Theoretical Calculations of Heavy Atom Effects in Magnetic Resonance Spectroscopy

Corneliu I. Oprea

Theoretical Chemistry
School of Biotechnology
Royal Institute of Technology
Stockholm 2006
Abstract

This thesis presents quantum chemical calculations, applications of the response function formalism recently implemented within the framework of density functional theory (DFT) 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 (NMR) 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 \textit{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 and II.
- I participated in the implementation of code and performed a part of calculations in paper III.
- I participated in the analysis of results and in the preparation of manuscripts of all papers.
Acknowledgments

I would like to thank my supervisors Dr. Olav Vahtras and Prof. Hans Ågren for their guidance and constant support during the preparation of this work. I also thank Dr. Zilvinas Rinkevicius for the help he gave me in many aspects of my work. I express my gratitude to my close collaborators Lyudmyla Telyatnyk, Guangde Tu, and Prof. Kenneth Ruud. At last, I wish to thank all members of Theoretical Chemistry group at KTH for creating a stimulating and pleasant working environment.
## Contents

1 **Introduction** ..... 1

2 **Magnetic Resonance Spectroscopy** ..... 3
   2.1 The EPR spin Hamiltonian ..... 4
   2.2 The NMR spin Hamiltonian ..... 7

3 **Molecular Hamiltonian** ..... 11
   3.1 The Dirac Equation ..... 11
   3.2 The Breit-Pauli Hamiltonian ..... 12
      3.2.1 The Foldy-Wouthuysen transformations ..... 13
      3.2.2 Expansion of Hamiltonian terms ..... 14
      3.2.3 Field dependence of Hamiltonian terms ..... 14

4 **Magnetic Resonance Parameters** ..... 17
   4.1 Density Functional Response Theory ..... 17
   4.2 Relativistic corrections to NMR parameters ..... 19
      4.2.1 Nuclear spin-spin coupling tensor ..... 19
      4.2.2 Nuclear shielding tensor ..... 21
   4.3 Hyperfine coupling tensor ..... 22

5 **Summary of Papers** ..... 25
Biochemical processes are guided by the physical and chemical properties arising from the electronic molecular structure of participant compounds. Thorough investigations required for a comprehensive description of the electronic structure, may be carried out by means of magnetic resonance spectroscopy techniques. Techniques pertaining to electron paramagnetic resonance (EPR) spectroscopy are dedicated to 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]. 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 [4]. The behavior of nuclear spin in the case of nuclei possessing magnetic properties is studied with the help of nuclear magnetic resonance (NMR) spectroscopy. A successful application of NMR spectroscopy is the determination of geometrical structure of biomolecules by analysis of dipolar shifts [5]. However, it is difficult to accomplish the analysis of experimental results in most cases which EPR and NMR spectra have very complicated structure. The evaluation of magnetic resonance parameters by quantum chemistry methods offers the possibility of reliably connecting the EPR and NMR spectra to the electronic molecular structure, with the help of spectral parameters.

Past decades have witnessed important steps in the development of methods to provide accurate wave function and molecular properties, including EPR and NMR parameters. However, the study of heavy element compounds and compounds with large number of atoms is often hampered by the present computing capabilities. This shortcoming becomes more obvious for the heavy atom compounds which experience important relativistic effects [6] with increasing mass of elements, since the treatment of these effects requires more
computationally demanding algorithms. To overcome this problem, physically justified approximations to the full treatment have to be employed. Although significant progress has been made over the past years, there are still possibilities for further improvement of methods in this direction. The work presented in this thesis contributes to this area of quantum chemistry and consists of development, implementation and applications of density functional response theory methods for calculation of EPR and NMR parameters including the heavy atom effects.

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 is neglected by spin-restricted methods. We seek to address this issue by employing a version of the so-called restricted-unrestricted (RU) approach [7], 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 generalization of the implementation of RU method at DFT level of theory [8] which accounts for the full unrestricted response of the system to hyperfine perturbations.
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 the molecules [9].

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 dipole interactions or indirectly via interactions with the 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.

