Density Functional Studies of EPR and NMR Parameters of Paramagnetic Systems

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Akademisk avhandling

som med tillstånd av Kungliga Tekniska Högskolan i Stockholm framlägges till offentlig granskning för avläggande av teknologie doktorsexamen, fredagen den 6 oktober 2006, kl. 10.00 i FD5, AlbaNova, Stockholm.
Avhandlingen försvaras på engelska.

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Abstract

Experimental methods based on the magnetic resonance phenomenon belong to the most widely used experimental techniques for investigations of molecular and electronic structure. The difficulty with such experiments, usually a proper interpretation of data obtained from high-resolution spectra, opens new challenges for pure theoretical methods. One of these methods is density functional theory (DFT), that now has an advanced position among a whole variety of computational techniques. This thesis constitutes an effort in this respect, as it presents theory and discusses calculations of electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) parameters of paramagnetic molecules. It is known that the experimental determination of the magnetic resonance parameters of such molecules, especially in the case of NMR, is quite complicated and requires special techniques of spectral detection. On the other hand, paramagnetics play an important role in many areas, such as molecular magnets, active centers in biological systems, and defects in inorganic conductive materials. Therefore, they have spurred great interest among experimentalists, motivating us to facilitate the interpretation of spectral data through theoretical calculations. This thesis describes new methodologies for the determination of magnetic properties of paramagnetic molecules in the framework of DFT, which have been developed in our laboratory, and their applications in calculations of a wide range of molecular systems.

The first two papers of this thesis deal with the theoretical determination of NMR parameters, such as nuclear shielding tensors and chemical shifts, in paramagnetic nitroxides that form core units in molecular magnets. The developed methodology is aimed to realize a high calculational accuracy for these systems. The effects of hydrogen bonding are also described in that context. Our theory for the evaluation of nuclear shielding tensors in paramagnetic molecules is consistent up to second order in the fine structure constant and considers orbital, fully anisotropic dipolar, and isotropic contact contributions to the shielding tensor.

The next projects concern electron paramagnetic resonance. The well-known EPR parameters, such as the g-tensors and the hyperfine coupling constants are explored. Calculations of electronic g-tensors were carried out in the framework of a spin-restricted open-shell Kohn-Sham method combined with the linear response theory recently developed in our laboratory and allowing us to avoid by definition the spin-contamination problem. The inclusion of solvent effects, described by the polarizable continuum model, extends the possibility to treat molecular systems often investigated in solution. For calculations of the hyperfine coupling constants a so-called restricted-unrestricted approach to account for the spin polarization effect has been developed in the context of DFT. To examine the validity of the approximations implicit in this scheme, the neglect

of singlet operators, a generalized RU methodology was implemented, which includes a fully unrestricted treatment with both singlet and triplet operators. The small magnitude of the changes in hyperfine coupling constants confirms the validity of the original scheme.

Acknowledgments

I would like to express my sincere gratitude to my supervisor Dr. Olav Vahtras, who supported me in many respects with kind understanding and helped with big and small things. Thank you for all of that!

I warmly thank the chief of Laboratory of Theoretical Chemistry Prof. Hans Ågren for allowing me to think and to do a lot by myself, but pointing my research in the right direction.

I wish to thank my university teacher in Quantum Chemistry Prof. Boris Minaev who introduced me into this area of science.

A lot of thanks to my colleague Dr. Zilvinas Rinkevicius for all good work together.

Many thanks to my office neighbor Corneliu Oprea for the scientific as well as non-scientific discussions.

I am grateful to my collaborators Dr. Juha Vaara and Prof. Kenneth Ruud. I also would like to thank all members of the Theoretical Chemistry group.

And finally, all of my heart belongs to little daughter Anastasia, my husband Pavel and my parents.

List of papers included in the thesis

Paper I. Z. Rinkevicius, J. Vaara, L. Telyatnyk and O. Vahtras, **Calculations of nuclear magnetic shielding in paramagnetic molecules.** *J. Chem. Phys.*, **118**, 2550-2561 (2003).

Paper II. L. Telyatnyk, J. Vaara, Z. Rinkevicius and O. Vahtras, **Influence of hydrogen bonding in the paramagnetic NMR spectra of nitronylnitroxide derivative molecules.** *J. Phys. Chem. B*, **108**, 1197 (2004).

Paper III. Z. Rinkevicius, L. Telyatnyk, P. Salek, O. Vahtras and H. Ågren, **Restricted density functional linear response theory calculations of electronic g-tensors.** *J. Chem. Phys.*, **119**, 10489 (2003).

Paper IV. Z. Rinkevicius, L. Telyatnyk, K. Ruud and O. Vahtras, **Electronic g-tensors of solvated molecules: application of the polarizable continuum model.** *J. Chem. Phys.*, **121**, 5051 (2004).

Paper V. Z. Rinkevicius, L. Telyatnyk, O. Vahtras and H. Ågren, **Density functional theory for hyperfine coupling constants with the restricted-unrestricted approach.** *J. Chem. Phys.*, **121**, 7614 (2004).

Paper VI. C. Oprea, L. Telyatnyk, Z. Rinkevicius, O. Vahtras and H. Ågren, **Time-dependent density functional theory with the generalized restricted-unrestricted approach.** *J. Chem. Phys.*, **124**, 174103 (2006).

Paper VII. L. Telyatnyk, C. Oprea, Z. Rinkevicius and O. Vahtras, **Density functional theory for spin Hamiltonian parameters of azurin. Part I. EPR parameters.** *in manuscript*, (2006).

Paper VIII. Z. Rinkevicius, L. Telyatnyk and O. Vahtras, **Restricted density functional response theory for open-shell systems.** *Adv. Quant. Chem. (ed. Hans Jensen)*, vol. 50, 231 (2005).

My contribution to the papers in the thesis

- I carried out the calculations of nuclear shielding tensors of small main-group organic molecules using the DALTON code and participated in the preparation of the manuscript for paper I.

- I proposed the subject and a way of realization of the investigation presented in paper II, and carried out all calculations using the Gaussian 98 code. I was responsible for the preparation of the manuscript.

- I performed all calculations of the main group radicals and, partly, of the transition metal compounds in paper III and participated in the preparation of the manuscript.

- In paper IV all calculations using the Gaussian 98 and DALTON codes were fulfilled by me. I also realized the part of the work connected with the preparation of the manuscript.

- I calculated hyperfine coupling constants of transition metal compounds in paper V and participated in the preparation of the manuscript.

- I calculated hyperfine coupling constants for the transition metal compounds in paper VI and participated in the preparation of the manuscript.

- I proposed the idea behind paper VII, realized the calculations of spin Hamiltonian parameters and prepared the manuscript.

- Paper VIII is review paper. I performed the calculations of g-tensors of transition metal radicals, g-tensors in solution using the PCM model, hyperfine-coupling in transition metal radicals and prepared the tables for this manuscript.

Contents

Chapter 1

Introduction

Magnetic resonance techniques have a prominent position in current investigations of different objects. New areas based on the Overhauser effect, masers, Fourier transform spectroscopy, magnetic resonance imaging and many others, as well as classical experiments have been successfully applied to investigations of important systems, e.g. biological molecules, inorganic materials and organic magnets.

The first ideas behind the notion of magnetic resonance appeared in the beginning of the twentieth century [1]. The earliest reported, but unfortunately unsuccessful, experimental work regarding the dependence of magnetic susceptibility on frequency was carried out by M. H. Belz in 1922 [2]. After that, in the beginning of 1930's, Gorter, using a calorimetric detection technique, observed a frequency dependence of the paramagnetic relaxation of a number of alums. However, no resonance effects were found [3].

The real beginning of the magnetic resonance era occurred almost ten years later. In 1937 I. I. Rabi's paper "Space Quantization in a Gyrating Magnetic Field" was published. It provided a fundamental theory for all magnetic resonance experiments. Despite that the problem of charges in magnetic fields was first proposed and partly solved by C. G. Darwin in 1927, Rabi is usually considered to be the founder of magnetic resonance theory. Moreover, the first successful observation of magnetic resonance was done in his laboratory in experiments on beams of $LiCl$ molecules [4]. In 1944 he was awarded the Nobel Prize in Physics for his discoveries in this area.

The first successful electron spin resonance (ESR) experiments in condensed matter, or electron paramagnetic resonance (EPR) as we also call it, were carried out by E. Zavoisky in an investigation of $CuCl_2 \cdot 2H_2O$ [5], in 1944. The first nuclear magnetic resonance (NMR) experiments were independently carried out at the same time by E. M. Purcell, H. C. Torrey and R. V. Pound at Harvard University [6]; and by F. Bloch, W. W. Hansen and M. Packard at Stanford University [7], in 1945. For this discovery Bloch and Purcell were awarded the Nobel Prize in Physics in 1952. A little earlier, in 1942, C. J. Gorter proposed the name for the new technique - "nuclear magnetic resonance".

Along with the experimental developments, there was also progress in theoretical aspects. The history of theoretical investigations of magnetic resonance parameters begins with the excellent works of Abragam and Harriman [8, 9]. With the development of new theories, extensive investigations were made at the semiempirical level, Hartree-Fock (HF) and post-HF methods (see for example [10]). However, the great boom in this area was really caused by density functional theory.

