonian as:

$$\tilde{\mathcal{H}}_{NMR}^{iso} = -\mu_p g_n (1 - \sigma)(I_{z_1} + I_{z_2})B + K \left[ \frac{1}{2}(I_{1+}I_{2-} + I_{1-}I_{2+}) + I_{z_1}I_{z_2} \right]. \quad (2.21)$$

One obtains for the representation of $\tilde{\mathcal{H}}_{NMR}^{iso}$ in the nuclear spin function basis:

$$ \begin{pmatrix} -\mu_p g_n (1 - \sigma)B + \frac{1}{4}K & 0 & 0 & 0 \\ 0 & -\frac{1}{4}K & \frac{1}{2}K & 0 \\ 0 & \frac{1}{2}K & -\frac{1}{4}K & 0 \\ 0 & 0 & 0 & \mu_p g_n (1 - \sigma)B + \frac{1}{4}K \end{pmatrix}. \quad (2.22)$$

As one expects, states with total spin null are split and coupled only by the nuclear spin-spin interactions. The eigenstates of NMR Hamiltonian are linear combinations of nuclear spin functions, symmetric or antisymmetric with respect to the permutation of the magnetic nuclei:

$$\begin{align*}
|1\rangle &= |\uparrow, \uparrow\rangle \\
|2\rangle &= \frac{1}{\sqrt{2}} \left( |\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle \right) \\
|3\rangle &= \frac{1}{\sqrt{2}} \left( -|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle \right) \\
|4\rangle &= |\downarrow, \downarrow\rangle.
\end{align*} \quad (2.23)$$

If one examines the eigenvalues of the NMR Hamiltonian Eq. 2.22, one sees that only the energy level of parallel orientated spins state is split in two sub-levels by the applied field, while the nuclear spin-spin interactions split in two sub-levels the total spin zero state, and also shifts the Zeeman energy spin sub-levels:

$$\begin{align*}
E_1 &= -\mu_p g_n (1 - \sigma)B + \frac{1}{4}K \\
E_2 &= \frac{1}{2} |K| - \frac{1}{4}K \\
E_3 &= -\frac{1}{2} |K| - \frac{1}{4}K \\
E_4 &= \mu_p g_n (1 - \sigma)B + \frac{1}{4}K.
\end{align*} \quad (2.27 - 2.30)$$

The observed transitions in NMR spectroscopy, obey the selection rule $\Delta m_I = \pm 1$. There is a number of four allowed transitions for any size of the field.
strength, \( |1\rangle \leftrightarrow |2\rangle, |1\rangle \leftrightarrow |3\rangle, |2\rangle \leftrightarrow |4\rangle, \) and \( |3\rangle \leftrightarrow |4\rangle \). The frequencies of these transitions may be calculated as corresponding energy differences:

\[
E_1 - E_2 = E_3 - E_4 = -\mu_pg_n(1 - \sigma)B - \frac{1}{2}(|K| - K) \tag{2.31}
\]

\[
E_1 - E_3 = E_2 - E_4 = -\mu_pg_n(1 - \sigma)B + \frac{1}{2}(|K| - K) \tag{2.32}
\]

yielding that only two spectral peaks are to be observed in the NMR spectra of this molecule, since some of the transition frequencies are equal. The separation of this two peaks is \(|K| - K\). If the resonant electromagnetic field oscillates along \(x\)-axis, the transition intensities are to be determined computing the matrix elements of spin projection \(S_z\) operator, taken between the states of respective transitions. The intensities of transitions are all equal to

\[
|\langle 1|S_z|2\rangle|^2 = \frac{1}{2}. \tag{2.33}
\]

To conclude this section, we employed the spin Hamiltonian approach to find that the NMR spectrum of a particular diamagnetic molecule having two equivalent magnetic nuclei, reduces to two lines separated by the nuclear spin-spin interaction. Variations of this method apply successfully in the determination of NMR and EPR spectral parameters of more complex diamagnetic or paramagnetic molecules.

The NMR spin Hamiltonian of paramagnetics

The presence of unpaired electrons in paramagnetic molecules cause hyperfine shifts of the absorption peaks, they affect the relaxation times as well as influence other parameters of the NMR spectra. From the NMR spectroscopy point of view we are interested in the ensemble average of the molecular electronic spin projection \(\langle S_z \rangle\) along the external magnetic field \(B\) which defines the molecule induced magnetic moment average [8]

\[
\langle \mu \rangle = -\mu_Bg_e\langle S_z \rangle \tag{2.34}
\]

We consider a molecule with non-vanishing electronic spin angular momentum \(S\), implying \(2S + 1\) degenerate states that correspond to the different \(m_S\) quantum numbers, i.e. the spin projection \(S_z\) values. In a magnetic field the energy levels corresponding to the states with different \(m_S\) quantum numbers may be expressed in the form

\[
E(m_S) = \mu_Bg_eBm_S \tag{2.35}
\]

As the different states of the ensemble can be populated with certain probability according the Boltzmann statistics the averaged value of spin projection along the magnetic field is

\[
\langle S_z \rangle = \frac{\sum m_S \exp(-\mu_Bg_eBm_S/kT)}{\sum \exp(-\mu_Bg_eBm_S/kT)} \tag{2.36}
\]
2.2. THE NMR SPIN HAMILTONIAN OF DIAMAGNETICS

In the high temperature limit \( \mu_B g_e B m S << kT \) equation for \( \langle S_z \rangle \) may be simplified [18] to

\[
\langle S_z \rangle = -\mu_B g_e \frac{S(S + 1)B}{3kT}
\]

This form will be used in the following description of NMR spectral parameters of paramagnetic molecules.

In the time scale of the NMR experiment the resonating nuclei experience an additional magnetic field created by the averaged magnetic moment of unpaired electrons. Therefore, it is appealing to introduce the hyperfine interaction terms with the ensemble averaged effective spin \( \langle S \rangle \) into the NMR spin Hamiltonian for a paramagnetic molecule and neglect the electronic spin degrees of freedom

\[
\mathcal{H}_{pNMR} = -\sum_i \mu_p g_{ni} B^T \cdot (1 - \sigma) \cdot I_i + \sum_i \langle S \rangle^T \cdot A_i \cdot I_i + \frac{1}{2} \sum_{i \neq j} I_i^T \cdot (D_{ij} + K_{ij}) \cdot I_j
\]

In Eq. 2.38 the hyperfine interaction term depends on the external magnetic field \( B \) and temperature \( T \) and this term corresponds to the additional magnetic field due to the magnetic moments of the unpaired electrons interacting with nuclear spins. Therefore, by analogy to nuclear shielding the hyperfine interaction term of the Spin Hamiltonian will change the frequency by affecting the strength of magnetic field at the resonating nucleus.
Chapter 3

Molecular Hamiltonian

Properties of a molecular system can be derived from the solution of a quantum mechanical wave equation for the Hamiltonian operator that describes the system under particular conditions. The specific terms in the Hamiltonian account for the different interactions in the molecule. The Dirac equation [19] is the natural choice for the investigation of relativistic effects in the framework of quantum mechanics, as it incorporates both special relativity and electronic spin. However, a relativistic quantum mechanical approach is complicated, even for the simplest of molecular systems; an alternative approach is to use non-relativistic quantum mechanics and treat the relativistic effects as perturbations.

In the present chapter, four-component and two-component formalisms are related, reducing the many electron-generalization of the Dirac Hamiltonian to the Breit-Pauli Hamiltonian [13, 20]. The terms of the Breit-Pauli Hamiltonian that are relevant for EPR and NMR parameters are discussed. We study the influence of relativity on the parameters of magnetic resonance spectroscopy because the relativistic corrections are important for many types of problems in both chemistry and physics. Two examples of relativistic effects, with totally different origins, are the mass-velocity correction and the electronic spin-orbit interaction. Their dependence on electronic spin separates them into two classes with a predominant influence either on the molecular properties of heavy element compounds (such as binding energies, activation energies, geometries), or on the dynamical properties of light molecules, e.g. transitions that are allowed due to a strong spin-orbit coupling [10].

3.1 The Dirac Equation

The origin of Dirac’s assertion regarding the relativistic treatment of an electron, is the desire to have an equation which is relativistically covariant and whose solutions have a probability interpretation. This drove Dirac to postulate the following relativistic equation of motion [19] linear in both the time derivative
CHAPTER 3. MOLECULAR HAMILTONIAN

and momentum $p$

$$ih \frac{\partial \Phi}{\partial t} = (c \mathbf{\alpha} \cdot \mathbf{p} + mc^2 \beta)\Phi. \tag{3.1}$$

The requirements on this ansatz lead to non-commutative coefficients ($\alpha, \beta$) which could be represented by matrices of dimension 4 and the interpretation of this internal structure is that electronic spin is explicitly present. In the most common representation, the components of $\alpha, \alpha_u, u = x, y, z$, and $\beta$ are defined as

$$\alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{3.2}$$

with the help of spin one-half Pauli matrices:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{3.3}$$

The operator in the right-hand side of time-dependent Dirac equation (Eq. 3.1) is the one-electron Dirac Hamiltonian, acting on the four-component Dirac spinor $\Phi$.