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

\[ \hat{H}_{\text{ESR}} = \mu_B S^T \cdot g \cdot B + \sum_{N} S^T \cdot A_N \cdot I_N + S^T \cdot D \cdot S \]  

(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 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 more than one unpaired electrons. The corresponding parameter is named 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 [9]. 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, \( g \) represents 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 \( \mathcal{H}_{\text{EPR}}^{\text{iso}} \), we represent 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: \( m_S = \pm \frac{1}{2} = m_I \). There are four linearly independent spin states in this basis, denoted for convenience as

\[
\left\{|m_S, m_I\rangle\right\}_{m_S, m_I = \pm \frac{1}{2}} = \{|\uparrow, \uparrow\rangle, |\uparrow, \downarrow\rangle, |\downarrow, \uparrow\rangle, |\downarrow, \downarrow\rangle\}. \tag{2.3}
\]

To evaluate the \( \mathcal{H}_{\text{EPR}}^{\text{iso}} \) 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,

\[
S_\pm = S_x \pm iS_y \tag{2.4}
\]
\[
I_\pm = I_x \pm iI_y. \tag{2.5}
\]

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:

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

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

\[
\begin{pmatrix}
\frac{1}{2}g\mu_B B + \frac{1}{4}A & 0 & 0 & 0 \\
0 & \frac{1}{2}g\mu_B B - \frac{1}{4}A & \frac{1}{2}A & 0 \\
0 & \frac{1}{2}A & -\frac{1}{2}g\mu_B B - \frac{1}{4}A & 0 \\
0 & 0 & 0 & -\frac{1}{2}g\mu_B B + \frac{1}{4}A
\end{pmatrix}. \tag{2.7}
\]

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

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

$$E_1 = \frac{1}{2} g \mu_B B + \frac{1}{4} A$$

$$E_2 = \frac{1}{2} g \mu_B B \sqrt{1 + \tan^2(2\theta)} - \frac{1}{4} A$$

$$E_3 = -\frac{1}{2} g \mu_B B \sqrt{1 + \tan^2(2\theta)} - \frac{1}{4} A$$

$$E_4 = -\frac{1}{2} g \mu_B B + \frac{1}{4} A.$$

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.

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 $A_{iso} < < g_{iso} \mu_B B$, the allowed EPR transitions
of this system are between states $|1\rangle$ ↔ $|3\rangle$ and states $|2\rangle$ ↔ $|4\rangle$ (see Fig. 2.1). The frequencies of these transitions can be computed from Eqs. 2.12-2.15 as:

$$E_1 - E_3 \approx g\mu_B B + \frac{1}{2} A$$

$$E_2 - E_4 \approx g\mu_B B - \frac{1}{2} A$$

yielding that the separation between the two transitions equals the hyperfine coupling constant $A$. Additionally, within 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:

$$|\langle 1|S_x|3\rangle|^2 = |\langle 2|S_x|4\rangle|^2 = \cos^2 \theta .$$

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.

## 2.2 The NMR spin Hamiltonian

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:

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

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:

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

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 $|m_1, m_2\rangle = |I_1, m_{I_1}\rangle|I_2, m_{I_2}\rangle$, 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:

$$\hat{\mathcal{H}}_{\text{NMR}}^{\text{iso}} = -\mu_p g_n (1 - \sigma)(I_{z1} + I_{z2})B + K \left[ \frac{1}{2}(I_{+1}I_{-2} + I_{-1}I_{+2}) + I_{z1}I_{z2} \right]. \quad (2.21)$$

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

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

As one expected, 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:
2.2. THE NMR SPIN HAMILTONIAN

\[ |1\rangle = |\uparrow, \uparrow\rangle \]
\[ |2\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle \right) \]
\[ |3\rangle = \frac{1}{\sqrt{2}} \left( -|\uparrow, \downarrow\rangle + |\downarrow, \uparrow\rangle \right) \]
\[ |4\rangle = |\downarrow, \downarrow\rangle . \]

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:

\[ E_1 = -\mu_p g_n (1 - \sigma) B + \frac{1}{4} K \]
\[ E_2 = \frac{1}{2} |K| - \frac{1}{4} K \]
\[ E_3 = -\frac{1}{2} |K| - \frac{1}{4} K \]
\[ E_4 = \mu_p g_n (1 - \sigma) B + \frac{1}{4} K . \]

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:

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

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 \( S_x \) operator, taken between the states of respective transitions. The intensities of transitions are all equal to

\[ |\langle 1 | S_x | 2 \rangle|^2 = \frac{1}{2} . \]

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.
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 [10] 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 [9, 11]. 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 because of a strong spin-orbit coupling [6].