The popularity of density functional calculations can be explained by the possibility to explore comparatively large molecular systems that were previously available only at the HF and semiempirical levels, but with a substantially increased calculational accuracy. The presence of a large variety of exchange-correlation functionals that can be combined with proper basis sets allows one to realize calculations of magnetic properties of high quality at low cost. Therefore, different molecular geometries can be investigated during a comparatively short time for probing the correct molecular structures, not only of stable compounds, but also of intermediate ones in many chemical reactions and biochemical processes; it is also possible to explain the observed magnetic behavior in organic materials. Moreover, density functional theory is probably the only method able to predict more or less accurate results for large molecules containing transition metal centers, a subject of increasing interest in experimental sciences. Due to these features, density functional theory can be seen as one of the most promising tools currently existing for the investigation of magnetic resonance parameters.

On the basis of the evident advantages of density functional theory, I chose it as the theoretical tool for investigations of EPR and NMR parameters of paramagnetic molecular systems. This thesis describes three types of calculations: electronic g-tensor calculations based on the restricted density functional response theory for molecules in vacuum and solution; hyperfine coupling tensor calculations in the framework of time-dependent density functional theory with the restricted-unrestricted approach; and calculations of nuclear shielding tensors of paramagnetic molecules. The thesis is arranged in the following order: fundamentals of density functional theory with a special topic regarding spin-restricted methodology; time-dependent response theory; basics of experimental magnetic resonance, this part also presents the spin Hamiltonian concept; theoretical aspects of magnetic resonance with a detailed formulation for calculations of electronic g-tensors, hyperfine coupling tensors and nuclear shieldings. The last part also contains a brief presentation of the Breit-Pauli Hamiltonian and short historical review of theoretical calculations of magnetic resonance parameters within DFT. A description of the essential points and general conclusions about each of the works presented in this thesis is given in the summary.

Chapter 2

Density Functional Theory

Density functional theory (DFT) is comparatively new in the field of computational chemistry despite that the idea to use the electron density rather than the wave function for obtaining information about atomic and molecular systems is old and dates back to the works of Thomas and Fermi [11, 12]. Following the theoretical ideas an approximate density functional theory finds its first applications in chemistry only in the late eighties and early nineties, and since then the popularity of DFT has rapidly increased every year. This process is highly influenced by the development of new exchange-correlation functionals with better performance and the implementation of DFT in many popular quantum chemistry packages. The 1998 Noble Prize in chemistry awarded to John Pople and Walter Kohn placed density functional theory on equal footing to traditional quantum chemistry.

The present chapter contains of two main parts. The first part describes the theoretical foundations of DFT, such as the Hohenberg-Kohn theorems, and its general methodology, the Kohn-Sham approach. The second part is more specific and concerns the topic of this thesis, the treatment of open-shell molecular systems in DFT. One should note here that such a treatment is not a trivial task. The expectation value of the square of the total spin angular momentum operator, S^2, is an important characteristic of any molecular system. And generally speaking the quality of reproduction of this value defines the ability of a calculational method to properly describe the system under investigation. The evaluation of $\langle S^2 \rangle$ requires the knowledge of the two-electron density matrix, and this requirement consequently belongs to a problem area for DFT, where only diagonal elements of the one-electron density matrix of the real interacting system are defined. Therefore, the direct evaluation of the expectation values of two-electron operators is not possible. One of the ways of solving this problem is the possibility to express the two-electron density matrix in terms of the diagonal and off-diagonal elements, extracted by the use of a core hole function, of the one-electron density matrix. In our implementations we used the core hole function of the homogeneous electron gas under the condition that $\rho_\alpha(\mathbf{r}) > \rho_\beta(\mathbf{r})$ is obeyed. That allows us to get an exact total spin angular mo-

mentum of the molecule. The methodology mentioned above is realized in the spin-restricted Kohn-Sham response formalism described in detail in this chapter. The unrestricted Kohn-Sham formalism is also considered in order to show the differences and final advantages of both methods.

2.1   The theoretical foundation of DFT, Hohenberg-Kohn theorems

The central quantity in DFT is the electron density, $\rho(\mathbf{r})$, that can be defined as the multiple integral over the spin coordinates of all electrons and over all but one of the spatial variables,

$$\rho(\mathbf{r}_1) = N \int \cdots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)|^2 ds_1 d\mathbf{x}_2 \cdots d\mathbf{x}_N \qquad (2.1)$$

where $\mathbf{x} = (\mathbf{r}, s)$ is a composite space-spin coordinate and Ψ is the wave-function of the system. $\rho(\mathbf{r})$ determines the probability of finding any of the N electrons with arbitrary spin within a volume element $d\mathbf{r}_1$ while the other N-1 electrons have arbitrary positions and spins. $\rho(\mathbf{r})$ is a non-negative function that integrates to the total number of electrons and vanishes at infinity.

   The birth of modern density functional theory is considered to be the publishing of two fundamental theorems by Hohenberg and Kohn [13] in 1964. In the first theorem they established the ground state electron density as a quantity which uniquely determines the Hamilton operator and therefore all properties of the studied system: *the external potential $v_{ext}(\mathbf{r})$ is (to within a constant) a unique functional of $\rho(\mathbf{r})$; since, in turn $v_{ext}(\mathbf{r})$ fixes $\hat{H}$ we see that the full many-particle ground state is a unique functional of $\rho(\mathbf{r})$.* The second Hohenberg-Kohn theorem provides a lower bound for approximate densities: *the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density, $\rho(\mathbf{r})$* [14].

   Consider the basic energy expression

$$E[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + E_{ee}[\rho(\mathbf{r})] + E_{Ne}[\rho(\mathbf{r})] \qquad (2.2)$$

where the complete ground state energy is a functional of the ground state density. Each of the terms of this expression can be characterized as dependent or independent on the actual system. The potential energy due to the nuclear-electron attraction, is obviously of the first kind, and can be defined as:

$$E_{Ne}[\rho(\mathbf{r})] = \int \rho(\mathbf{r}) V_{Ne} d\mathbf{r} \qquad (2.3)$$

   The system independent parts, the kinetic energy, $T[\rho(\mathbf{r})]$, and the electron-electron interaction, $E_{ee}[\rho(\mathbf{r})]$, are usually collected into the Hohenberg-Kohn

functional, $F_{HK}[\rho(\mathbf{r})]$. Its explicit form is unfortunately unknown, only the classical Coulomb part, $J[\rho(\mathbf{r})]$, of the electron-electron interaction can easily be extracted as:

$$E_{ee}[\rho(\mathbf{r})] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{ncl}[\rho(\mathbf{r})] = J[\rho(\mathbf{r})] + E_{ncl}[\rho(\mathbf{r})] \qquad (2.4)$$

where $E_{ncl}[\rho(\mathbf{r})]$ is the non-classical contribution to the electron-electron interaction. In this way, the ground state energy of a system can be written as

$$E = \min_{\rho \to N}(F[\rho(\mathbf{r})] + \int \rho(\mathbf{r})V_{Ne}d\mathbf{r}) \qquad (2.5)$$

and the universal functional $F_{HK}[\rho(\mathbf{r})]$ accounts for the individual contributions of the kinetic energy, the classical Coulomb interaction and the non-classical part due to the exchange and electron correlation effects.

2.2 The Kohn-Sham approach

The terms defined by $F_{HK}[\rho(\mathbf{r})]$ are functionals of the electron density and their explicit form is only known for $J[\rho(\mathbf{r})]$ while the other parts are usually approximated in the framework of different methods. Evidently, the way of treating the kinetic energy is a crucial aspect of the problem, which to a great extent defines the final accuracy of results. With the goal of calculating the kinetic energy part as well as possible, Kohn and Sham proposed to consider a non-interacting reference system with a Hamiltonian consisting of an effective local potential $v_s(\mathbf{r})$ [15]

$$\hat{H}_s = -\frac{1}{2}\sum_i^N \nabla_i^2 + \sum_i^N v_s(\mathbf{r}) \qquad (2.6)$$

which is defined such that the ground state density is the same as that of the interacting system. The ground state wave function of a non-interacting system can be represented by a Slater determinant with the diagonal elements given by:

$$\Theta_s = \frac{1}{\sqrt{N!}} det[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)\cdots\varphi_N(\mathbf{x}_N)] \qquad (2.7)$$

The spin orbitals, Kohn-Sham orbitals φ_i, are determined by

$$\hat{f}_s^{KS}\varphi_i(\mathbf{r}, s) = \varepsilon_i\varphi_i(\mathbf{r}, s) \qquad (2.8)$$

where the one-electron Kohn-Sham operator is defined as

$$\hat{f}_s^{KS} = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}) \qquad (2.9)$$

From the treatment above an essential part of the exact kinetic energy can be obtained as the kinetic energy of the non-interacting reference system

$$T_s = -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle \tag{2.10}$$

The part of the true kinetic energy, not included in (2.10), is usually included in the so-called exchange-correlation energy, E_{XC}, along with the non-classical contributions from the electron-electron interaction:

$$F[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})] \tag{2.11}$$

Therefore the energy of the interacting system is

$$
\begin{aligned}
E[\rho(\mathbf{r})] &= T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})] + E_{Ne}[\rho(\mathbf{r})] = -\frac{1}{2} \sum_i^N \langle \varphi_i | \nabla^2 | \varphi_i \rangle \\
&+ \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' d\mathbf{r} + E_{XC}[\rho(\mathbf{r})] - \int \sum_A^M \frac{Z_A}{r_{1A}} \rho(\mathbf{r}) d\mathbf{r}
\end{aligned}
\tag{2.12}
$$

where the exact form of only one term, i.e. E_{XC}, remains unknown and therefore needs to be approximated in some way.