A form of the many-electron relativistic Hamiltonian can be obtained by adding some two-electron interaction terms to the sum of one-electron Dirac Hamiltonians. A popular choice is to correct the two-electron Coulomb interaction operator with the two-electron Breit operator [21], which describes the electron-electron interaction of the order $O(c^{-2})$. Thus, we will consider the following expression for the so-called relativistic Dirac-Coulomb-Breit (DCB) Hamiltonian:

$$\hat{H}^{\text{DCB}} = \sum_i \hat{H}^D_i + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{i>j} \hat{H}^B_{ij} \tag{3.4}$$

where $\hat{H}^D_i$ denotes the relativistic Dirac Hamiltonian of electron $i$, $r_{ij}$ is the distance between electrons $i$ and $j$, and $\hat{H}^B_{ij}$ denotes the Breit interaction corresponding to electrons $i$ and $j$. The two-electron Breit operator $\hat{H}^B_{ij}$ is defined as the magnetic Gaunt [22] term corrected for retardation:

$$\hat{H}^B_{ij} = -\frac{e^2}{2} \left[ \frac{\mathbf{\alpha}_i \cdot \mathbf{\alpha}_j}{r_{ij}} + \frac{(\mathbf{\alpha}_i \cdot \mathbf{r}_{ij})(\mathbf{\alpha}_j \cdot \mathbf{r}_{ij})}{r^2_{ij}} \right]. \tag{3.5}$$

The use of 4-component methods involving this approximate form of the Hamiltonian is computationally expensive, unsuitable for the study of relative large molecules.

3.2 The Breit-Pauli Hamiltonian

The Breit-Pauli Hamiltonian is the result of reducing the 4-component DCB Hamiltonian (Eq. 3.4) to a two-component form which in the non-relativistic
limit can be incorporated in the Schrödinger equation. The Breit-Pauli Hamiltonian gives an adequate partitioning of the Hamiltonian operator into a non-relativistic part and relativistic corrections, which is a starting point for the study of relativistic effects in molecular systems. One way of obtaining these corrections is through the Foldy-Wouthuysen (FW) transformation\cite{FW} of which the purpose is to uncouple the positive and negative-energy solutions of the Dirac equation.

### 3.2.1 The Foldy-Wouthuysen transformations

The Dirac Hamiltonian for an electron in a static electro-magnetic field can be written as

\[ \hat{H} = mc^2 (\beta + \mathcal{O} + \mathcal{E}) \]  

where \( \mathcal{O} \) is linear and \( \mathcal{E} \) is quadratic in \( c^{-1} \)

\[ \mathcal{O} = \frac{\mathbf{\pi} \cdot \mathbf{\alpha}}{mc} \]  

\[ \mathcal{E} = -\frac{\varepsilon \phi}{mc^2} \]  

Here \( \phi \) is the electrostatic potential and \( \mathbf{\pi} \) is the kinetic momentum for an electron in a magnetic vector potential \( \mathbf{A} = \mathbf{p} + e\mathbf{A} \).

For the discussion of magnetic resonance parameters it is only necessary to consider magnetostatic fields. \( \mathcal{O} \) is odd and anti-commutes with \( \beta \) and \( \mathcal{E} \) is even and commutes with \( \beta \). Odd terms in the Hamiltonian couple positive and negative energy solutions and the purpose of the transformations is to eliminate odd terms to a given order. It can be shown\cite{FW} that the exponential transformation

\[ \hat{H}' = e^S \hat{H} e^{-S} \]  

has this property for

\[ S = \frac{\beta \mathcal{O}}{2} \]  

i.e. the transformed Hamiltonian can be written

\[ \hat{H}' = mc^2 (\beta + \mathcal{O}' + \mathcal{E}') \]  

where the new odd term \( \mathcal{O}' \) is of third-order in \( c^{-1} \). To zero:th order in the inverse speed of light Eq. 3.12 is block diagonal with respect to positive and negative energy parts. Consecutive applications of the FW transformations reduces the current odd term and for each transformation the off-diagonal blocks are reduced by an order \( c^2 \). In molecular applications the negative energy part of a (block diagonal) Hamiltonian can be ignored and only the two-component positive-energy Hamiltonian need to be considered.
3.2.2 Expansion of Hamiltonian terms

In this section the principles are outlined for identifying Hamiltonian terms contributing to a magnetic resonance parameter. The lowest-order even term is just the electrostatic potential term and for clarity we may write

$$ E = E^{(2)} . $$  \hspace{1cm} (3.13)

The odd-term has contributions of different order due to different types of field dependencies

$$ O = O^{(1)} + O^{(3)} . $$  \hspace{1cm} (3.14)

On a molecular energy scale relevant for a magnetic resonance experiment, the first term contains the canonical momentum and the external field, while the second term contains magnetic fields due to internal sources, such as magnetic nuclei in which magnetic vector potential is

$$ A = A^{(0)} + A^{(2)} = \frac{1}{2} B \times r + \sum_{N} \frac{\mu_0 M_N}{4\pi} \frac{r_N}{r^3} $$ \hspace{1cm} (3.15)

where \( r \) is the field point relative to a gauge origin, \( \mu_0 \) is the magnetic permeability in vacuum, and \( r_N \) is the position of nuclear \( N \) with magnetic dipole moment \( M_N = g_N \mu_p I_N \). On an energy scale that is adequate in quantum chemistry calculations it is convenient to subtract the rest mass term of the Hamiltonian. Thus a sequence of FW transformations gives Hamiltonian expansion in orders of the inverse speed of light. After two transformations we have

$$ \hat{H}'' - mc^2 \beta = \hat{H}^{(0)} + \hat{H}^{(2)} + o(c^{-3}) $$ \hspace{1cm} (3.16)

where

$$ \hat{H}^{(0)} = mc^2 \left( \beta \frac{O^{(1)}^2}{2} + E^{(2)} \right) $$ \hspace{1cm} (3.17)

$$ \hat{H}^{(2)} = mc^2 \left( \beta \frac{[O^{(1)}, O^{(3)}]}{2} - \frac{1}{8} \frac{O^{(1)}^4}{8} - \frac{1}{8} [O^{(1)}, [O^{(1)}, E^{(2)}]] \right) . $$ \hspace{1cm} (3.18)

3.2.3 Field dependence of Hamiltonian terms

For each order the field dependence of the Hamiltonian can be separated off according to the following expansion around the zero field point [24]:

$$ \hat{H}^{(k)}(B, I_N) = \hat{H}^{(k)}_0 + \hat{H}^{(k)}_B \cdot B + \sum_{N} \hat{H}^{(k)}_{I_N} \cdot I_N + \frac{1}{2} B \cdot \hat{H}^{(k)}_{BB} \cdot B $$ \hspace{1cm} (3.19)

$$ + \sum_{N} I_N \cdot \hat{H}^{(k)}_{I_N B} \cdot B + \sum_{M > N} I_M \cdot \hat{H}^{(k)}_{I_M I_N} \cdot I_N . $$ \hspace{1cm} (3.20)
3.2. THE BREIT-PAULI HAMILTONIAN

The lowest order derivatives of the Hamiltonian are then given by

\[ \hat{H}_0^{(0)} = \frac{\mathbf{p}^2}{2m} - e\phi \]  
\[ \hat{H}_B^{(0)} = \frac{e}{2m} (\ell + 2S) = \hat{H}^{OZ} + \hat{H}^{SZ} \]  

i.e. the non-relativistic field free Hamiltonian, and the orbital (OZ) and spin Zeeman (SZ) operators. In Eq. 3.22 it is denoted by \( \ell \) and \( S \) the electronic orbital momentum and the electron spin, respectively.

The lowest order non-vanishing dipole-field derivatives are one order smaller in \( c^{-2} \) and these are the paramagnetic spin-orbit (PSO), Fermi-contact (FC), spin-dipole (SD) and the diamagnetic spin-orbit (DSO) terms defined as follows:

\[ \hat{H}_N^{(2)} = \frac{e}{4\pi m} \frac{m \mathbf{r}_N \times \mathbf{p}}{r_N^3} + \frac{e}{m} \mathbf{S} \cdot \mathbf{B}_{X} = \hat{H}^{PSO} + \hat{H}^{FC} + \hat{H}^{SD} \]  
\[ \hat{H}_{B_N}^{(2)} = \frac{e^2\hbar}{4\pi m} \frac{m (\mathbf{r}_N \cdot \mathbf{r}) \mathbf{1} - rr_N}{r_N^3} = \hat{H}^{DSO} \]  

Eq. 3.23 is a vector property and Eq. 3.24 is a tensor property, where \( \mathbf{1} \) is a unit tensor, the dot product is the ordinary scalar product and the other vector product a dyadic.

The FC and SD terms are obtained from the magnetic dipole field

\[ \mathbf{B}_{X} = \frac{\mu_0}{4\pi m} \left( \frac{8\pi}{3} \delta(\mathbf{r}_N) + \frac{3r_Nr_N - r_N^2}{r_N^5} \mathbf{1} \right) \]  

Other Hamiltonian operators of the same order include

\[ \hat{H}_0^{(2)} = -\frac{\mathbf{p}^4}{8m^3c^2} + \frac{e\hbar^2}{8m^2c^2} (\nabla \cdot \mathbf{E}) + \frac{e}{2m^2c^2} \mathbf{S} \cdot \mathbf{E} \times \mathbf{p} \]  
\[ = \hat{H}^{mv} + \hat{H}^{Dar} + \hat{H}^{SO(1-el)} \]  

where the field-free parts are the mass-velocity (mv) term, the so called Darwin (Dar) term and the one-electron spin-orbit interaction. It can be noted that the two-electron spin-orbit operators can also be recovered in this context if we consider the other electrons as field sources as well; as sources of electric fields the last term of Eq. 3.26 provides the spin-own-orbit interaction while as sources of magnetic fields the spin-Zeeman term (c.f. Eq. 3.22) provides the spin-other-orbit interaction.