### 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 [10] linear in both the time derivative
and momentum $\mathbf{p}$
\[ i\hbar \frac{\partial \Phi}{\partial t} = (c \mathbf{\alpha} \cdot \mathbf{p} + mc^2 \beta)\Phi . \] (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
\[ \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \] (3.2)

with the help of spin one-half Pauli matrices:
\[ \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} . \] (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[12], which describes the electron-electron interaction to second order in inverse speed of light. Thus, we will consider the following expression for the so-called relativistic Dirac-Coulomb-Breit (DCB) Hamiltonian:
\[ \hat{H}_{DCB} = \sum_i \hat{H}^D_i + \sum_{i>j} \frac{e^2}{r_{ij}} + \sum_{i>j} \hat{H}^B_{ij} \] (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 [13] term corrected for retardation:
\[ \hat{H}^B_{ij} = -\frac{e^2}{2} \left[ \frac{\mathbf{\alpha}_i \cdot \mathbf{\alpha}_j}{r_{ij}} + \frac{(\mathbf{\alpha}_i \cdot \mathbf{r}_{ij})(\mathbf{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^3} \right] . \] (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[14] 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

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

(3.6)

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

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

(3.7)

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

(3.8)

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

\[ \mathbf{\pi} = \mathbf{p} + e\mathbf{A} \]  

(3.9)

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[14] that the exponential transformation

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

(3.10)

has this property for

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

(3.11)

i.e. the transformed Hamiltonian can be written

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

(3.12)

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

$$\mathcal{E} = \mathcal{E}^{(2)}.$$  

(3.13)

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

$$\mathcal{O} = \mathcal{O}^{(1)} + \mathcal{O}^{(3)}.$$  

(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

$$\mathbf{A} = \mathbf{A}^{(0)} + \mathbf{A}^{(2)} = \frac{1}{2} \mathbf{B} \times \mathbf{r} + \sum_N \frac{\mu_0}{4\pi} \mathbf{M}_N \times \mathbf{r}_N$$  

(3.15)

where $\mathbf{r}$ is the field point relative to a gauge origin, $\mu_0$ is the magnetic permeability in vacuum, and $\mathbf{r}_N$ is the position of nuclear $N$ with magnetic dipole moment $\mathbf{M}_N = g_N \mu_p \mathbf{I}_N$. 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

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

(3.16)

where

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

(3.17)

$$\hat{H}^{(2)} = mc^2 \left( \beta \left[ \mathcal{O}^{(1)}, \mathcal{O}^{(3)} \right]_+ + \beta \frac{\mathcal{O}^{(1)}^4}{8} - \frac{1}{8} \left[ \mathcal{O}^{(1)}, \left[ \mathcal{O}^{(1)}, \mathcal{O}^{(2)} \right] \right] \right).$$  

(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 [15]:

$$\hat{H}^{(k)}(\mathbf{B}, \mathbf{I}_N) = \hat{H}_0^{(k)} + \hat{\mathbf{H}}_B^{(k)} \cdot \mathbf{B} + \sum_N \hat{\mathbf{H}}_{I_N}^{(k)} \cdot \mathbf{I}_N + \frac{1}{2} \mathbf{B} \cdot \hat{\mathbf{H}}_{BB}^{(k)} \cdot \mathbf{B}$$  

(3.19)

$$+ \sum_N \mathbf{I}_N \cdot \hat{\mathbf{H}}_{I_NB}^{(k)} \cdot \mathbf{B} + \sum_{M > N} \mathbf{I}_M \cdot \hat{\mathbf{H}}_{IMI_N}^{(k)} \cdot \mathbf{I}_N.$$  

(3.20)
The lowest order derivatives of the Hamiltonian are then given by

\[ \hat{H}_0^{(0)} = \frac{\mathbf{p}^2}{2m} - e\phi \quad \text{(3.21)} \]
\[ \hat{H}_B^{(0)} = \frac{e}{2m}(\ell + 2\mathbf{S}) = \hat{H}^{OZ} + \hat{H}^{SZ} \quad \text{(3.22)} \]

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 \( \mathbf{S} \) 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:

\[ \hat{H}_{1N}^{(2)} = \frac{e}{m} \frac{\mu_0}{4\pi} \gamma_N \frac{\mathbf{r}_N \times \mathbf{p}}{r_N^3} + \frac{e}{m} \mathbf{S} \cdot \mathbf{B}_1N = \hat{H}^{PSO} + \hat{H}^{FC} + \hat{H}^{SD} \quad \text{(3.23)} \]
\[ \hat{H}_{B1N}^{(2)} = \frac{e^2\hbar}{m} \frac{\mu_0}{4\pi} \frac{(\mathbf{r}_N \cdot \mathbf{r})\mathbf{1} - \mathbf{r}\mathbf{r}}{r_N^3} = \hat{H}^{DSO}. \quad \text{(3.24)} \]