As we can see from the discussion above, the Kohn-Sham equations (2.8) are a complicated system of coupled integro-differential equations containing a differential kinetic energy operator and an integral Coulomb contribution operator. Therefore, an easy and compact way of solving it is strictly required for obtaining the Kohn-Sham molecular orbitals corresponding to the ground state density associated with a particular exchange-correlation functional. A purely numerical approach has only been used for small molecules and has not found a wide range of application because of the computational cost associated with discretizing the differential equations. A more efficient way is use the linear combination of atomic orbitals (LCAO) expansion of the Kohn-Sham orbitals, along the ideas introduced by Roothan in Hartree-Fock theory. In this case the Kohn-Sham orbitals can be expressed as a linear combination of a predefined set of basis functions $\{\eta_\mu\}$:

$$\varphi_i = \sum_{\mu=1}^L c_{\mu i} \eta_\mu \tag{2.13}$$

where L is a number of functions. Then, instead of solving what is originally a non-linear optimization problem, a set of linear equations can be obtained and solved iteratively, where the coefficients $\{c_{\mu i}\}$ are the only variables.

After several mathematical manipulations with equations (2.8) and (2.13) we can get a compact matrix equation

$$\mathbf{F}^{KS}\mathbf{C} = \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon} \tag{2.14}$$

On the left hand side of this equation we have the Kohn-Sham matrix with the matrix elements represented as:

$$F_{\mu\nu}^{KS} = \int \eta_\mu(\mathbf{r}_1) \hat{f}_s^{KS}(\mathbf{r}_1) \eta_\nu(\mathbf{r}_1) d\mathbf{r}_1 \tag{2.15}$$

and the matrix C containing the expansion vectors. On the right hand side we have the overlap matrix, S, with matrix elements

$$S_{\mu\nu} = \int \eta_\mu(\mathbf{r}_1) \eta_\nu(\mathbf{r}_1) d\mathbf{r}_1 \tag{2.16}$$

and a diagonal matrix of the orbital energies, ε. Both matrices $\mathbf{F}^{KS}$ and S are symmetric and $L \times L$ dimensional.

2.3 DFT for open-shell systems

Until now we have considered Kohn-Sham equations without any reference to the spin of the system. The effective local potential $v_s(\mathbf{r})$ included in the one-electron Kohn-Sham operator $\hat{f}_s^{KS}$ deals with a total spin density as the all-decisive variable. But in some cases the energy of a system should be considered as a function of the individual spin densities, for example, if the potential energy contains spin dependent parts. This is certainly the case for this thesis, which describes the evaluation of magnetic resonance parameters of open-shell systems.

In the case of open-shell systems, equation (2.12) should be rewritten in a spin dependent form:

$$\begin{aligned} E[\rho_\alpha(\mathbf{r})\rho_\beta(\mathbf{r})] = T_s[\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})] \quad &+ \quad J[\rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})] + E_{XC}[\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})] \\ &+ \quad E_{Ne}[\rho_\alpha(\mathbf{r}) + \rho_\beta(\mathbf{r})] \end{aligned} \tag{2.17}$$

where the corresponding α and β spin densities for Kohn-Sham orbitals φ_i can be expressed in the following way

$$\rho_\alpha(\mathbf{r}) = \sum_i n_{\alpha i} |\varphi_i(\mathbf{r}, \alpha)|^2 \text{ and } \rho_\beta(\mathbf{r}) = \sum_i n_{\beta i} |\varphi_i(\mathbf{r}, \beta)|^2 \tag{2.18}$$

where $n_{\sigma i}$ is the occupation number of the $\varphi_i(\mathbf{r}, \sigma)$ spin orbital in the Kohn-Sham determinant, equation (2.7), with possible values zero or one.

Further minimization of the energy functional $E[\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})]$ should now be carried out with respect to the densities of different spin. There are two methods that differ only by a condition of constraint imposed in the minimization: the unrestricted Kohn-Sham approach and the spin-restricted Kohn-Sham approach. In the following a rather brief description of the unrestricted Kohn-Sham method will be presented, while more attention will be paid to the spin-restricted method, used in the projects included in this thesis.

2.3.1   The unrestricted Kohn-Sham approach

The minimization of the molecular energy functional $E[\rho_\alpha, \rho_\beta]$ is carried out with separate constraints on the α and β densities [16]

$$\int \rho_\alpha(\mathbf{r})d\mathbf{r} = N_\alpha \text{ and } \int \rho_\beta(\mathbf{r})d\mathbf{r} = N_\beta \tag{2.19}$$

which means that the number of electrons with α and β spins remains constant during the variational procedure. Under this condition one can obtain a separate set of Kohn-Sham equations for the Kohn-Sham orbitals corresponding to the different spin orientations:

$$\hat{f}_\alpha \varphi_i(\mathbf{r}, \alpha) = \frac{\epsilon'_{\alpha i}}{n_{\alpha i}} \varphi_i(\mathbf{r}, \alpha) \ \ i = 1, 2, .., N_\alpha \tag{2.20}$$

$$\hat{f}_\beta \varphi_i(\mathbf{r}, \beta) = \frac{\epsilon'_{\beta i}}{n_{\beta i}} \varphi_i(\mathbf{r}, \beta) \ \ i = 1, 2, .., N_\beta \tag{2.21}$$

where the Kohn-Sham operators for $\varphi_i(\mathbf{r}, \alpha)$ and $\varphi_i(\mathbf{r}, \beta)$ spin orbitals are defined now as

$$\begin{aligned}
\hat{f}_\alpha = -\frac{1}{2}\nabla^2 + v_s^\alpha(\mathbf{r}) &= -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
&+ \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\mathbf{r})}
\end{aligned} \tag{2.22}$$

$$\begin{aligned}
\hat{f}_\beta = -\frac{1}{2}\nabla^2 + v_s^\beta(\mathbf{r}) &= -\frac{1}{2}\nabla^2 + v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \\
&+ \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\mathbf{r})}
\end{aligned} \tag{2.23}$$

and where the $\epsilon'_{\sigma i}$ is a Lagrangian multiplier for the corresponding spin-orbital $\varphi_i(\mathbf{r}, \sigma)$. The Kohn-Sham equations for $\varphi_i(\mathbf{r}, \alpha)$ and $\varphi_i(\mathbf{r}, \beta)$ spin orbitals, (2.20) and (2.21), are connected only by the electron spin densities entering the equations and the off-diagonal Lagrangian multipliers do not appear, which is a main advantage of the unrestricted method. Furthermore, two Kohn-Sham matrices should be constructed and diagonalized independently in each iteration. However, a main disadvantage with the unrestricted Kohn-Sham approach is the spin contamination problem.

2.3.2   The spin-restricted Kohn-Sham approach

The same constraints, equation (2.19), to the number of electrons with α and β spins are also used in the spin-restricted Kohn-Sham approach. In addition the spatial parts of $\varphi_i(\mathbf{r}, \alpha)$ and $\varphi_i(\mathbf{r}, \beta)$ spin orbitals are assumed to be the same during the minimization of the energy functional.

Let us consider a molecule in the ground state represented by N_d doubly occupied and N_s singly occupied orbitals. If the constraints mentioned above are taken into account, the Kohn-Sham equations, can be presented as

$$\hat{f}_d \varphi_k(\mathbf{r}) = \sum_j \epsilon'_{kj} \varphi_j(\mathbf{r}) \ \ k = 1, 2, .., N_d \tag{2.24}$$

$$\frac{1}{2} \hat{f}_o \varphi_m(\mathbf{r}) = \sum_j \epsilon'_{mj} \varphi_j(\mathbf{r}) \ \ m = 1, 2, .., N_s \tag{2.25}$$

where j runs over doubly and singly occupied orbitals $j = 1, 2, ..., N_d + N_s$. The corresponding Kohn-Sham operators here are

$$\hat{f}_d = -\frac{1}{2} \nabla^2 + v(\mathbf{r})_s^d = -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$+ \ \frac{1}{2} \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\mathbf{r})} + \frac{1}{2} \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\mathbf{r})} \tag{2.26}$$

$$\hat{f}_o = -\frac{1}{2} \nabla^2 + v(\mathbf{r})_s^o = -\frac{1}{2} \nabla^2 + v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

$$+ \ \frac{\delta E_{XC}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\mathbf{r})} \tag{2.27}$$

while the α and β spin densities are defined as

$$\rho_\alpha(\mathbf{r}) = \sum_{i=1}^{N_d} |\varphi_i(\mathbf{r}, \alpha)|^2 + \sum_{j=1}^{N_s} |\varphi_j(\mathbf{r}, \alpha)|^2 \text{ and } \rho_\beta(\mathbf{r}) = \sum_{i=1}^{N_d} |\varphi_i(\mathbf{r}, \beta)|^2 \tag{2.28}$$

Contrary to the unrestricted Kohn-Sham equations, the coupling of the equations for doubly and singly occupied orbitals, (2.24) and (2.25), gives us off-diagonal Lagrangian multipliers. Methods adopted from restricted open shell Hartree-Fock (ROHF) theory can be used to handle them also in the Kohn-Sham formalism. There are two ways to realize that: one could solve the equations for singly and doubly occupied orbitals separately or solve these equations as a combined effective equation with the off-diagonal Lagrangian multipliers absorbed into the Kohn-Sham Hamiltonian. The latter method was chosen in the applications presented in this thesis; in analogy to ROHF theory the effective Kohn-Sham matrix is defined in the following form

$$\hat{H} = \begin{pmatrix} F_c & F_{co} & F_c \\ F_{co} & F_c & F_{ov} \\ F_c & F_{ov} & F_c \end{pmatrix} \tag{2.29}$$

which has two modified blocks F_{co} and F_{ov} corresponding to off-diagonal elements between doubly (c) and singly (o) occupied orbitals and between singly occupied and virtual (v) orbitals, respectively. The off-diagonal elements are

modified to be proportional to the orbital gradient in such a way that a diagonalization of the effective Fock matrix leads to a stationary state. The matrix elements in equation (2.29) are defined as

$$F_c = \frac{1}{2}(f_\alpha + f_\beta) \, , F_{co} = f_\beta \text{ and } F_{ov} = f_\alpha \tag{2.30}$$

where f_α and f_β are ordinary matrix elements of Kohn-Sham operators for the $\varphi_j(\mathbf{r}, \alpha)$ and $\varphi_j(\mathbf{r}, \beta)$ spin orbitals given in equations (2.20) and (2.21). The eigenvalues of the effective Hamiltonian, (2.29), do not have any physical meaning; only the final spin-densities obtained from the optimized Kohn-Sham determinant are relevant.