Once the Hamiltonian derivatives have been identified it is straightforward to define a magnetic resonance parameter to a given order. As an example, the lowest-order contributions to the NMR shielding tensor for a closed shell molecule are [24]

\[ \sigma_N^{(2)} = \langle \hat{H}_N^{(2)} \rangle + \langle \hat{H}_B^{(2)} ; \hat{H}_B^{(0)} \rangle \]  

known as the diamagnetic and paramagnetic terms expressed as an expectation value and a static linear response function, respectively. The relativistic corrections to the shielding tensor of order $c^{-4}$ and all possible contributions here have the form

$$
\sigma^{(4)}_N = \langle \hat{H}^{(4)}_{NB} \rangle + \langle \hat{H}^{(2)}_{NB} ; \hat{H}^{(2)}_B \rangle + \langle \hat{H}^{(4)}_N ; \hat{H}^{(0)}_B \rangle + \langle \hat{H}^{(2)}_N ; \hat{H}^{(2)}_B \rangle + \langle \hat{H}^{(2)}_B ; \hat{H}^{(0)}_B \rangle 
$$

(3.28)

where the last term is a static quadratic response function corresponding to the third-order energy contribution in Rayleigh-Schrödinger perturbation theory.

A part of this thesis is devoted to the influence of relativistic effects on magnetic resonance parameters in the context of density functional theory. In paper I, density functional calculations are carried for the spin-orbit corrections to the nuclear spin-spin coupling tensor, and in paper II, a number of corrections of the form Eq. 3.28 are devoted to the nuclear shielding tensor.
Chapter 4

Computational Methods

The response theory introduces an elegant mathematical description of electronic response to static and dynamic perturbations. Early implementation of codes capable to determine high order response functions for Hartree-Fock and multiconfigurational self-consistent field wave functions provided essential tools necessary for investigations of optical, magnetic and mixed molecular properties, and laid the ground for "blackbox modeling" of arbitrary properties of molecules and materials. The development of density functional theory in combination with response theory produces a versatile approach for determination of properties of large molecules beyond the reach of correlated \textit{ab initio} methods. Recently one has witnessed the implementation of a density functional response theory (DFRT) formalism, which is capable to determine up to cubic response functions as well as their residues in a automated way. However, this advance in DFRT focused on closed-shell molecules and only a limited development has taken place for open-shell molecules. This chapter presents our attempt to elevate the situation by developing a general purpose spin-restricted DFRT capable of computing arbitrary quadratic response functions in molecules with a high spin ground state.

4.1 Density Functional Theory

The idea to consider the energy of the system as a functional of the electronic density, emerged in the early stages of quantum physics from the work of Thomas and Fermi [25, 26], but it wasn’t until 1964 [27] when density functional theory (DFT) recieved a theoretical justification, and became a modeling tool extensively used by physicists due to the practical formulation of Kohn and Sham [28]. Relatively late, in the 90’s it achieved its current status as the most widely applied quantum chemistry approach for determining electronic structure and properties of various compounds. This delay was caused by the rather disappointing description of molecular systems, i.e. the poor description of chemical bonding by exchange-correlation functionals available at that time [29, 30,
The breakthrough came with the development of more accurate hybrid exchange-correlation functionals [32], when first successful applications of DFT in the investigation of molecular electronic structures began to appear. An alert rhythm in the development of functionals resulted in one of the most accurate and fastest approaches for the calculation of electronic structure and properties of large molecular systems. The key to this remarkable success of DFT in quantum chemistry was its capability to include a large part of the dynamic electron correlation via the exchange-correlation functional, which allowed one to obtain the accuracy in the evaluation of molecular properties comparable with sophisticated \textit{ab initio} methods but with computational efforts similar to the ordinary Hartree-Fock method.

The ground state energy of the molecular electronic system in DFT can be found by minimization of the energy functional

$$E[\rho] = \int \rho(r)v(r)dr + F[\rho]$$  \hspace{1cm} (4.1)

where first term is the nuclear potential uniquely defined by electronic density $\rho(r)$ [27], while the universal potential $F[\rho]$ can be decomposed into the electron kinetic energy and electron-electron interaction functionals, respectively:

$$F[\rho] = T[\rho] + V_{ee}[\rho]$$  \hspace{1cm} (4.2)

Applying the variational principle with constraint

$$\int \rho(r)dr = N$$  \hspace{1cm} (4.3)

where $N$ is the number of electrons in the system, one may write a condition for the minimum of the energy functional $E[\rho]$ as

$$\delta\{E[\rho] - \mu \int \rho(r)dr\} = 0.$$  \hspace{1cm} (4.4)

The stationary condition (Eq. 4.4) for $E[\rho]$ can be rewritten for the determination of Lagrange multiplier $\mu$

$$\mu = v(r) + \frac{\delta F[\rho]}{\delta \rho}$$  \hspace{1cm} (4.5)

\textbf{4.1.1 The Kohn-Sham method for closed shell systems}

Early failure in producing reasonable results in electronic structure investigations were attributed to an inaccurate evaluation of kinetic energy functional $T[\rho]$. Kohn and Sham proposed a solution in 1965 [28] by expressing the kinetic energy functional in a basis of Kohn-Sham orbitals in similar fashion as in wave function methods

$$T_s[\rho] = -\frac{1}{2} \sum^N_i \langle \psi_i | \nabla^2 | \psi_i \rangle.$$  \hspace{1cm} (4.6)
Here the electron density is defined using KS orbitals

\[ \rho (r) = \sum_i^N \sum_s |\psi_i(r, s)|^2 \]  

(4.7)
implying that the ground state of the molecule is represented by a single Slater determinant

\[ \Psi_s = \frac{1}{\sqrt{N!}} \det [\psi_1 \psi_2 \ldots \psi_N] \]  

(4.8)
constructed from KS orbitals. \( T_s[\rho] \) corresponds to the exact kinetic energy functional \( T[\rho] \) within a small residual correction. The energy functional becomes

\[ E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + \int \rho(r) v(r) dr \]  

(4.9)
where the electron-electron interaction functional \( V_{ee}[\rho] \) is partitioned into the classical electron Coulomb interaction energy \( J[\rho] \) and exchange-correlation functional \( E_{xc}[\rho] \), which accounts for the non-classical electron-electron interaction and the residual kinetic energy correction.

### 4.1.2 The Kohn-Sham method for open shell systems

The energy functional capable of describing open shell molecules has the slightly more sophisticated form

\[ E[\rho_\alpha, \rho_\beta] = T_s[\rho_\alpha, \rho_\beta] + J[\rho_\alpha + \rho_\beta] + E_{xc}[\rho_\alpha, \rho_\beta] + \int (\rho_\alpha(r) + \rho_\beta(r)) v(r) dr \]  

(4.10)
dependent on electrons spin densities, \( \rho_\alpha \) and \( \rho_\beta \), is required. Here the spin densities are defined in the KS orbital basis as

\[ \rho_\alpha(r) = \sum_i n_{\alpha i} |\psi_i(r, \alpha)|^2 \quad \text{and} \quad \rho_\beta(r) = \sum_i n_{\beta i} |\psi_i(r, \beta)|^2, \]  

(4.11)
where \( n_{\sigma i} \) is the occupation number of \( \psi_i(r, \sigma) \) spin orbital in the Kohn-Sham determinant with possible values zero or one. The kinetic energy expression in Eq. 4.10

\[ T_s[\rho_\alpha, \rho_\beta] = -\frac{1}{2} \sum_{i\sigma} n_{\sigma i} \langle \psi_i(r, \sigma) | \nabla^2 | \psi_i(r, \sigma) \rangle \]  

(4.12)
slightly differs from the previous one for closed shell molecule (see Eq. 4.6). The variational search for a minimum of the \( E[\rho_\alpha, \rho_\beta] \) functional can be carried out by spin unrestricted or spin restricted approaches. The two methods essentially differ only by conditions of constraint imposed in the energy functional minimization that lead to different sets of Kohn-Sham equations for spin orbitals. The unrestricted Kohn-Sham approach is the most commonly used and is implemented in various standard quantum chemistry software packages. However this method has a major disadvantage, the spin contamination
problem, and in recent years the alternative restricted Kohn-Sham approach has become more popular. At first we discuss the conventional unrestricted Kohn-Sham method and later we switch our attention to the restricted Kohn-Sham approach, the development and implementation of which have been one of the goals of this thesis.

The unrestricted Kohn-Sham method

The unrestricted Kohn-Sham method relies on the minimization of the molecular energy functional $E[\rho_\alpha, \rho_\beta]$ with separate constrains [33]

$$
\int \rho_\alpha(r)dr = N_\alpha \text{ and } \int \rho_\beta(r)dr = N_\beta,
$$

which implies that the number of electrons with $\alpha$ and $\beta$ spins should remain constant under variational minimization of the energy functional. The minimization of $E[\rho_\alpha, \rho_\beta]$ under given constrains leads to separate sets of Kohn-Sham equations for $\psi_i(r, \alpha)$ and $\psi_i(r, \beta)$ spin orbitals:

$$
\hat{f}_\alpha \psi_i(r, \alpha) = \left\{ -\frac{1}{2} \nabla^2 + v_{\text{eff}}^\alpha \right\} \psi_i(r, \alpha) = \frac{\epsilon_\alpha^i}{n_{\alpha i}} \psi_i(r, \alpha) \quad i = 1, 2, ..., N_\alpha \quad (4.14)
$$

$$
\hat{f}_\beta \psi_i(r, \beta) = \left\{ -\frac{1}{2} \nabla^2 + v_{\text{eff}}^\beta \right\} \psi_i(r, \beta) = \frac{\epsilon_\beta^i}{n_{\beta i}} \psi_i(r, \beta) \quad i = 1, 2, ..., N_\beta \quad (4.15)
$$

where the spin dependent effective potentials are

$$
v(r)^\alpha_{\text{eff}} = v(r) + \int \frac{\rho_\alpha(r') + \rho_\beta(r')}{|r - r'|} d^3r' + \frac{\delta E_{\text{ex}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(r)} \quad (4.16)
$$

$$
v(r)^\beta_{\text{eff}} = v(r) + \int \frac{\rho_\alpha(r') + \rho_\beta(r')}{|r - r'|} d^3r' + \frac{\delta E_{\text{ex}}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(r)} \quad (4.17)
$$

and $\epsilon_\alpha^i$ is the Lagrange multiplier for the corresponding spin-orbital $\psi_i(r, \sigma)$. Equations 4.14-1.15 are coupled only by means of the electron spin densities entering the equations and the off-diagonal Lagrange multipliers do not appear. This is one of the major advantages of unrestricted Kohn-Sham theory. However, there is a price for this simple mathematical formulation of this method, namely the two Kohn-Sham matrices must be constructed and diagonalized in each iteration of the energy functional $E[\rho_\alpha, \rho_\beta]$ minimization instead of just one effective Kohn-Sham matrix used in the spin-restricted Kohn-Sham method.