Eq. (3.23) is a vector property and Eq. (3.24) is a tensor property, where \( 1 \) 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

\[ \mathbf{B}_1N = \frac{\mu_0}{4\pi} \left( \frac{8\pi}{3} \delta_N(r_N) + \frac{3r_Nr_N - r^2}{r_N^5} \mathbf{1} \right). \quad \text{(3.25)} \]

Other Hamiltonian operators of the same order include

\[ \hat{H}_0^{(2)} = -\frac{\mathbf{p}^4}{8m^3c^2} + \frac{e\hbar^2}{8m^2c^2} (\nabla \cdot \mathbf{E}) + \frac{e}{2m^2c^2} \mathbf{S} \cdot \mathbf{E} \times \mathbf{p} \]
\[ = \hat{H}_{mv}^{(2)} + \hat{H}_{Dar}^{(2)} + \hat{H}_{SO1}^{(2)} \quad \text{(3.26)} \]

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 [15]

\[ \sigma_N^{(2)} = \langle \tilde{H}_{NB}^{(2)} \rangle + \langle \langle \tilde{H}_N^{(2)}; \tilde{H}_B^{(0)} \rangle \rangle \quad \text{(3.27)} \]
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

$$
\sigma^{(4)}_N = \langle \hat{H}^{(4)}_{NB} + \langle \hat{H}^{(2)}_{NB}; \hat{H}^{(0)}_0 \rangle + \langle \hat{H}^{(4)}_N; \hat{H}^{(0)}_B \rangle + \langle \hat{H}^{(0)}_N; \hat{H}^{(2)}_B \rangle + \langle \hat{H}^{(2)}_N; \hat{H}^{(2)}_B; \hat{H}^{(2)}_0 \rangle \rangle
$$

(3.28)

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

The main aim of this thesis is to study 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

Magnetic Resonance Parameters

4.1 Density Functional Response Theory

Since its birth in 1964 [16], Density Functional Theory (DFT) has come a long way from being a modeling tool primarily used by physicists to its current status as the most widely applied quantum chemistry approach for determining electronic structure and properties of various compounds. However, early attempts to use DFT for the description of molecular systems were rather disappointing due to poor description of chemical bonding by exchange-correlation functionals available at that time [17, 18, 19]. Only in the 1990’s with the development of more accurate exchange-correlation functionals [20], the first successful applications of DFT for the investigation of molecular electronic structure began to appear. Inspired by this success, a rapid development of exchange–correlation functionals followed and as results of these efforts DFT methods emerged as 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 inherent capability to include a large part of the dynamic electron correlation via the exchange-correlation functional, something that 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. Despite these achievements, evaluation of molecular properties remained mostly in domain of \textit{ab initio} quantum chemistry methods and only with recent extension of response theory to the Kohn-Sham [21] method, the first reliable methodologies for performing calculations of this kind have been developed and implemented.

Density functional response theory i.e. response theory applied to the Kohn-Sham method, employ same basic principle as the response formalism [22] used in the framework of \textit{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

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

(4.1)

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

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

(4.2)

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

$$(\hat{H}(t) + \hat{V}(t))|\hat{0}\rangle = i \frac{d}{dt} |\hat{0}\rangle$$

(4.3)

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

$$\hat{H}(t) + \hat{V}(t) = \sum_\sigma \int d\tau \hat{\Psi}_\sigma^\dagger(r) [f_\sigma(r, t) + v(r, t)] \hat{\Psi}_\sigma(r, t) .$$

(4.4)

In Eq. 4.4 the fermion field operator $\hat{\Psi}_\sigma(r)$ is restricted to spin orbitals with equal spatial parts

$$\hat{\Psi}_\sigma(r) = \sum_j \varphi_j(r) a_{j\sigma}$$

(4.5)

and therefore employs optimized spin orbitals obtained by solution of spin restricted KS equations. The time development of the Kohn-Sham determinant $|\hat{0}\rangle$ is parametrized by the exponential operator

$$|\hat{0}\rangle = \exp [-\hat{\kappa}(t)] |0\rangle$$

(4.6)