2.4 Exchange-correlation functionals

In the Kohn-Sham approach almost all contributions to the electronic energy of the studied system, including a major part of the kinetic energy, can be calculated exactly. The parts of unknown form are collected in the so-called exchange-correlation term, E_{XC}, which needs to be calculated according to some approximate model. Therefore, the quality of the approximation made for E_{XC} defines the final quality of the whole DFT procedure.

Several strategies for the approximation of the exchange-correlation functional are known by now:

- *Local density (LDA) and local spin-density approximations (LSD).* Central to this model is the assumption that a simple dependence exists between E_{XC} and the electron density defined locally in space :

$$E_{XC}^{LDA}[\rho] = \int \rho(\mathbf{r})\varepsilon_{XC}(\rho(\mathbf{r}))d\mathbf{r} \tag{2.31}$$

  ε_{XC} is the exchange-correlation energy per particle of a uniform electron gas, consisting of two parts: exchange and correlation. The exchange contribution has the form, apart from a pre-factor, equal to that in the Slater approximation of the Hartree-Fock (HF) exchange [17, 18]. The correlation contribution is usually represented by analytical expressions based on the basis of highly accurate numerical quantum Monte-Carlo simulations of the homogeneous electron gas [19]. When the LDA scheme is extended to the unrestricted case, we arrive at the local spin-density approximation, where not only the total electron density $\rho(\mathbf{r})$, but two spin densities $\rho_\alpha(\mathbf{r})$ and $\rho_\beta(\mathbf{r})$ are considered.

  Despite that LDA is based on a very crude model the results are in general better than in the Hartree-Fock approximation. Properties such as equilibrium structures, harmonic frequencies or charge moments can be

successfully calculated with LDA. However, the deviation from the experimental atomization energies for the so-called G2 data set is rather large, 36 kcal/mol [20]. G2 contains chemical compounds consisting of the first- (Li-F) and second-row (Na-Cl) atoms with well-defined experimental energetic parameters, as atomization energies, ionization potentials, electron affinities and proton affinities, and is usually used for systematic studies of the performance of new methods of calculations.

- *The generalized gradient approximation.* The uniform electron gas model does not correspond to any real chemical system and by only considering the value of the electron density at a given point one cannot always reproduce the energetic parameters of a studied system.

  In order to get a description that is closer to truth, information on the gradient of the charge density, $\nabla\rho(\mathbf{r})$, can be added to account for the non-homogeneity of the true electron density. Functionals that include the gradients of the charge density and where the hole constraints have been restored such that the exchange and correlation holes contain one and zero electron charges, respectively, are known as the generalized gradient approximation (GGA) and have a general form:

$$E_{XC}^{GGA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha, \nabla\rho_\beta)d\mathbf{r} \tag{2.32}$$

  Usually E_{XC}^{GGA} is split into exchange and correlation contributions, the approximations of which are made separately. The mean error in the atomization energies for the G2 set with this type of functionals is 5-7 kcal/mol [20].

- *Hybrid functionals.* The basic idea in this type of approximation of E_{XC} is to use a fraction of the exact exchange energy computed with the Slater determinant in the same manner as in the HF picture and to approximate only the electron correlation.

$$E_{XC} = E_X^{exact} + E_C^{KS} \tag{2.33}$$

  The technique was developed by Becke [21] and is based on the adiabatic connection scheme. Currently, the most popular functional of this type is B3LYP suggested by Stephens *et al.* [22]. The error with respect to the G2 data set has been shown to be slightly above 2 kcal/mol [20].

Chapter 3

Time-dependent Response Theory

Time-dependent response theory describes the interaction between a time dependent field and a system. The influence of such a field on a molecule, treated as perturbation, causes corresponding changes in the wave function, which also becomes time-dependent. Molecular properties can be obtained from time-dependent expectation values in the framework of time-dependent response theory. The response functions define the changes of observables when the system is influenced by one or several perturbing fields. In the limit of a static perturbation time-dependent perturbation theory becomes identical to time-independent perturbation theory. When the field is oscillating with a frequency that corresponds to the excitation energy of the molecule a large response in the wave function will occur; the excitation energy corresponds to a pole in the response function. Residues of the response functions determine the corresponding transition matrix elements.

This chapter is organized in the following way. First, the basic definitions of time-dependent response theory are presented. Second, the two most widely used methods for the calculation of molecular properties for molecular systems influenced by time-dependent perturbations are considered. One of them, the sum-over-state method, is given only at introductory presentation. The response method is described in more detail.

3.1 Basic definitions

Suppose that the molecular system can be described by the Hamilton operator containing the time-independent part, $\hat{H}_0$ and the time-dependent perturbation, $\hat{V}(t)$:

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \tag{3.1}$$

If the perturbation caused by a field of frequency ω has a Fourier transform we may write [23]

$$\hat{V}(t) = \int_{-\infty}^{\infty} \hat{V}^{\omega} \exp[(-i\omega + \varepsilon)t]d\omega \tag{3.2}$$

where ε is a small positive infinitesimal indicating that the perturbed field is switched on adiabatically and that the perturbation operator vanishes at $t = -\infty$. The perturbation operator is required to be Hermitian.

The influence of the perturbing field causes changes in the molecular wave function, that at some finite time t can be expanded in the series:

$$\begin{aligned}
|\overline{0}(t)\rangle &= |0\rangle + \int_{-\infty}^{\infty} |0_1^{(\omega_1)}\rangle \exp[(-i\omega_1 + \varepsilon)t]d\omega_1 \\
&+ \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |0_2^{(\omega_1,\omega_2)}\rangle \exp[(-i(\omega_1 + \omega_2) + 2\varepsilon)t]d\omega_1 d\omega_2 + \cdots
\end{aligned} \tag{3.3}$$

where the second term describes changes in the wave function that are linear in the perturbation, the third term is quadratic in the perturbation, *etc.* The time development of observables can be represented by expectation values of the time-independent operator $\hat{A}$ when the system is influenced by the time-dependent perturbation $\hat{V}(t)$:

$$\langle \overline{0}(t)|\hat{A}|\overline{0}(t)\rangle = \langle 0|\hat{A}|0\rangle + \int_{-\infty}^{\infty} \langle\langle \hat{A}; \hat{V}^{\omega_1} \rangle\rangle_{\omega_1} exp[(-i\omega_1 + \varepsilon)t]d\omega_1 \tag{3.4}$$

$$+ \quad \frac{1}{2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \langle\langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle\rangle_{\omega_1,\omega_2} \exp[(-i(\omega_1 + \omega_2) + 2\varepsilon)t]d\omega_1 d\omega_2 + \cdots$$

In Eq. 3.4 $\langle 0|\hat{A}|0\rangle$ defines the expectation value of operator $\hat{A}$ in the absence of perturbation, while $\langle\langle \hat{A}; \hat{V}^{\omega_1} \rangle\rangle_{\omega_1}$ and $\langle\langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle\rangle_{\omega_1,\omega_2}$ are the linear and quadratic response functions, respectively. The latter is defined to be symmetric with respect to interchange of the frequencies. The unique determination of the response functions forms a basis for calculating molecular properties with different methods.

3.2   The sum-over-states method

There are different approaches to the calculation of molecular properties which correspond to time-dependent response functions. In a sum-over-states framework the linear response function is expanded in the basis of eigenfunctions $(|0\rangle, |n\rangle)$ of $\hat{H}_0$ written as [23]:

$$\langle\langle \hat{A}; \hat{V}^{\omega} \rangle\rangle_{\omega} = \sum_{n\neq0} \frac{\langle 0|\hat{A}|n\rangle\langle n|\hat{V}^{\omega}|0\rangle}{\omega - (E_n - E_0)} - \sum_{n\neq0} \frac{\langle 0|\hat{V}^{\omega}|n\rangle\langle n|\hat{A}|0\rangle}{\omega + (E_n - E_0)} \tag{3.5}$$

where E_0 is the ground state energy and E_n is the energy of state $|n\rangle$.