The restricted Kohn-Sham method

In addition to the constrains on the number of $\alpha$ and $\beta$ electrons (see Eq. 4.13) we require in the spin-restricted Kohn-Sham method that spatial parts of $\psi_i(r, \alpha)$ and $\psi_i(r, \beta)$ spin orbitals remain the same under the $E[\rho_\alpha, \rho_\beta]$ minimization. Assuming a high spin ground state of a molecule with $N_\alpha$ doubly occupied
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orbitals and $N_s$ singly occupied orbitals the Kohn Sham equations under these constraints become

$$\{-\frac{1}{2}\nabla^2 + v_{\text{eff}}^d\} \psi_k(r) = \sum_j \epsilon'_{kj} \psi_j(r) \quad k = 1, 2, ..., N_d,$$  \hspace{1cm} \text{(4.18)}

$$\frac{1}{2}\{-\frac{1}{2}\nabla^2 + v_{\text{eff}}^s\} \psi_m(r) = \sum_j \epsilon'_{mj} \psi_j(r) \quad m = 1, 2, ..., N_s,$$  \hspace{1cm} \text{(4.19)}

where $j$ runs over doubly and singly occupied orbitals $j = 1, 2, ..., N_d + N_s$. In Eq.4.18-4.19 the effective potentials are defined as

$$v(r)_{\text{eff}}^d = v(r) + \int \frac{\rho_\alpha(r') + \rho_\beta(r')}{|r - r'|} dr' + \frac{1}{2} \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(r)}$$  \hspace{1cm} \text{(4.20)}

$$v(r)_{\text{eff}}^s = v(r) + \int \frac{\rho_\alpha(r') + \rho_\beta(r')}{|r - r'|} dr' + \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(r)},$$  \hspace{1cm} \text{(4.21)}

where the spin densities are given by the expressions

$$\rho_\alpha(r) = \sum_{i=1}^{N_d} |\psi_i(r)|^2 + \sum_{j=1}^{N_d} |\psi_j(r)|^2 \text{ and } \rho_\beta(r) = \sum_{i=1}^{N_d} |\psi_i(r)|^2.$$  \hspace{1cm} \text{(4.22)}

In the spin restricted Kohn-Sham equations above the off-diagonal Lagrangian multipliers appear in the coupling of the equations for doubly and singly occupied orbitals and therefore the ordinary solution methods can not be applied. However, the method for handling off-diagonal Lagrange multipliers developed in restricted open shell Hartree-Fock theory can be adapted to the Kohn-Sham formalism. There are two possibilities: to solve the equations for singly and doubly occupied orbitals separately or to combine both sets of equations into the one effective with off-diagonal Lagrange multipliers absorbed into the Kohn-Sham Hamiltonian. The second approach is more appealing from the computational point of view and has been chosen for implementation of a spin restricted Kohn-Sham method in papers included in this thesis. In analogy to ROHF theory the effective Kohn-Sham matrix is defined in the following form

$$\hat{H} = \begin{pmatrix} F_c & F_{co} & F_c \\ F_{co} & F_c & F_{ov} \\ F_c & F_{ov} & F_c \end{pmatrix},$$  \hspace{1cm} \text{(4.23)}

which has two modified blocks $F_{co}$ and $F_{ov}$ corresponding to off-diagonal elements between doubly and singly occupied orbitals and between singly occupied and virtual orbitals, respectively. Off-diagonal elements are modified to be proportional to the orbital gradient such that diagonalizing the effective Fock matrix leads to a stationary state. The matrix elements in Eq. 4.23 are defined as

$$F_c = \frac{1}{2}(f_\alpha + f_\beta), F_{co} = f_\beta \text{ and } F_{ov} = f_\alpha,$$  \hspace{1cm} \text{(4.24)}
where \( f_\alpha \) and \( f_\beta \) are ordinary matrix elements of Kohn-Sham operators for \( \psi_j(r, \alpha) \) and \( \psi_j(r, \alpha) \) spin orbitals given in Eqs. 4.14-4.15. The eigenvalues of the effective Hamiltonian Eq. 4.23 do not have physical meaning and only the final spin-densities obtained from the optimized Kohn-Sham determinant are relevant.

### 4.1.3 Exchange-correlation functionals

The Kohn-Sham exchange-correlation functional defines as the universal potential \( F[\rho] \) (see Eq. 4.2) from which the exact kinetic energy and inter-electron Coulomb repulsion are subtracted. Since the form of the exchange-correlation functional is unknown, one has to use physically justified approximations. The development of DFT is oriented on the improvement of exchange-correlation functionals to describe energetics and molecular structure more accurately within the framework of the Kohn-Sham method. One may classify the functionals into three major groups: local density approximation, generalized gradient approximation, and hybrid functionals.

**Local density approximation (LDA) functionals**

LDA functionals depend only on the electron density \( \rho(r) \). The combination of Dirac exchange [34] and Vosko-Wilk-Nussair [29] correlation functionals introduced in the 80's provides the most accurate results in DFT calculations at this level of approximation and for this reason is recognized as the standard LDA type exchange-correlation functional. The Dirac exchange functional has the analytical form of the energy of the electron gas

\[
E_x^{LDA}[\rho] = C_1 \rho^{1/3}
\]  

and it provides in general a poor description of bonding regions in molecules.

**Generalized gradient approximation (GGA) functionals**

In GGA exchange-correlation functionals a dependence on the gradient of electron density \( \nabla \rho(r) \) is included in order to describe more accurately the region with fast varying electron density in the molecular system. However, the first attempts of development of such functionals carried out by Sham [35] and Herman [36] in the 1970's was unsuccessful and only in 1986 the first reliable GGA exchange functional appeared, namely the one proposed by Becke [30]. Later development driven by the success of the Becke functional led to a variety of GGA functionals, including the Perdew-Wang exchange (PW) [37], Lee-Yang-Parr (LYP) correlation [31], and Perdew-Burke-Ernzerhof (PBE) exchange-correlation [38] functionals.
4.2. RESPONSE THEORY

Hybrid functionals

The hybrid functionals [32] were introduced by Becke and are based on the adiabatic connection. The most successful among these functionals is B3LYP, which has proved to be the most accurate functional for energetic calculations of molecular systems within the Kohn-Sham method. The B3LYP functional combines Dirac, exact Hartree-Fock exchange, and Becke exchange functionals with VWN and LYP correlation functionals in the form

$$E_{xc}^{B3LYP} = a_{xc}E_{xc}^{LDA} + (1 - a_{xc})E_{xc}^{HF} + a_xE_{x}^{B} + E_c^{VWN} + a_cE_c^{LYP} \quad (4.26)$$

where coefficients $a_{xc}$, $a_x$, $a_c$ are empirically determined.

4.2 Response Theory

Density functional response theory, i.e. response theory applied to the Kohn-Sham method, employs same basic principle as the response formalism [39] used in the framework of ab initio methods, which postulates that the time development of the time independent operator $\hat{A}$ in the presence of a time dependent perturbation $\hat{V}(t)$ acting on the system can be expressed

$$\langle 0 | \hat{A} | 0 \rangle = \langle 0 | \hat{A} | 0 \rangle + \int \langle \hat{A}; \hat{V}^{\omega_1} \rangle_{\omega_1} \exp(-i\omega_1 t) \, d\omega_1$$

$$+ \frac{1}{2} \int \int \langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle_{\omega_1,\omega_2} \exp(-i(\omega_1 + \omega_2)t) \, d\omega_1 d\omega_2 + \ldots \quad (4.27)$$

where $\langle 0 | \hat{A} | 0 \rangle$ is the expectation value of operator $\hat{A}$ for the unperturbed system, $\langle \hat{A}; \hat{V}^{\omega_1} \rangle_{\omega_1}$ is the linear, and $\langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle_{\omega_1,\omega_2}$ is the quadratic response functions, respectively. $\hat{V}^{\omega}$ is the time dependent perturbation $\hat{V}(t)$ in the frequency domain given by a Fourier transformation

$$\hat{V}(t) = \int_{-\infty}^{\infty} \hat{V}^{\omega} \exp(-i\omega t) \, d\omega \quad . \quad (4.28)$$

Therefore, the evolution of the expectation value of an operator $\hat{A}$ is fully described up to chosen order of perturbation by the corresponding response functions and the determination of the response functions is equivalent to the evaluation of corresponding molecular properties.