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

$$\hat{\kappa}(t) = \sum_{r\sigma} \kappa_{rs}(t) E_{r\sigma}^\sigma \equiv \sum_{r\sigma} \kappa_{rs}(t) a_{r\sigma}^\dagger a_{s\sigma}$$

(4.7)
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

$$\rho_\sigma(r, t) = \langle 0 | \hat{\rho}_\sigma(r) | 0 \rangle = \langle 0 | \exp[\hat{\kappa}(t)] \rho_\sigma(\vec{r}) \exp[-\hat{\kappa}(t)] | 0 \rangle$$

(4.8)

where the electron spin-density operator is

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

(4.9)

The Ehrenfest principle for a one electron operator $\hat{Q}$ using Eq. 4.3 and Eq. 4.6 may be written as

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

(4.10)

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:

$$\hat{\kappa}(t) = \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + \ldots$$

(4.11)

Inserting this expansion of variational parameters into Eq. 4.10 and collecting the terms at corresponding orders one can readily identify equations for the determination of the response functions. The linear response function can be obtained by keeping only first order term in Ehrenfest’s equation which in the frequency domain becomes

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

(4.12)

where non-redundant excitation operators $E_{pq}^\sigma$ have been collected in the column vector $\hat{q}$. The solution of Eq. 4.12 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

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

(4.13)

In a similar way, quadratic response equations can be obtained and formulae for the evaluation of properties described by the quadratic response function can be derived.

### 4.2 Relativistic corrections to NMR parameters

#### 4.2.1 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:

$$K_{MN} = \frac{\partial^2 E}{\partial M_M \partial M_N} \bigg|_{M_M, M_N=0} - D_{MN}$$  \hspace{1cm} (4.14)

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 [23]

$$K_{MN} = K_{MN}^{DSO} + K_{MN}^{PSO/PSO} + K_{MN}^{FC/FC} + K_{MN}^{SD/SD} + K_{MN}^{FC/SD}$$  \hspace{1cm} (4.15)

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 $\hat{H}_{MN}^{DSO}$, and is evaluated as an expectation value over the ground state:

$$K_{MN}^{DSO} = \langle 0 | \hat{H}_{MN}^{DSO} | 0 \rangle.$$  \hspace{1cm} (4.16)

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:

$$K_{MN}^{PSO/PSO} = \langle \hat{H}_M^{PSO} ; \hat{H}_N^{PSO} \rangle_0$$  \hspace{1cm} (4.17)

$$K_{MN}^{FC/FC} = \langle \hat{H}_M^{FC} ; \hat{H}_N^{FC} \rangle_0$$  \hspace{1cm} (4.18)

$$K_{MN}^{SD/SD} = \langle \hat{H}_M^{SD} ; \hat{H}_N^{SD} \rangle_0$$  \hspace{1cm} (4.19)

$$K_{MN}^{FC/SD} = \langle \hat{H}_M^{SD} ; \hat{H}_N^{FC} \rangle_0 + \langle \hat{H}_N^{SD} ; \hat{H}_M^{FC} \rangle_0.$$  \hspace{1cm} (4.20)

The expression in Eq. 4.15 for the indirect nuclear spin-spin coupling tensor in the non-relativistic limit of theory is exact up to fourth 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 $\hat{H}^{SO}$:

\[ K_{MN}^{FC/SO/PSO} = \langle \hat{H}^{FC}_M; \hat{H}^{SO}_N, \hat{H}^{PSO}_M \rangle_{0,0} + \langle \hat{H}^{FC}_N; \hat{H}^{SO}_M, \hat{H}^{PSO}_M \rangle_{0,0} \quad (4.21) \]

\[ K_{MN}^{SD/PSO} = \langle \hat{H}^{SD}_M; \hat{H}^{SO}_N, \hat{H}^{PSO}_M \rangle_{0,0} + \langle \hat{H}^{SD}_N; \hat{H}^{SO}_M, \hat{H}^{PSO}_M \rangle_{0,0} \quad (4.22) \]

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

\[ \langle \hat{H}_1; \hat{H}_2, \hat{H}_3 \rangle_{0,0} = \sum_{k,m>0} \frac{(0|\hat{H}_1|k) \left( \langle k|\hat{H}_2|m \rangle - \delta_{km} \langle 0|\hat{H}_2|0 \rangle \right) \langle m|\hat{H}_3|0 \rangle}{(E_0 - E_k)(E_0 - E_m)} + \text{perm.} \quad (4.23) \]