The evaluation of the linear response function requires summation over all excited states. Such a procedure is quite expensive, and, moreover cannot be easily realized in DFT where a proper treatment of excited states still is an open question. An approximate scheme based on the sum-over-states approach combined with density functional theory was proposed by V. Malkin *et al.* [24]. Two central questions were defined: how to find the many-electron wave function for the ground and excited states and their corresponding total energies. In the framework of Kohn-Sham theory the exact many-electron wave function for a non-interacting reference system, Eq. 2.7, is used instead of the many-electron wave function. The ground state Kohn-Sham total energy is defined as a functional of electron density. Then the excited state wave function is approximated by the excited state Slater determinant which differs from the ground state one by one spin-orbital with a replacement of an occupied molecular orbital (MO) with a virtual MO. The remaining question therefore is how to approximate the energy of this excited state. The proposition was to use the Kohn-Sham orbital energies for ground and excited states along with some corrections to Coulomb and exchange-correlation contributions derived from other orbital-based techniques. The energy difference in the denominator of Eq. 3.5 is therefore replaced by the corresponding difference between Kohn-Sham energies corrected by the approximate exchange-correlation term. The method is rather sensitive to the quality of approximations made for the exchange-correlation energy and can only be applied to calculations of certain types of molecular properties.

3.3 The response method

The response method, considered below, deals with the perturbational treatment of closed- and open-shell molecular systems, being described by a Kohn-Sham Hamiltonian [25]. An initial small perturbation disturbs the ground state density, and corresponding static and dynamic molecular properties, which involves the interaction between ground and excited states, are derived.

Suppose that the time development of the KS determinant $|\overline{0}\rangle$ is represented in the form:

$$\hat{H}|\overline{0}\rangle = i\frac{\mathrm{d}}{\mathrm{d}t}|\overline{0}\rangle \tag{3.6}$$

As in Eq. 3.1, the $\hat{H}_0$ term can be seen as the Kohn-Sham operator $f_\sigma(\mathbf{r}, t)$, that in the static field limit has the same form as the ordinary Kohn-Sham Hamiltonian and covers the kinetic energy term, the Coulomb part of electron-electron interaction, the electron-nuclear interaction and the exchange-correlation potentials, Eq. 2.11. The $\hat{V}(t)$ term is now treated as an explicit perturbation $v(\mathbf{r}, t)$.

$$\hat{H}_0 + \hat{V}(t) = \sum_\sigma \int \hat{\Psi}_\sigma^\dagger(\mathbf{r})[f_\sigma(\mathbf{r}, t) + v(\mathbf{r}, t)]\hat{\Psi}_\sigma(\mathbf{r})d\tau \tag{3.7}$$

$\hat{\Psi}_\sigma$ is a traditional fermion field operator, where the spin-orbitals are restricted to have equal spatial parts:

$$\hat{\Psi}_\sigma(\mathbf{r}) = \sum_i \varphi_i(\mathbf{r})a_{i,\sigma} \tag{3.8}$$

The electron spin-density operator can, therefore, be defined in the following way:

$$\hat{\rho}_\sigma(\mathbf{r}) = \hat{\Psi}_\sigma^\dagger(\mathbf{r})\hat{\Psi}_\sigma(\mathbf{r}) = \sum_{ij} \varphi_i^*(\mathbf{r})\varphi_j(\mathbf{r})E_{ij}^\sigma \tag{3.9}$$

The time development of the unperturbed Kohn-Sham determinant $|0\rangle$ can in analogy to Eq. 3.3 be parametrized in an exponential form including an anti-Hermitian operator $\hat{\kappa}(t)$, the elements of which are the variational parameters and form the orbital rotation matrix.

$$|\overline{0}\rangle = exp[-\hat{\kappa}(t)]|0\rangle \tag{3.10}$$

$$\hat{\kappa}(t) = \sum_{rs\sigma} \kappa_{rs}(t)E_{rs}^\sigma \equiv \sum_{rs\sigma} \kappa_{rs}(t)a_{r\sigma}^\dagger a_{s\sigma} \tag{3.11}$$

The spin density can be obtained as the expectation value of the corresponding electron spin density operator from Eq. 3.9 and, if the exponential parameterization is taken into account, it is given by

$$\rho_\sigma(\mathbf{r}, t) = \langle\hat{0}|\hat{\rho}_\sigma(\mathbf{r})|\hat{0}\rangle = \langle 0|exp[\hat{\kappa}(t)]\hat{\rho}_\sigma(\mathbf{r})exp[-\hat{\kappa}(t)]|0\rangle \tag{3.12}$$

The use of Ehrenfest's theorem, which forms the basis for the time-dependent variational principle, allows one to identify the response functions and obtain the corresponding response equations. From Eq. 3.6 and Eq. 3.10:

$$\langle 0|\left[\hat{Q}, exp[\hat{\kappa}(t)]\left(\hat{H}(t) - i\frac{\mathrm{d}}{\mathrm{d}t}\right)exp[-\hat{\kappa}(t)]\right]|0\rangle = 0 \tag{3.13}$$

where $\hat{Q}$ is the arbitrary one-electron operator. The parameters $\hat{\kappa}(t)$ of a given order are uniquely defined in the expansion

$$\hat{\kappa}(t) = \hat{\kappa}(t)^{(1)} + \hat{\kappa}(t)^{(2)} + \cdots \tag{3.14}$$

Each term in this equation is Fourier expanded, and neglecting the small infinitesimal, the linear term can be written as

$$\hat{\kappa}(t)^{(1)} = \int \hat{\kappa}^{\omega_1} exp(-i\omega_1 t)d\omega_1 \tag{3.15}$$

If, in addition, the corresponding expansions for the spin densities and the Kohn-Sham Hamiltonian are carried out and only first order terms are included, the Ehrenfest's equation can be written as

$$\langle 0|[\hat{\mathbf{q}}, [\hat{\boldsymbol{\kappa}}^\omega, \hat{H}_0^{(0)}] + \hat{H}_0^\omega]|0\rangle + \omega\langle 0|[\hat{\mathbf{q}}, \hat{\boldsymbol{\kappa}}^\omega]|0\rangle = -\langle 0|[\hat{\mathbf{q}}, \hat{V}^\omega]|0\rangle \tag{3.16}$$

where $\hat{q}$ collects the non-redundant excitation operators E_{rs}^{σ}. The solution of this equation determines the linear response function for an arbitrary operator $\hat{A}$,

$$\langle\langle \hat{A}; \hat{V}^{\omega} \rangle\rangle_{\omega} = \langle 0|[\hat{\kappa}^{\omega}, \hat{A}]|0\rangle \tag{3.17}$$

The response method has been implemented for all important electronic structure approaches and, despite, it is not widely used for calculations of general molecular properties this thesis presents a wide range of works based on the response methodology.

Chapter 4

Basics of Magnetic Resonance Phenomena

The aspiration of humanity to solve the mystery of the nature of living systems was expressed by Thomas Huxby more than a century ago [26]: *what an enormous revolution would be made in biology if physics or chemistry could supply the physiologist with a means of making out the molecular structure of living tissues comparable to that which spectroscopy affords to the inquirer into the nature of the heavenly bodies.*

Recent progress in magnetic resonance experiments makes this hope tangible and close. Magnetic resonance includes several spectroscopic techniques for studying the interaction of molecules with an applied magnetic field. When a molecule is influenced by a magnetic field the perturbation causes interactions between magnetic moments associated with nuclear or electron spins and local electronic currents induced by this field. The specific case where the interaction involves the unpaired electron spin is considered within the framework of electron paramagnetic resonance, EPR, also known as electron spin resonance, ESR. Central quantities in EPR are the so-called g-tensor, g, and the hyperfine coupling constant, A, describing the influence on the unpaired electron spin density by the local chemical environment and the presence of unpaired spin density at the nuclear positions, respectively. Naturally, the nuclear spin levels can also be perturbed by an externally applied magnetic field and studied by the nuclear magnetic resonance technique, NMR. The result of the interaction is observable in the spectrum as the so-called chemical shift, δ.

Over the past few years extensive studies of many biological systems have been carried out: heme-proteins and amino acid model systems; bacterial and plant photosynthetic systems; radicals from reaction centers, e.g. quinones and tyrosine; enzymes - oxidases and reductases; and spin labeled compounds. Now special features of metabolic processes in the skeletal muscle, heart and brain of intact organisms can be successfully studied by EPR and NMR [27, 28, 29, 30, 31]. Many of the inorganic solids, defects in crystal structures, dynamic effects on colloidal systems and porous materials are of particular interest due to

their usage in electro-technical production [32]. Therefore, magnetic resonance based methods are now among of the most popular experimental techniques allowing one to explore the electronic and chemical structures in relatively easy and elegant ways.

4.1   The spin Hamiltonian concept

Due to the complex nature of the interactions between the unpaired spin and the molecular environment, the interpretation of the resulting experimental spectra is usually a complicated task. When the dynamical effects are not taken into account, and only the transitions themselves are considered, i.e. the transition energies, line positions and the corresponding line intensities and amplitudes, the data can be analyzed in terms of a spin Hamiltonian. The one to one relation between experimental investigation and theoretical calculation is shown in Figure 4.1. Every molecule or molecular system has its own unique spectrum. Theoretical calculations of such spectra require the solving of the molecular Schrödinger equation at the first stage, from which one can get the molecular wave function, and definition of the spin Hamiltonian parameters at the second stage. An experimental spectrum can be simulated after that on the basis of defined theoretical parameters or, on the other hand, experimentally evaluated spectral features can be compared with the calculated ones.