The DFT response methodology for the evaluation of molecular properties can be formulated in density matrix or second quantization domains. The second way, namely second quantization form of DFT response, is more general in a sense that it allows for a uniform treatment of time dependent and time independent perturbations. All calculations presented here have been carried out using the DFT response implementation based on the second quantization
formalism mentioned above. In the remaining part of this paragraph the basic principles of this formalism will be briefly described. The derivation of the response equations start from the time dependent Kohn-Sham equation

$$\left( \hat{H}(t) + \hat{V}(t) \right) |\tilde{0}\rangle = i \frac{d}{dt} |\tilde{0}\rangle$$  \hspace{1cm} \text{(4.29)}$$

where the Kohn-Sham (KS) Hamiltonian is defined via Kohn-Sham operators $f_\sigma(r, t)$ for spin orbitals and an explicit perturbation potential $v(r, t)$:

$$\hat{H}(t) + \hat{V}(t) = \sum \int d\tau \, \hat{\Psi}_\sigma^\dagger(r) \left[ f_\sigma(r, t) + v(r, t) \right] \hat{\Psi}_\sigma(r, t).$$  \hspace{1cm} \text{(4.30)}$$

In Eq. 4.30 the fermion field operator $\hat{\Psi}_\sigma(r)$ is restricted to spin orbitals with equal spatial parts

$$\hat{\Psi}_\sigma(r) = \sum_j \varphi_j(r) a_{j\sigma}$$  \hspace{1cm} \text{(4.31)}$$

and therefore employs optimized spin orbitals obtained by solution of spin restricted KS equations.

The time development of the Kohn-Sham determinant $|\tilde{0}\rangle$ is parametrized by the exponential operator

$$|\tilde{0}\rangle = \exp \left[ -\hat{\kappa}(t) \right] |0\rangle$$  \hspace{1cm} \text{(4.32)}$$

where $\hat{\kappa}(t)$ is an anti-Hermitian operator of the form

$$\hat{\kappa}(t) = \sum_{r,s} \kappa_{rs}(t) E_{rs}^\sigma = \sum_{r,s} \kappa_{rs}(t) a_{r\sigma}^\dagger a_{s\sigma}$$  \hspace{1cm} \text{(4.33)}$$

with variational parameters $\kappa_{rs}(t)$, which form the so-called orbital rotation matrix. It follows that the spin densities $\rho_\sigma(r)$ can be obtained from

$$\rho_\sigma(r, t) = \langle \tilde{0} | \hat{\rho}_\sigma(r) |\tilde{0}\rangle = \langle 0 | \exp[\hat{\kappa}(t)] \hat{\rho}_\sigma(r) \exp[-\hat{\kappa}(t)] |0\rangle$$  \hspace{1cm} \text{(4.34)}$$

where the electron spin-density operator is

$$\hat{\rho}_\sigma(r) = \hat{\Psi}_\sigma^\dagger(r) \hat{\Psi}_\sigma(r) = \sum_{pq} \varphi_p^* \varphi_q(r) E_{pq}^\sigma.$$  \hspace{1cm} \text{(4.35)}$$

The Ehrenfest principle for a one electron operator $\hat{Q}$ using Eq. 4.29 and Eq. 4.32 may be written as

$$\left\langle 0 \left| \left[ \hat{Q}, \exp[\hat{\kappa}(t)] \right] \left( \hat{H}(t) + \hat{V}(t) - i \frac{d}{dt} \exp[-\hat{\kappa}(t)] \right) \right| 0 \right\rangle = 0.$$  \hspace{1cm} \text{(4.36)}$$

This equation represents the time-dependent variational principle and allows to identify the linear response as well as higher order response functions with corresponding response equations through the expansion of $\hat{\kappa}(t)$ in order of the perturbation:

$$\hat{\kappa}(t) = \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + \ldots$$  \hspace{1cm} \text{(4.37)}$$

Inserting this expansion of variational parameters into Eq. 4.36 and collecting the terms at corresponding orders one can readily identify equations for the determination of the response functions.
4.2. RESPONSE THEORY

4.2.1 Linear response function

The linear response function can be obtained by keeping only first order term in Ehrenfest’s equation which in the frequency domain becomes

\[
\langle 0 \left| [\mathbf{q}, \hat{\kappa}^\omega, \hat{H}^{(0)} + \hat{H}^\omega] \right| 0 \rangle + \omega \langle 0 \left| [\mathbf{q}, \hat{\kappa}^\omega] \right| 0 \rangle = - \langle 0 \left| [\mathbf{q}, \hat{V}^\omega] \right| 0 \rangle \tag{4.38}
\]

where non-redundant excitation operators \( E_{pq}^\omega \) have been collected in the column vector \( \mathbf{q} \). The solution of Eq. 4.38 allows one to evaluate the linear response function for arbitrary one-electron operator \( \hat{A} \) in the presence of a perturbation \( \hat{V}^\omega \) acting on the molecular system in the following way

\[
\langle \hat{A}; \hat{V} \rangle_\omega = \langle 0 \left| [\hat{\kappa}^\omega, \hat{A}] \right| 0 \rangle . \tag{4.39}
\]

4.2.2 Quadratic response function

In a similar way, quadratic response equations can be obtained by allowing first and second order terms in \( \hat{\kappa}(t) \) to remain in Ehrenfest’s equation. Under these conditions quadratic response equation along with two accompanying linear response equations reads

\[
\langle 0 \left| \mathbf{q}, \hat{\kappa}^{\omega_1, \omega_2} + 2P_{12} \left[ \hat{\kappa}^{\omega_1}, \hat{H}^{\omega_2} + \hat{V}^{\omega_2} \right] + (\omega_1 + \omega_2) \hat{\kappa}^{\omega_1, \omega_2} \\
+ P_{12} \left[ \hat{\kappa}^{\omega_1, \omega_2}, \hat{H}^{(0)} \right] + (\omega_2 - \omega_1) \left[ \hat{\kappa}^{\omega_1}, \hat{\kappa}^{\omega_2} \right] \right| 0 \rangle = 0 \tag{4.40}
\]

\[
\langle 0 \left| \mathbf{q}, \hat{\kappa}^{\omega_1}, \hat{H}^{\omega_1} + \hat{H}^{\omega_1} \right| 0 \rangle \rangle + \omega \langle 0 \left| [\mathbf{q}, \hat{\kappa}^{\omega_1}] \right| 0 \rangle = - \langle 0 \left| [\mathbf{q}, \hat{V}^{\omega_1}] \right| 0 \rangle \tag{4.41}
\]

\[
\langle 0 \left| \mathbf{q}, \hat{\kappa}^{\omega_2}, \hat{H}^{\omega_2} + \hat{H}^{\omega_2} \right| 0 \rangle \rangle + \omega \langle 0 \left| [\mathbf{q}, \hat{\kappa}^{\omega_2}] \right| 0 \rangle = - \langle 0 \left| [\mathbf{q}, \hat{V}^{\omega_2}] \right| 0 \rangle \tag{4.42}
\]

where we introduced symmetrization operator

\[
P_{12}f(1)g(2) = \frac{f(1)g(2) + f(2)g(1)}{2}. \tag{4.43}
\]

The solution of Eq. 4.42 allows one to evaluate the quadratic response function for arbitrary one-electron operator \( \hat{A} \) in the presence of a perturbation \( \hat{V}^{\omega_1} \) and \( \hat{V}^{\omega_2} \) in the following way

\[
\langle \hat{A}; \hat{V}, \hat{V} \rangle_{\omega_1, \omega_2} = \langle 0 \left| [\hat{\kappa}^{\omega_1, \omega_2}, \hat{A}] \right| 0 \rangle + P_{12} \left[ \hat{\kappa}^{\omega_1}, \left[ \hat{\kappa}^{\omega_2}, \hat{A} \right] \right] \left| 0 \rangle \right. \tag{4.44}
\]
4.2.3 Spin symmetry in open-shell response theory

The linear and quadratic response equations for closed and open shell molecules [40, 41, 42] have the same basic form, but there are fundamental differences in the spin symmetry handling between the two cases. First of all, in open shell molecules single and double excitations are mixed (see Fig. 4.1) and can therefore not be strictly separated as in the case of closed shell molecules. This feature of open shell molecules have far reaching consequences for response theory methods, while the time evolution of the density operator using only single excitation operators has more restricted applicability. A more sophisticated description of the time evolution in open-shell molecules is thus needed.

Another important aspect of the linear and quadratic response formalisms in open-shell molecules is the treatment of spin-dependent (triplet) operators. Contrary to the case of closed shell molecules, triplet excitation operators do not generate excited states in open shell molecules with well defined spin symmetry, but produce instead mixed states with contributions from various multiplicities. This implies that Eqs. 4.38-4.42 in their present form can not be used for determination of molecular properties, which involves perturbations capable to couple the high spin ground state with excited states of different multiplicities,
as the excitation operators $\hat{q}$ lack correct symmetry adaptation. In view of the above outlined arguments it is evident that the handling of the triplet perturbations in the linear and quadratic response formalisms renders meaningful applications to complicated spin dependent molecular properties, like spin-orbit contributions to electronic spin-spin coupling constants.
Chapter 5

Evaluation of NMR and EPR parameters

Resulting from the dependence of molecular electronic energy on internal and external magnetic fields, the magnetic resonance parameters can be computed as second-order properties employing a perturbational approach. In the following, we use in the evaluation of parameters the density functional response formalism introduced in Sec. 4.2.