### 4.2.2 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 $\mathbf{M}_N$ and external field $\mathbf{B}$:

\[ \sigma_N = \frac{\partial^2 E}{\partial M_N \partial B} \bigg|_{M_N = B = 0}. \quad (4.24) \]

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 $\mathcal{O}(c^{-4})$ 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:

\[ \sigma_N = \sigma_N^{nr} + \sigma_N^{so} + \sigma_N^{sr}. \quad (4.25) \]

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. 4.21,4.22), or for the current subject:

\[ \sigma_N^{SO/FC+SD} = \langle \hat{H}^{FC}_N + \hat{H}^{SD}_N; \hat{H}^{SO}_N, \hat{H}^{OZ}_B \rangle_{0,0}. \quad (4.26) \]

The hyperfine interaction $\hat{H}^{FC}$ and $\hat{H}^{SD}$ 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 $\hat{H}^{mv}$ and the one-electron Darwin $\hat{H}^{Dar}$ corrections.

$$p = mv + \hat{H}^{Dar}$$

$$d = mv + \hat{H}^{Dar}$$

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.

### 4.3 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:

$$\mathbf{A}_N = \left. \frac{d^2 E}{dSdI_N} \right|_{S,I_N=0}$$

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 coupling constant. 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. It is well-known that spin polarization is over-estimated 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. [7] for HF/MCSCF wave functions, and extended to DFT by Rinkevicius et al. [8] it was not fully unrestricted; there was a neglect of singlet excitations
4.3. HYPERFINE COUPLING TENSOR

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 $\hat{H}_{FC}$, and spin-dipole $\hat{H}_{SD}$ operators, are applied adiabatically to the unperturbed Kohn-Sham Hamiltonian $\hat{H}_{KS}$:

$$\hat{H} = \hat{H}_{KS} + x(\hat{H}_{FC} + \hat{H}_{SD})$$  \hspace{1cm} (4.30)

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. (4.30), may be evaluated from its first derivative with respect to $x$:

$$\frac{dE[\hat{\rho}, x]}{dx} = \frac{\partial E[\hat{\rho}, x]}{\partial x} + \int \frac{\partial E[\hat{\rho}, x]}{\partial \hat{\rho}} \frac{\partial \hat{\rho}}{\partial x} d\mathbf{r} .$$  \hspace{1cm} (4.31)

In the limit $x \to 0$, the first term in Eq. (4.31) corresponds to the expectation value of hyperfine interaction operators,

$$\frac{\partial E[\hat{\rho}, x]}{\partial x}\bigg|_{x=0} = \langle 0 | \hat{H}_{FC} + \hat{H}_{SD} | 0 \rangle$$  \hspace{1cm} (4.32)

while the last term in Eq. (4.31) 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. (4.31) as the zero-frequency linear response function:

$$\int \frac{\delta E[\hat{\rho}, x]}{\delta \hat{\rho}} \frac{\partial \hat{\rho}}{\partial x} d\mathbf{r} \bigg|_{x=0} = \langle \hat{H}_{KS}; \hat{H}_{FC} + \hat{H}_{SD} \rangle_0 .$$  \hspace{1cm} (4.33)

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:

$$\begin{bmatrix}
\frac{\partial^2 E}{\partial \hat{\rho}^2} & \frac{\partial^2 E}{\partial \hat{\rho} \partial \xi} \\
\frac{\partial^2 E}{\partial \hat{\rho} \partial \xi} & \frac{\partial^2 E}{\partial \xi^2}
\end{bmatrix}
\begin{bmatrix}
\pi \\
\tau
\end{bmatrix} = -\begin{bmatrix}
0 \\
\tau
\end{bmatrix} .$$  \hspace{1cm} (4.34)

In Eq. (4.34) 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 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. [8] within the approximation of the restricted-unrestricted approach.
Chapter 5

Summary of Papers

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 this 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.

A partial solution to the problem of improper description of the electronic spin polarization is investigated in paper III. The determination of EPR pa-
parameters, of hyperfine coupling constant in particular require 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 the approximation of neglecting singlet-triplet orbital rotations, was performed on organic radicals and transition metal compounds, and yielded that the RU results differ by less than one percent from the generalized approach results.
Bibliography