The spin Hamiltonian can be defined as a Hermitian operator containing only spin operators and parameters. It can be written in the general form:

$$\mathcal{H} = \sum_{ij} H_{ij} |i\rangle\langle j| \tag{4.1}$$

for any orthonormal basis set in the appropriate spin space $|i\rangle$. The matrix elements H_{ij} can be expressed as a linear combination of spin operators and products of spin operators. The corresponding expansion coefficients are parameters that are adjusted so that the experimentally determined set of relative energy levels is reproduced. In general, the energy levels are functions of molecular orientation and magnetic field strength. Neglecting terms which do not contribute to the splitting, the spin Hamiltonian is usually written in the form [9]:

$$\begin{aligned}
\mathcal{H} &= \mathbf{S}^T \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{S}^T \cdot \mathbf{g} \cdot \mathbf{B} - \sum_N \mathbf{I}_N^T \cdot \gamma_N \cdot \mathbf{B} + \sum_N \mathbf{S}^T \cdot \mathbf{A}_N \cdot \mathbf{I}_N \\
&\quad + \frac{1}{2} \sum_N \sum_{M \neq N} \mathbf{I}_N^T \cdot \mathbf{q}_{NM} \cdot \mathbf{I}_M + \frac{1}{2} \sum_N \sum_{M \neq N} \mathbf{I}_N^T \cdot (\mathbf{D}_{NM} + \mathbf{J}_{NM}) \cdot \mathbf{I}_M .
\end{aligned} \tag{4.2}$$

where $\mathbf{S}$ is the effective electronic spin, $\mathbf{I}_N$ - the spin of nucleus N, $\mathbf{B}$ - the external magnetic field, $\mathbf{g}$ - the electronic g-tensor, $\mathbf{D}$ - the zero-field splitting tensor, and $\mathbf{A}$ - the hyperfine coupling tensor.

The first term in Eq.4.2 defines the zero-field splitting of energy levels that occurs in the systems with more than one unpaired electron in the absence of
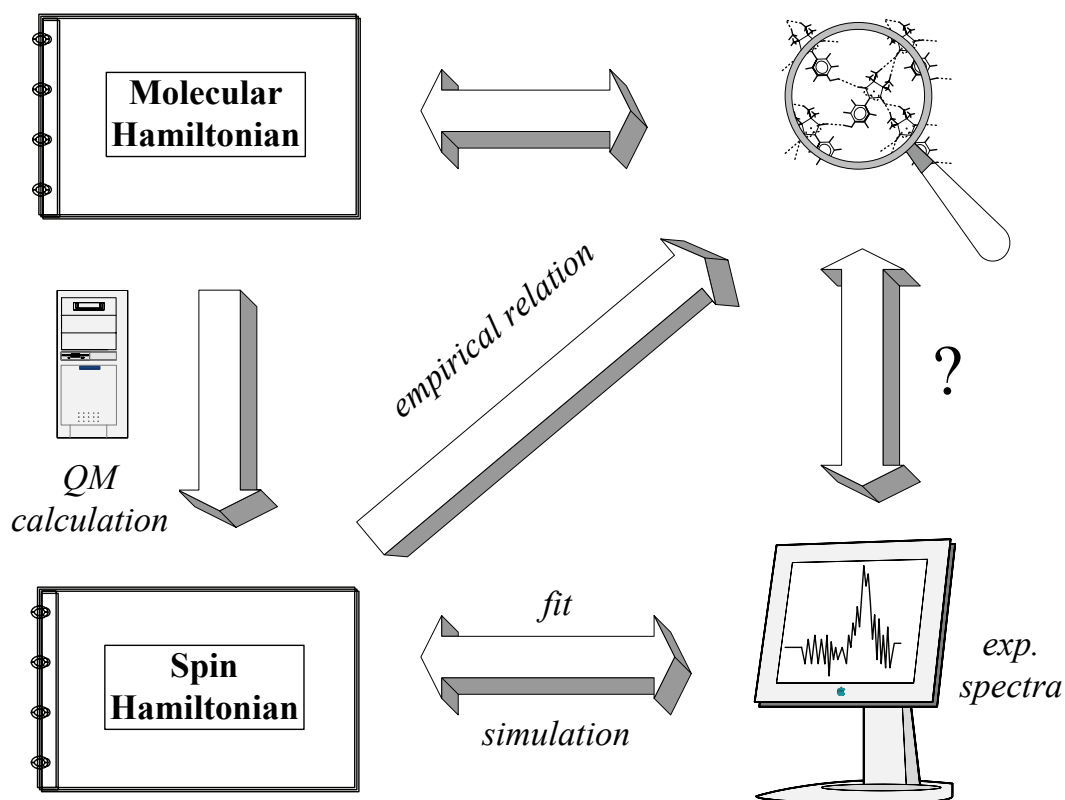
Figure 4.1: Relation between theory and experiment. Idea of the picture was taken from review of F. Neese [46]

an externally applied magnetic field. The next two terms describe the electron and nuclear Zeeman interactions, respectively. The fourth term arises from the hyperfine interaction between the unpaired electron spin density and the corresponding unpaired spin density localized at the magnetic nuclei. The last two terms originate from the nuclear spin-spin coupling interaction and include quadrupole, dipolar and indirect effects.

Without additional restrictions the spin Hamiltonian cannot be uniquely defined by the observed spectra. Therefore, it is helpful to consider different standard types of Hamiltonians that are adapted to the specific experimental situation. The treatment of spin Hamiltonians in EPR and NMR experiments will be exemplified in the following sections.

4.2 The EPR spin Hamiltonian

Suppose, that the tensor coupling of the spins to each other and to the field is orientation independent, which can easily be realized in an experiment in solution when the investigated molecules rotate rapidly. The isotropic spin Hamil-

tonian for a spin one-half system can be written in the form [9]:

$$\mathcal{H} = g\mu_B B S_z + \sum_{N=1}^{M} A_N \mathbf{S} \cdot \mathbf{I}_N \tag{4.3}$$

where the system containing M magnetic nuclei is influenced by an external magnetic field B in the z direction. μ_B is the Bohr magneton. Strictly speaking, the nuclear Zeeman interaction must also be included in Eq. 4.3, but in most cases its energy contribution is negligible on the EPR energy scale and can be neglected in the computation of EPR transitions.

When the z axis is chosen as the direction of the static magnetic field, the dot product in Eq. 4.3 can be expanded in terms of raising and lowering operators

$$
\begin{aligned}
S_\pm &= S_x \pm i S_y \\
I_\pm &= I_x \pm i I_y
\end{aligned}
\tag{4.4}
$$

such that

$$\mathbf{S} \cdot \mathbf{I} = S_z I_z + \frac{1}{2}(S_+ I_- + S_- I_+) \tag{4.5}$$

Consider as an example a system with an unpaired electron and a single nucleus of spin $\frac{1}{2}$. This system is characterized by only four linearly independent spin states: $|1\rangle = |1/2; 1/2\rangle$, $|2\rangle = |1/2; -1/2\rangle$, $|3\rangle = |-1/2; 1/2\rangle$, and $|4\rangle = |-1/2; -1/2\rangle$. The energy levels can be obtained by diagonalizing $\mathcal{H}$ in the basis of the spin function $|m_S; m_I\rangle$

$$
\begin{aligned}
E_1 &= \frac{1}{2}g\mu_B B + \frac{1}{4}A, \\
E_{2,3} &= -\frac{1}{4}A \pm \frac{1}{2}g\mu_B B \left[1 + \left(\frac{A}{g\mu_B B}\right)^2\right]^{\frac{1}{2}}, \\
E_4 &= -\frac{1}{2}g\mu_B B + \frac{1}{4}A
\end{aligned}
\tag{4.6}
$$

Transitions between these energy levels are usually initialized by an oscillating magnetic field applied in a direction perpendicular to B. If this direction is taken to be x, the transition probability between two states j and k is proportional to $|\langle j|S_x|k\rangle|^2$. In our four-state system the nonvanishing matrix elements for S_x are:

$$
\begin{aligned}
\langle 1|S_x|2\rangle = \sin\theta &\quad,\quad \langle 1|S_x|3\rangle = \cos\theta \\
\langle 2|S_x|4\rangle = \cos\theta &\quad,\quad \langle 3|S_x|4\rangle = -\sin\theta
\end{aligned}
\tag{4.7}
$$

where θ is defined by

$$\tan 2\theta = \frac{|A|}{g\mu_B B}. \tag{4.8}$$

In the strong field case, θ is small and the transitions 1→3 and 2→4, with intensities proportional to $\cos^2 \theta$, will be strong while 1→2 and 3→4, proportional to $\sin^2 \theta$, are weak. The special result for our example with a spin one-half nucleus is that the splitting between the lines corresponding to the each of these transition pairs, 1→3⇔2→4 and 1→2⇔3→4, is defined only by the hyperfine coupling constant and is independent of the field strength.

4.3 The NMR spin Hamiltonian

The appearance of NMR spectra, in analogy with EPR, arises from the discrete nature of the energy levels of the nuclear spin system influenced by a static magnetic field. The number of energy levels that can be found for each isotope is characterized by the nuclear spin quantum number, I, associated with the nuclear spin momentum operator, I. It must be non-zero integer or half-integer to be observed in the spectrum. The magnetic moment of such a nucleus can be defined by the simple expression [33]:

$$\boldsymbol{\mu}_N = \gamma_N \mathbf{I}_N \tag{4.9}$$

where γ_N is the magnetogyric ratio for nucleus N.