5.1 Relativistic effects on NMR parameters

NMR spin Hamiltonian parameters, the nuclear spin-spin coupling constants and the nuclear shieldings are sensitive to relativistic effects as they have large contributions coming from the atomic core region in the molecule. Generally, the relativistic effects on NMR tensors become non-negligible not only for the heavy element atom itself, but for the light element atoms in heavy elements compounds as well [24]. For example, relativistic effects in nuclear shieldings of proton is comparable in size to the whole range of proton chemical shifts. From a computational standpoint, calculations of the relativistic effect on nuclear shieldings can be most straightforwardly pursued by a fully relativistic four- or two-component approach, where scalar relativistic and spin-orbit interaction effects are incorporated in the wave function and the nuclear spin-spin coupling constants and the nuclear shieldings are evaluated as in conventional non-relativistic calculations using second order perturbation theory [43, 44, 45]. An alternative approach relies on the perturbational treatment of the relativistic corrections to the NMR parameters, which implies the use of third order perturbation theory in the evaluation of the nuclear shielding tensors [46, 47, 48].
5.1.1 Nuclear spin-spin coupling tensor

The theoretical evaluation of indirect nuclear spin-spin coupling constants (SSCC) allows one to connect rigorously these constants to the structural information about molecules, by using the dependence of SSCC on the electron density distribution and the arrangement of coupled nuclei in molecules. The indirect nuclear spin-spin coupling tensor $K_{MN}$ couples magnetic momenta of nuclei $M$ and $N$ through the electronic structure of the molecule, and it is determined in a perturbative treatment from the second derivative of the molecular electronic energy relative to the nuclear magnetic momenta:

$$K_{MN} = \frac{\partial^2 E}{\partial M_M \partial M_N} \bigg|_{M_M, M_N = 0} - D_{MN}$$ (5.1)

where $M_N = g_N \mu_p I_N$ is the magnetic dipole moment of nucleus $N$ with spin $I_N$ and nuclear $g$-factor $g_N$ ($\mu_p$ is the proton magneton). The direct nuclear spin–spin coupling tensor $D_{MN}$ which describes the classical interaction between the magnetic dipole moments $M_M$ and $M_N$ is subtracted from the energy derivative.

The non-relativistic description of the nuclear spin–spin coupling tensor for a singlet molecule consists of five contributions as shown by Ramsey [49, 50]

$$K_{MN} = K_{DSO}^{MN} + K_{PSO}^{PSO} + K_{FC/FC}^{MN} + K_{SD/SD}^{MN} + K_{FC/SD}^{MN}$$ (5.2)

which correspond to various ways of coupling two nuclear magnetic momenta via the electronic density of the molecule. The first term describes the coupling of the nuclear magnetic momenta by the nuclear diamagnetic spin-orbit operator $\hat{H}_{DSO}^{MN}$, and is evaluated as an expectation value over the ground state:

$$K_{DSO}^{MN} = \frac{\partial^2}{\partial M_M \partial M_N} \langle 0 | \hat{H}_{DSO}^{MN} | 0 \rangle$$ (5.3)

The remaining non-relativistic contributions are computationally more demanding as they are obtained using second-order perturbation theory, i.e. they involve explicit summations over singlet or triplet excited states. They can be expressed as linear response functions involving the paramagnetic nuclear spin-orbit interaction, or the hyperfine interactions, Fermi contact and the spin-dipole operators:

$$K_{PSO/PSO}^{MN} = \frac{\partial^2}{\partial M_M \partial M_N} \langle \hat{H}_{PSO}^M ; \hat{H}_{PSO}^N \rangle_0$$ (5.4)

$$K_{FC/FC}^{MN} = \frac{\partial^2}{\partial M_M \partial M_N} \langle \hat{H}_{FC}^M ; \hat{H}_{FC}^N \rangle_0$$ (5.5)

$$K_{SD/SD}^{MN} = \frac{\partial^2}{\partial M_M \partial M_N} \langle \hat{H}_{SD}^M ; \hat{H}_{SD}^N \rangle_0$$ (5.6)

$$K_{FC/SD}^{MN} = \frac{\partial^2}{\partial M_M \partial M_N} \left( \langle \hat{H}_{SD}^M ; \hat{H}_{FC}^N \rangle_0 + \langle \hat{H}_{SD}^N ; \hat{H}_{FC}^M \rangle_0 \right)$$ (5.7)
The expression in Eq. 5.2 for the indirect nuclear spin-spin coupling tensor in the non-relativistic limit of theory is exact up to forth order in the inverse speed of light. Eventual relativistic corrections to SSCC obtained by crossing particular terms in Breit-Pauli Hamiltonian are then of order $O(c^{-6})$. We limit our study to most important heavy element induced relativistic effects on SSCC, the spin-orbit (SO) corrections. These corrections are evaluated employing a recently implemented quadratic response formalism in the framework of DFT which is able to treat spin-independent, as well as spin-dependent perturbations. In the mentioned formalism, the relativistic corrections to SSCC are defined using the sum of one- and two-electron spin-orbit operator $\hat{H}^{SO}$:

$$K_{MN}^{FC/SO/PSO} = \frac{\partial^2}{\partial M_M \partial M_N} \langle \langle \hat{H}_M^{FC}; \hat{H}_N^{SO}; \hat{H}_N^{PSO} \rangle \rangle_{0,0}$$

$$K_{MN}^{SD/SO/PSO} = \frac{\partial^2}{\partial M_M \partial M_N} \langle \langle \hat{H}_M^{SD}; \hat{H}_N^{SO}; \hat{H}_N^{PSO} \rangle \rangle_{0,0}$$

(5.8)

(5.9)

where the sum-over-states expression of a quadratic response function for three operators $\hat{H}_1, \hat{H}_2, \hat{H}_3$ is defined as:

$$\langle \langle \hat{H}_1 ; \hat{H}_2 ; \hat{H}_3 \rangle \rangle_{0,0} = \sum_{k,m>0} \frac{\langle 0 | \hat{H}_1 | k \rangle \langle k | \hat{H}_2 | m \rangle - \delta_{km} \langle 0 | \hat{H}_2 | 0 \rangle \langle m | \hat{H}_2 | 0 \rangle}{(E_0 - E_k)(E_0 - E_m)} + \text{perm.}$$

(5.10)

### 5.1.2 Nuclear shielding tensor

The nuclear shielding tensor is the parameter of NMR spectroscopy which couples a nuclear magnetic momentum to the external magnetic field. It is calculated as described in Section 3.2.3 from the derivatives of the molecular Hamiltonian which cross to form terms bilinear in nuclear magnetic moment $M_N$ and external field $B$:

$$\sigma_N = \frac{\partial^2 E}{\partial M_N \partial B} \bigg|_{M_N,B=0}.$$ 

(5.11)

It was pointed out that in the non-relativistic limit, the shielding tensor is represented by the diamagnetic and the paramagnetic terms calculated as expectation value and linear response, respectively (see Eq. 3.27). Not all of the relativistic contributions of $O(c^{-4})$ listed in Eq. 3.28 have an important influence on the final shielding tensor. The terms that will be considered as entering the total nuclear shielding tensor, are the spin-orbit and the scalar relativistic corrections:

$$\sigma_N = \sigma_N^{nr} + \sigma_N^{so} + \sigma_N^{sr}.$$ 

(5.12)
In the evaluation of spin-orbit effects, the fact that one and two-electron spin-orbit operators have triplet symmetry has to be considered similarly to the case of nuclear spin-spin coupling constants. The mixing of singlet and triplet states in closed-shell molecules requires summation over all excited singlet and triplet states in the quadratic response functions of SSCC (Eqs. 5.8-5.9), or for the current parameter:

\[
\sigma_{N}^{\text{FC/SD/OZ}} = \frac{\partial^2}{\partial M_N \partial B} \langle \hat{H}_N^{\text{FC}}; \hat{H}_B^{\text{SO}}, \hat{H}_B^{\text{OZ}} \rangle_{0,0}
\]

(5.13)

\[
\sigma_{N}^{\text{SD/SD/OZ}} = \frac{\partial^2}{\partial M_N \partial B} \langle \hat{H}_N^{\text{SD}}; \hat{H}_B^{\text{SO}}, \hat{H}_B^{\text{OZ}} \rangle_{0,0}
\]

(5.14)

The hyperfine interaction \(\hat{H}^{\text{FC}}\) and \(\hat{H}^{\text{SD}}\) operators, also of triplet symmetry, are needed to preserve the singlet character of the response functions. We found that the employed response DFT implementation suffers from the so-called triplet-instability problem, as all DFT and HF methods do, i.e. it is not able to handle perturbation operators of triplet symmetry.

Scalar relativistic effects rise from the non-relativistic shielding terms, for whom states are perturbed by mass-velocity \(\hat{H}^{\text{mv}}\) and the one-electron Darwin \(\hat{H}^{\text{Dar}}\) corrections.

\[
\sigma_{N}^{p/mv+Dar} = \frac{\partial^2}{\partial M_N \partial B} \langle \hat{H}_N^{\text{pSO}}; \hat{H}_N^{\text{OZ}}, \hat{H}^{\text{mv}} + \hat{H}^{\text{Dar}} \rangle_{0,0}
\]

(5.15)

\[
\sigma_{N}^{d/mv+Dar} = \frac{\partial^2}{\partial M_N \partial B} \langle \hat{H}_N^{\text{dSO}}; \hat{H}^{\text{mv}}, \hat{H}^{\text{Dar}} \rangle_{0,0}
\]

(5.16)

The scalar relativistic effects are in general more important for the heavy nuclei, while the spin-orbit interaction contributes noticeably only to the shielding constants of light element atoms in heavy elements compounds.

### 5.2 Relativistic effects on electronic \(g\)-tensor

The electronic \(g\)-tensor plays a key role in EPR spectroscopy [13], being the fundamental parameter of the electronic Zeeman effect. The electronic \(g\)-tensor enters the EPR spin-Hamiltonian (Eq. 2.1) in a form like \(\mu_B S^T \cdot g \cdot B\), that allows one to operate with the following definition as second derivative of molecular electronic energy \(E\) with respect to the effective electronic spin \(S\) of a paramagnetic molecule and the external magnetic field \(B\)

\[
g = \frac{1}{\mu_B} \frac{\partial^2 E}{\partial S \partial B} \bigg|_{S,B=0}.
\]

(5.17)

One usually evaluates the \(g\)-shift tensor

\[
\Delta g = g - g_e 1
\]

(5.18)
5.2. RELATIVISTIC EFFECTS ON ELECTRONIC G-TENSOR

where the free electron g-factor \( g_e = 2.0023 \) is subtracted in order to account only for the effects of electrons interaction in the molecule. The \( g \)-shift tensor is conventionally evaluated using perturbation theory, implying that the molecular wave function is calculated for an isolated molecule and all relevant terms of the Breit-Pauli Hamiltonian are treated as perturbation operators.