Suppose that a static magnetic field B is in the z direction, then the NMR spin Hamiltonian is:

$$\mathcal{H} = -\gamma_N B I_z \tag{4.10}$$

When in addition to the static field B, a weak radiative electro-magnetic field is applied perpendicularly to z, transitions between the energy levels are realized. Time-dependent perturbation theory shows that the transition probability has a maximum when the frequency of the radiative field is equal to the classical Larmor frequency

$$\nu_0 = \frac{\gamma_N B}{2\pi}. \tag{4.11}$$

However, such a simple expression does not explain the features of real NMR spectra. Separate patterns corresponding to the different atomic groups in the molecule and the splitting of such patterns is observed in the spectrum. The chemical environment modifies the resonance frequency, and is modeled in the isotropic NMR spin Hamiltonian by a multiplicative factor. If we consider a real molecule with some electronic structure, the "electronic clouds" and associated electronic magnetic moments will act as a perturbation and modify the local magnetic field B. The local field at the nucleus is expressed in terms of the shielding tensor $\boldsymbol{\sigma}_N$ of nucleus N; in the case of an isotropic tensor the resonance frequency is now

$$\nu_0 = \frac{\gamma_N (1 - \sigma_N) B}{2\pi}, \tag{4.12}$$

which is a function of the local electronic environment.

In addition, if there are other magnetic nuclei in the molecule, the effects of nuclear spin-spin interaction must also be considered. In this case the NMR spin Hamiltonian of a diamagnetic molecule can be written in the form [8]:

$$\mathcal{H} = -\sum_N \gamma_N \mathbf{B}^T \cdot (1 - \boldsymbol{\sigma}_N) \cdot \mathbf{I}_N + \frac{1}{2} \sum_N \sum_{M \neq N} \mathbf{I}_N^T \cdot (\mathbf{D}_{NM} + \mathbf{J}_{NM}) \cdot \mathbf{I}_M. \qquad (4.13)$$

where $\mathbf{D}_{NM}$ and $\mathbf{J}_{NM}$ are direct and indirect nuclear spin-spin interaction tensors, respectively.

4.4   Magnetic resonance experiments

The principal routine providing the magnetic resonance experiments contains three main steps. In the first stage a static magnetic field produces a splitting of the energy levels. Then an additional electro-magnetic field is applied to excite transitions between energy levels. And finally, the absorbed radiation is measured.

To derive the necessary condition that defines the alternating magnetic field, we consider the system described by Eq. 4.10 containing two possible states $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$, or $|\alpha\rangle$ and $|\beta\rangle$. In addition to the static field B the weak radiative electro-magnetic field with the resonant or Larmor frequency ν_0 can be defined as $\mathbf{B}_1 \cos(2\pi\nu_0 t)$. The spin Hamiltonian describing an interaction between nuclear spin system and alternating field is:

$$\mathcal{H}_1 = -\gamma_N \cos(2\pi\nu_0 t)[B_{1x} I_x + B_{1y} I_y + B_{1z} I_z] \qquad (4.14)$$

or using Eq. 4.4

$$\mathcal{H}_1 = -\gamma_N \cos(2\pi\nu_0 t) \left[\frac{1}{2}(B_{1x} - iB_{1y})I_+ + \frac{1}{2}(B_{1x} + iB_{1y})I_- + B_{1z} I_z \right] \qquad (4.15)$$

Transitions between the two states α and β is allowed if $\langle\alpha|\mathcal{H}_1|\beta\rangle \neq 0$ and it can be shown that for

$$\langle\alpha|\mathcal{H}_1|\beta\rangle = -\gamma_N \cos(2\pi\nu_0 t) \left[\frac{1}{2}\langle\alpha|(B_{1x} - iB_{1y})I_+|\beta\rangle \right]$$

$$-\gamma_N \cos(2\pi\nu_0 t) \left[\frac{1}{2}\langle\alpha|(B_{1x} + iB_{1y})I_-|\beta\rangle + \langle\alpha|B_{1z} I_z|\beta\rangle \right] \qquad (4.16)$$

only $\langle\alpha|(B_{1x} - iB_{1y})I_+|\beta\rangle$ leads to a non-zero result. Therefore *a transition is possible if and only if the alternating magnetic field* $\mathbf{B}_1$ *is polarized perpendicularly to the static field* $\mathbf{B}$.
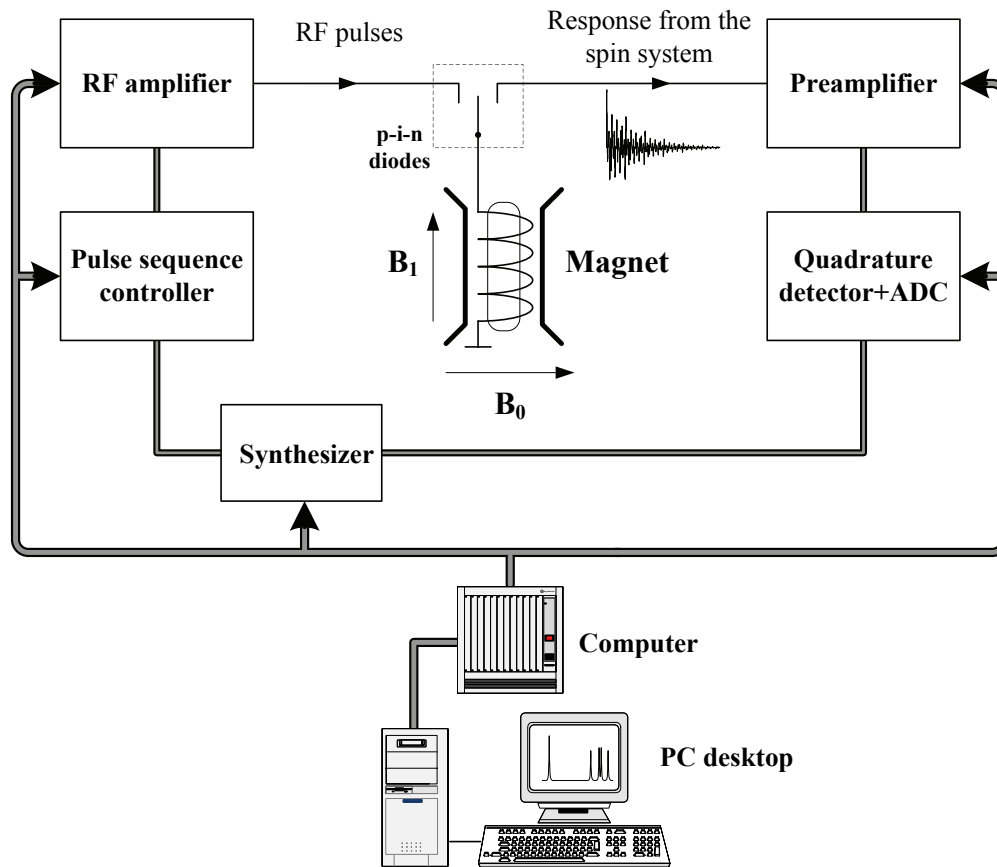
Figure 4.2: NMR spectrometer.

4.4.1 Nuclear magnetic resonance experiments

Nuclear magnetic resonance can be detected in substances that contain nuclei with non-zero magnetic moments. We already defined this magnetic moment in Eq. 4.9 and found that resonance between spin levels can be achieved by applying the radiative field with the frequency due to Eq. 4.12. Such radiation stimulates up and downward transitions equally and when the equilibrium situation is reached there is no net absorption any more - the signal is saturated. The non-radiative process that tends to bring the system to equilibrium is the exchange of the energy of the spin system and the surrounding called lattice. The settlement of equilibrium occurs through exponentially decaying processes characterized by the time constants called longitudinal and transverse relaxation times. Generally speaking, the first describes the system losing energy to the surrounding. It is also called spin-lattice relaxation. The second characterizes the system with spin-spin relaxation due to the interactions between nuclear spins. The NMR spectrometer (see Figure 4.2) provides the static magnetic field producing the splitting of the energy levels. The transitions between them for nuclear mag-
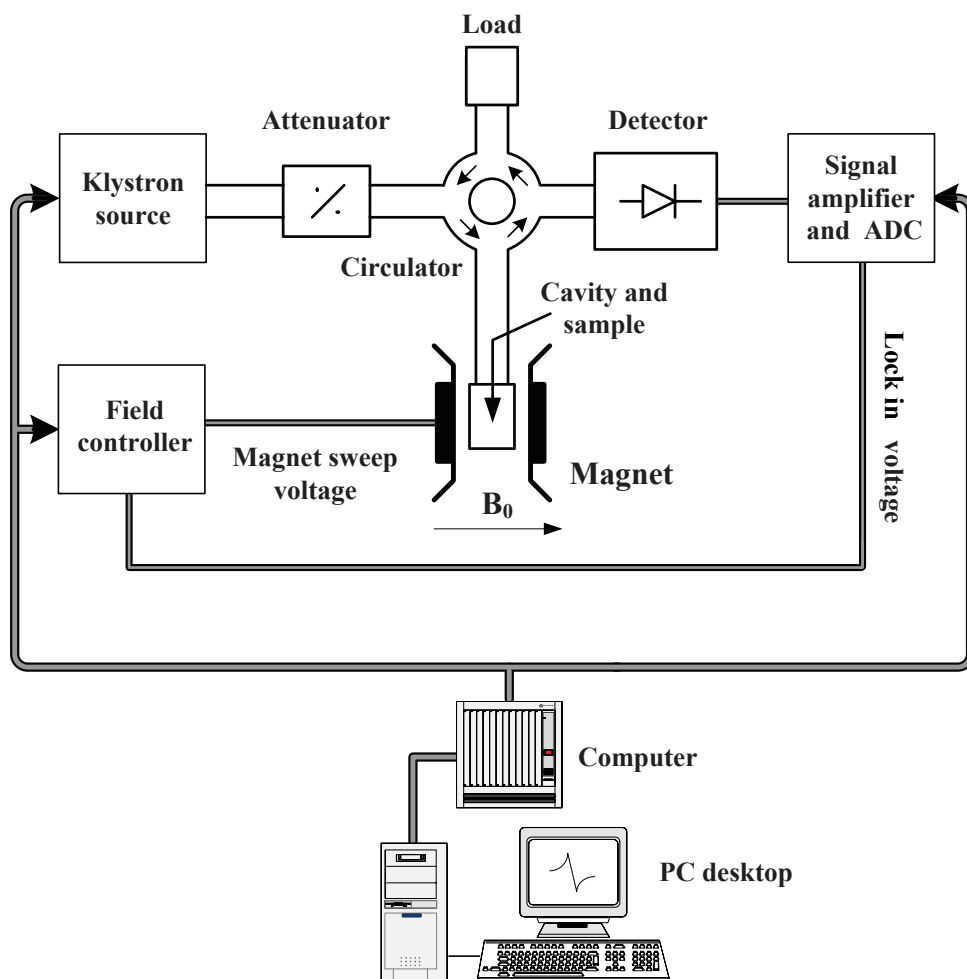
Figure 4.3: EPR spectrometer.