To a first approximation we consider contributions proportional to the square of inverse speed of light \( c^{-1} \) and the \( g \)-shift can be written as

\[
\Delta g(O(c^{-2})) = \Delta g^{\text{RMC}} + \Delta g^{\text{GC}} + \Delta g^{\text{SO/OZ}}
\]

(5.19)

where the first term denotes the mass-velocity correction to electronic Zeeman effect and the last two terms are gauge and spin-orbit corrections, respectively. The \( \Delta g^{\text{RMC}} \) and \( \Delta g^{\text{GC}} \) terms are simply evaluated as the expectation value of \( \hat{H}^{\text{RMC}} \) and \( \hat{H}^{\text{GC}} \) operators

\[
\Delta g^{\text{RMC}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \langle 0 | \hat{H}^{\text{RMC}} | 0 \rangle
\]

(5.20)

\[
\Delta g^{\text{GC}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \langle 0 | \hat{H}^{\text{GC}} | 0 \rangle
\]

(5.21)

The evaluation of \( \Delta g^{\text{SO/OZ}} \) is more demanding as it requires a determination of linear response functions

\[
\Delta g^{\text{SO/OZ}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \langle \langle \hat{H}^{\text{SO}} ; \hat{H}^{\text{OZ}} \rangle \rangle_0
\]

(5.22)

The formulae described above for the electronic \( g \)-tensor calculations in paramagnetic molecules can be relatively easily treated in DFT theory using response or sum-over-states methods, but special attention is required as evaluation of the \( \Delta g^{\text{GC}} \) and \( \Delta g^{\text{SO}} \) shifts are dependent on two-electron operators while DFT is in essence a one-electron theory.

The leading relativistic corrections to the electronic \( g \)-tensor arise in perturbation theory by inclusion of scalar relativistic effects resulting in the increase of the order in \( c^{-1} \) for each term in Eq. 5.19:

\[
\Delta g_{\text{RMC/mv+Dar}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \left( \langle \langle \hat{H}^{\text{RMC}} ; \hat{H}^{\text{mv}} \rangle \rangle_0 + \langle \langle \hat{H}^{\text{RMC}} ; \hat{H}^{\text{Dar}} \rangle \rangle_0 \right)
\]

(5.23)

\[
\Delta g_{\text{GC/mv+Dar}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \left( \langle \langle \hat{H}^{\text{GC}} ; \hat{H}^{\text{mv}} \rangle \rangle_0 + \langle \langle \hat{H}^{\text{GC}} ; \hat{H}^{\text{Dar}} \rangle \rangle_0 \right)
\]

(5.24)

\[
\Delta g_{\text{SO/OZ/mv+Dar}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \left( \langle \langle \hat{H}^{\text{SO}} ; \hat{H}^{\text{OZ}} \rangle \langle \hat{H}^{\text{mv}} \rangle \rangle_{0,0} \right)
\]

(5.25)

From the enumerated terms, the last one \( \Delta g_{\text{SO/OZ/mv+Dar}} \) is expected to give major contributions to the total scalar relativistic correction. The evaluation of
CHAPTER 5. EVALUATION OF NMR AND EPR PARAMETERS

Eq. 5.25 requires the solution of a quadratic response equations which has become possible after the implementation of the spin restricted open shell quadratic response DFT (see Sec. 4.2). One more correction of fourth power in \( c^{-1} \) accounts for the coupling between the kinetic energy-corrected orbital Zeeman operator \( \hat{H}_{OZ-KE} \) and the spin-orbit interaction \( \hat{H}_{SO} \) [51]

\[
\Delta g^{OZ-KE/SO} = \frac{1}{\mu_B} \frac{\partial^2}{\partial S \partial B} \langle \hat{H}_{OZ-KE}; \hat{H}_{SO}^0 \rangle_0
\]  

(5.26)

Adding this term to the scalar relativistic corrections, we obtain the final equation for the evaluation of the relativistic \( g \)-shift tensor

\[
\Delta g(\mathcal{O}(c^{-4})) = \Delta g^{RMC/mv+Dar} + \Delta g^{GC/mv+Dar} + \Delta g^{SO/OZ/mv+Dar} + \Delta g^{OZ-KE/SO}
\]  

(5.27)

The calculations of \( g \)-tensors have been performed using a spin restricted DFT quadratic response formalism, the development and implementation of which is presented in paper III.

5.3 Hyperfine coupling tensor

The hyperfine coupling tensor parameterizes the electron-nuclear spin interaction, thus being derived from molecular electronic energy terms that are bilinear in electronic spin and nuclear spin. One defines the hyperfine coupling tensor relative to a magnetic nucleus \( N \), as the second derivative of molecular electronic energy with respect to total electronic \( S \), and nuclear \( I_N \) spins:

\[
A_N = \frac{\partial^2 E}{\partial S \partial I_N} \bigg|_{S, I_N = 0}.
\]  

(5.28)

In the non-relativistic limit the HFC tensor is determined by Fermi contact and classical spin-dipole interactions that occur between electronic spin and nuclear magnetic momenta. Averaging over molecular orientations, relevant for EPR experiments in solution, only the Fermi contact interaction produces a contribution to the total hyperfine couplings.

5.3.1 Generalized restricted-unrestricted approach

The simple formalism which allows for the evaluation of hyperfine coupling constants finds an impediment in the inability of various wave function models to describe properly the electronic spin polarization that is induced by the hyperfine interactions. The spin polarization arises from the fact that the unpaired electron interacts differently with the two electrons of a spin-paired bond or inner shell, because the exchange interaction is operative only for the electrons with parallel spins. It is well-known that spin polarization is over-estimated
5.3. HYPERFINE COUPLING TENSOR

by spin-unrestricted Hartree-Fock and DFT methods, as they introduce spin contamination of the electronic density, while in restricted approaches such as Hartree-Fock or multi-configurational self-consistent field (MCSCF) the spin polarization is not properly accounted for by the doubly occupied core orbitals. An alternative to these methods is the restricted-unrestricted (RU) approach, which is based on a spin restricted optimization of the wave function, followed by a spin unrestricted treatment in the presence of hyperfine perturbations. The method was introduced by Fernandez et al. [11] for HF/MCSCF wave functions, then extended to DFT by Rinkevicius et al. [12] it is not fully unrestricted; there is a neglect of singlet excitations of electrons when applying the perturbation. In order to examine the validity of this approximation, we implemented recently the so-called generalized restricted-unrestricted (GRU) approach, which accounts for all excitations of a single determinant self-consistent field DFT.

One assumes that hyperfine interactions represented by Fermi contact $\hat{H}_{N}^{FC}$, and spin-dipole $\hat{H}_{N}^{SD}$ operators, are applied adiabatically to the unperturbed Kohn-Sham Hamiltonian $\hat{H}^{KS}$:

$$\hat{H} = \hat{H}^{KS} + x(\hat{H}^{FC}_{N} + \hat{H}^{SD}_{N})$$

where $x$ is the perturbation strength. The response of molecular energy functional $E[\hat{\rho}, x]$, which is independent of nuclear spins for the unperturbed system, to the spin relaxation induced by the triplet symmetry operators in Eq. 5.29, may be evaluated from its first derivative with respect to $x$:

$$\frac{dE[\hat{\rho}, x]}{dx} = \frac{\partial E[\hat{\rho}, x]}{\partial x} + \int \frac{\partial E[\hat{\rho}, x]}{\partial \hat{\rho}} \frac{\partial \hat{\rho}}{\partial x} \, dr .$$

In the limit $x \to 0$, the first term in Eq. 5.30 corresponds to the expectation value of hyperfine interaction operators,

$$\frac{\partial E[\hat{\rho}, x]}{\partial x} \bigg|_{x=0} = \langle 0 | \hat{H}^{FC}_{N} | 0 \rangle + \langle 0 | \hat{H}^{SD}_{N} | 0 \rangle$$

while the last term in Eq. 5.30 represents the linear response to the perturbation, as it involves the first derivative of the electronic density with respect to perturbation strength $x$. The latter term vanishes only in the unrestricted case, when the optimization of the energy functional $E[\hat{\rho}, x]$ has been carried out with respect to both singlet and triplet rotations of the Kohn-Sham spin-orbitals.

It is the task of the DFT restricted-unrestricted approach to transform the energy functional to a variational form with respect to triplet rotations of spin-orbitals, which would allow one to evaluate the last term in Eq. 5.30 as the zero-frequency linear response function:

$$\int \frac{\delta E[\hat{\rho}, x]}{\delta \hat{\rho}} \frac{\partial \hat{\rho}}{\partial x} \, dr \bigg|_{x=0} = \langle \hat{H}^{KS} ; \hat{H}^{FC}_{N} \rangle_{0} + \langle \hat{H}^{KS} ; \hat{H}^{SD}_{N} \rangle_{0} .$$

(5.32)
With the constraint of keeping the energy triplet gradient constant $\tau$ the Lagrange multipliers $\pi$ and $\tau$ corresponding to the singlet and triplet spin-orbital rotation operators, are to be determined from the coupled equations:

$$
\begin{bmatrix}
\frac{\partial^2 E}{\partial \tau_i^2} & \frac{\partial^2 E}{\partial \pi_i} \\
\frac{\partial^2 E}{\partial \pi_i} & \frac{\partial^2 E}{\partial \tau_i^2}
\end{bmatrix}
\begin{bmatrix}
\pi \\
\tau
\end{bmatrix} = -
\begin{bmatrix}
0 \\
\tau
\end{bmatrix}.
$$

(5.33)

In Eq. 5.33 the mixing of singlet and triplet rotations prevents the singlet multipliers $\pi$ from vanishing, although the wave function was optimized with respect to singlet rotations of the Kohn-Sham spin-orbitals. This is the consequence of allowing the electronic density to respond in a completely spin-unrestricted fashion to triplet character perturbations.

We investigated in paper V whether this generalization provides noticeable improvements in the evaluation of hyperfine coupling constants by performing computations on the set of organic radicals and transition metal compounds previously studied by Rinkevicius et al. [12] within the approximation of the restricted-unrestricted approach. The Fermi contact and spin-dipole components of the hyperfine coupling tensor $A_N$ were calculated as sum of the expectation values of the corresponding hyperfine operators and spin polarization terms in the form of linear response functions accounting for the relaxation of electron density in the presence of perturbations:

$$
A_{FC}^{N} = \frac{\partial^2 E}{\partial S \partial I_N} \left(\langle 0 | \hat{H}_{FC}^{N} | 0 \rangle + \langle \hat{H}_{KS}^{N} ; \hat{H}_{FC}^{N} \rangle_0 \right) 
$$

(5.34)

$$
A_{SD}^{N} = \frac{\partial^2 E}{\partial S \partial I_N} \left(\langle 0 | \hat{H}_{SD}^{N} | 0 \rangle + \langle \hat{H}_{KS}^{N} ; \hat{H}_{SD}^{N} \rangle_0 \right) 
$$

(5.35)

Equations 5.34-5.35 provide all needed information on the HFC tensors of free radicals, while this might not be true for transition metal atoms where spin-orbit effects turn out to be non-negligible.

### 5.3.2 Spin-orbit corrections

Additional contributions to HFC tensor come from cross term between one- and two-electron spin-orbit operators $\hat{H}^{SO}$, and the paramagnetic spin-orbit operator $\hat{H}^{PSO}$. 

$$
A_{SO/PSO}^{N} = \frac{\partial^2 E}{\partial S \partial I_N} \langle \hat{H}^{SO} ; \hat{H}^{PSO} \rangle_0 
$$

(5.36)

The computational demands for the full evaluation of two-electron SO operator using Kohn-Sham orbitals become very large for reasonably sized systems of biological interest, such as the metal center models of azurin studied in paper VI. The alternative we used for the evaluation of one- and two-electron SO operator is the atomic mean-field approximation (AMFI) [52, 53], which was previously proved to give compatible results with the full SO operator for an extended set
of properties including EPR parameters. To conclude the section, the total hyperfine coupling tensor is calculated in the framework of restricted open shell density functional response formalism as the sum

$$A_N = A_{N}^{FC} + A_{N}^{SD} + A_{N}^{SO/PSO}$$

(5.37)

where Fermi contact and spin-dipole terms include spin polarization effects through the restricted-unrestricted method.
Chapter 6

Summary of Papers

Present thesis encloses the development of novel DFT methods and their application to computational investigations of NMR and EPR spectral parameters. The subject of the first project presented in this thesis is the relativistic corrections of the indirect nuclear spin-spin coupling constants. Only spin-orbit effects consistent with the sixth power of inverse speed of light are considered in paper I. The calculations were carried out employing perturbation theory of second order for the non-relativistic coupling constants and of third order in the evaluation of spin-orbit corrections. A recent implementation of quadratic response density functional theory was applied to two sets of homologous systems in order to account for heavy atom effects on the spin-spin couplings between light nuclei in the molecular systems. We observed for one of the compound series that the electronic structure facilitates an efficient coupling of proton spins via the spin-orbit interaction. Moreover, only by accounting for the relativistic corrections, the experimental spin-spin coupling constants may be explained for heavier members of the series. The performance of our DFT response implementation in the calculation of indirect nuclear spin-spin coupling constants proved to be better than satisfactory, providing accurate spin-orbit contributions comparable with electron-correlated \textit{ab initio} methods and a weak dependency of the results on the exchange-correlation functionals.

In paper II we employed the perturbation theory of third order to compute the nuclear shielding tensor corrected with spin-independent and spin-orbit contributions. We found the spin-orbit correction to be important for light element atoms in the series of hydrogen halides. For the heavy element atoms, scalar relativistic contributions are comparable in size with spin-orbit effects. For a particular exchange-correlation functional the employed methodology is proved to handle satisfactorily instabilities arising from the use of triplet symmetry operators in evaluation of properties. The approach presented in this paper is an alternative to conventional two-component DFT methods for evaluating nuclear shielding constants with spin-orbit and scalar relativistic corrections, but also a practical approach which can be applied to large molecular systems of experimental interest.
In Paper III we developed spin restricted quadratic density functional response formalism for evaluation of time-dependent and time-independent non-linear properties of molecules with a high spin ground state. The designed approach is capable to handle the arbitrary perturbations and various electric, magnetic and mixed properties. The presented formalism treats singlet and triplet perturbation on equal footing, but only in singlet excitation manifold i.e. excited states which differ from ground state by the multiplicity are not included in response equations. The implemented quadratic density functional response code have been benchmarked by performing sample calculations of static and dynamic hyperpolarizabilities of small Si$_{(3n+1)}$H$_{(6n+3)}$ (n=0,1,2) clusters, which mimic Si(111) surfaces with dangling bond defects. The results also indicate that the first hyperpolarizability tensor components of Si$_{(3n+1)}$H$_{(6n+3)}$ show ordering compatible with results of second harmonic generation measurements in SiO$_2$/Si(111) interface (see Fig. 6.1) and therefore support the hypothesis that silicon surface defects with dangling bonds are responsible for this phenomenon.

Figure 6.1: Second harmonic generation intensity profiles.
Apart from investigating first hyperpolarizabilities of $\text{Si}_{(3n+1)}\text{H}_{(6n+3)}$, we also employed described quadratic density functional response formalism in studies of relativistic effects in electronic g-tensors of dihalide anions $X_2^-$ ($X=\text{F,Cl,Br,I}$) \textbf{(Paper IV)}. The obtained results indicates that the scalar relativistic play only minor role in electronic g-tensor shifts and the higher order spin-orbit contributions are responsible for large negative parallel component of g-tensor shift in $\text{Br}_2$ and $\text{I}_2$. Apart from testing applicability of the density functional response formalism in \textbf{Paper IV}, we also correct inappropriate handling of spin symmetry in previous work on the same topic.

A partial solution to the problem of improper description of the electronic spin polarization is investigated in \textbf{paper V}. The determination of EPR parameters, of hyperfine coupling constant in particular, requires the correct spin polarization, which is regularly over-estimated by spin-unrestricted methods, while lacking in spin-restricted methods. We implemented a generalization of the restricted-unrestricted (RU) approach which aims to control these shortcomings by performing a spin-restricted optimization of the electron density before the hyperfine interactions perturb the system, allowing then the spin density to relax in order to account for spin polarization. The method is a generalization in the sense of a completely unrestricted response of the density to spin polarization induced by hyperfine operators. Unlike the present implementation, only triplet orbital rotations were permitted in previous implementations of RU at MCSCF and DFT levels of theory. The verification of this approximation was performed on organic radicals and transition metal compounds, and yielded that the account of singlet-triplet orbital rotations improves the RU results by less than one percent.

\textbf{Paper VI} presents calculations of electronic g-tensors and hyperfine coupling tensors for azurin model compounds. The well-known model of the blue copper active site consisting of the Cu center and the closest residues Gly45, His46, Cys112, His117, and Met121, were investigated along with six other extended models. In these models, Met13, Met44, Asn47, Thr113, and Ser118, are individually added and subsequently both the Asn47 and Thr113 amino acids. By these means we explore the paramagnetic influence of the copper center on the protein surrounding and examine the direct unpaired spin density delocalization and the spin polarization effect important for each of the models. The electronic g-tensor of blue copper proteins is well determined by experimentalists. Therefore, a good recovery of experimental values in theoretical calculations is a sensitive test on the quality of molecular models as well as of the theory used in the calculations. We generally notice a good correlation between calculated results and experimental data. The dominating component of the electronic g-tensor, here denoted as $g_{zz}$, was best reproduced in the IM+Thr113 model, wherein the population balance between the sulfur and copper molecular orbitals is close to the ideal 50\% - 50\%.
Figure 6.2: Active site of the azurin. Protein data bank entry - 4AZU.

The spin restricted linear response formalism combined with the restricted-unrestricted approach allows to separate the contributions coming from the direct unpaired spin density delocalization and the spin polarization effect for each of the calculated amino acids. The correspondence between calculated and the rather limited set of experimental data does, however, not follow a clear trend. Generally, the isotropic hyperfine coupling constants of the remote nitrogens $N_{e_2}$ and hydrogens $H_{e_2}$ of His46 and His117 (see Fig. 6.2) are not satisfactorily reproduced causing a poor total hyperfine coupling tensor. We attributed the failure in the description of these HFC constants to the comparatively small spin polarization contribution obtained. The examination of average and response contributions to the HFC tensor shows a large influence of the paramagnetic copper center on the coordinated ligands. Far away from the metal site this influence diminishes. Exceptions from this rule are the $N_{NH}$, $H_{NH}$, and $H_{\alpha}$ atoms in Asn47 and Thr113, for which the HFC constants are quite large. Different mechanisms of the paramagnetic influence have been detected. The large average term in HFC of $N_{NH}$ and $H_{\alpha}$ of Asn47 signifies that the major contribu-
tion is coming from the direct unpaired spin density delocalization assisted to a great extent by the imidazole ring of His46. On the other hand, the HFC of $H_{NH}$ has a spin polarization nature, because of the (Cys112) $S_{\cdot\cdot\cdot}H_{NH}$ (Asn47) hydrogen bond. The large paramagnetic influence of the copper center on Thr113 has previously been suggested experimentally and is now confirmed by our calculations. We found here that the calculated and experimental results correlate reasonably well.
Bibliography