netic dipoles occur in the radio-frequency range. The resolution of the NMR spectrometer depends on the strength and homogeneity of the magnetic field and the constancy of radio-frequency radiation. In NMR the transition frequencies belong to the MHz region and characteristic relaxation times of the systems are 10^{-1}-10^{-5} s. In NMR spectrometers an oscillating magnetic field is applied in the direction perpendicular to the magnetic field produced by the magnet. This field rotates the magnetization vector of the sample from the equilibrium position to the direction of the applied field by an angle which is proportional to the magnetogyric ratio, the magnetic field strength and the duration of the pulse. Since the pulse is applied during a finite time, there is a transition energy associated with it. The output after the pulse is called a free induction decay. The period of the pulse gives the chemical shift of the studied system.

4.4.2 Electron paramagnetic resonance experiments

The basic formulation for EPR is very similar to NMR and many equations for EPR spin Hamiltonian can be found in Section 4.2. Electron paramagnetic resonance can be detected in substances containing unpaired electrons. These are free radicals, odd-electron molecules, triplet states of organic molecules and paramagnetic transition metal ions and their complexes. In EPR the transition frequencies belong to the microwave region (GHz), since the magnetic moment of the electron is almost 10^3-fold larger than for nuclei, with characteristic relaxation times being 10^{-4}-10^{-8} s. Because of the short relaxation times, pulsed experiments cannot easily be carried out in EPR. In a classical EPR spectrometer (see Figure 4.3) the frequency is held constant, and the magnetic field is swept through the resonance. When the transition between electronic levels occurs, part of the microwave radiation is absorbed, reducing microwave energy received at the detector.

Chapter 5

Theory of Magnetic Resonance Parameters

Magnetic resonance spectroscopy is a widely used area in the determination of molecular structures and dynamical processes in different materials. Along with the huge importance of experimental work in this area, theoretical calculations are also rapidly developing. In this chapter we discuss the recent state of the art in theoretical work concerning the calculations of magnetic resonance parameters. Following a short historical review, we will briefly describe the Breit-Pauli Hamiltonian which is used for a proper treatment of a molecular system influenced by an electromagnetic field. Formulations for calculation of electronic g-tensors, hyperfine coupling tensors and nuclear shielding tensors developed in this thesis are described in detail.

5.1   Magnetic resonance parameters in DFT

Our main focus in this section is the computational prediction of magnetic resonance parameters, such as electronic g-tensors, hyperfine coupling constants and nuclear shieldings, from a historical point of view. Here we make a general overview of DFT calculations that also form the main challenge of this thesis.

The electronic energy of a molecule placed in magnetic field is dependent on the perturbations caused by this field on the electrons. Such a perturbation is to lowest order proportional to the strength of the corresponding external field. Magnetic resonance parameters are second-order properties and can be expressed as second-order derivatives of the total electronic energy with respect to two perturbations: if the first perturbation is the magnetic field strength and the second is an electronic spin or nuclear magnetic moment one can obtain the g-tensor or nuclear shielding tensor, respectively; if the two perturbations are electronic and nuclear spins, hyperfine coupling can be investigated.

The usual way to solve the corresponding equations is by employing stationary perturbation theory, where the linear response of the molecular orbitals

to the external perturbation should be accounted for. The response of a particular molecular orbital depends on the linear response of all other occupied orbitals. This is formally a problem for DFT methods, because the local character of the exchange-correlation functional cancels the coupling between the linear responses of different molecular orbitals. In order to handle this problem, the standard exchange-correlation potential can be modified to enter both the electron density and the current density induced by the magnetic field dependences. Such a current density functional technique was employed by Vignale *et al.* in 1990 [34]. On the other hand we should notice here that almost all current implementations for computing magnetic resonance parameters are based on the common density functionals, as well as the work presented in this thesis.

Another problem arising in calculations of magnetic properties is the so-called gauge-problem. It is manifested in approximate schemes with finite one-electron basis sets as calculated magnetic parameters that depend on the choice of coordinate system. To handle this problem two widely used methods have been developed. The first one is called *individual gauges for localized orbitals* (IGLO) [35] and uses the gauge-dependent factor on localized orbitals. The second one is *gauge-including atomic orbitals* (GIAO) [36] , based on atom-centered basis functions with an explicit field dependence. Both methods give generally good results in comparison with experimental data. The work presented in this thesis treats the gauge origin problem by applying IGLO method.

A short and general description of the state of the art of calculations of electronic g-tensors, hyperfine coupling constants and nuclear shieldings is presented in the following.

- *Electronic g-tensors.* The theoretical determination of electronic g-tensors within density functional theory is a comparatively new field. The first significant implementations start to appear in the middle of the nineties. All of them can be divided on the basis of the method employed as one- and two-component methods. In the first group the Breit-Pauli Hamiltonian operators with approximated spin-orbit contributions are considered in the framework of perturbation theory. Schreckenbach and Ziegler [37] based their implementation on the GIAO scheme and derived an approximate two-electron spin-orbit (SO) operator from the exchange-correlation potential. The two-electron SO operator approximated with the atomic mean field (AMFI) concept is used in the work of Malkin and Kaupp [38]. And, finally, the so-called scaled SO approximation has been chosen by Neese [39].

  The second group of methods is based on the evaluation of the g-tensor as a first order property. The corresponding SO interaction here is included in the two-component Kohn-Sham equations. The first work based on this methodology belongs to van Lenthe *et al.* [40], who included relativistic effects through the ZORA technique. A similar two-component method was later used by Neyman *et al.* [41] in combination with the Douglas-

Kroll transformation of the Dirac-Kohn-Sham equation.

In the present thesis the evaluation of g-tensors is carried out by using spin-restricted open shell DFT linear response theory. The two-electron SO operators are approximated with the AMFI technique.

- *Hyperfine coupling.* The Fermi contact and magnetic dipole contributions to the hyperfine coupling tensor are first order properties and can be calculated as expectation values over the ground state wave function within almost all standard quantum chemistry packages. The critical requirement for obtaining accurate results of the hyperfine coupling tensor is a good description of the spin density at the position of the nucleus. Therefore, the choice of basis set is very important here. IGLO-type basis sets are recommended [42]. Also the EPR-II and EPR-III basis sets, specially designed by Barone and co-workers, are suitable [43]. Another important point is that spin-polarization and electron correlation should be as much as possible accounted for by the corresponding DFT method. There are a lot of works about calculations of hyperfine couplings with DFT. One should notice that generally there are good results only for light elements, while the corresponding values for transition metal compounds are still far from the ideal situation [44, 45, 46]. In this thesis we presented calculations of hyperfine couplings based on the spin-restricted Kohn-Sham formalism, while the spin-polarization problem is treated in the framework of the restricted-unrestricted approach.

- *Nuclear shielding.* A lot of experimental NMR data concerning different molecular systems provide good sources for theoretical investigations. The experimental identification of proton and carbon shieldings forms the main challenge of many works. But other, heavier nuclei, are also important. All of them can be calculated in an equal way in many DFT packages. Proton chemical shifts are comparatively difficult cases for calculation, because they are small and rovibrational and solvent effects can be comparable with the shifts themselves. Anyway, there are several successful investigations, for example the work of Rablen *et al.* reported the performance of popular hybrid functionals for 80 organic molecules [47]. ^{13}C, ^{15}N and ^{17}O chemical shifts calculated with the popular exchange-correlation and hybrid functionals were presented in the works of Cheeseman [48] and Barone [49] and many other authors. As was shown in these investigations the LDA functional gives the worst results, while BLYP the best ones. In any case, DFT systematically works better than HF and MP2. This means that DFT is the best tool for calculating nuclear shieldings with good accuracy, for molecules of various types and sizes.

Another important area of application for DFT is the calculation of chemical shifts of transition metal compounds. There are several reviews summarizing such investigations, for example the ones by Schreckenbach and

Ziegler [50], Kaupp and Malkin [51], Bühl [52]. They concluded that B3LYP and similar functionals give the best results, but none knows if the reason for that is to be explained by physics or in terms of a simple cancellation of errors. In any case, successful calculations of transition metal compounds open opportunities for investigations of biologically relevant molecules, since many of them contain metal centers.

5.2   The Breit-Pauli Hamiltonian

The energy of molecular systems can be obtained by solving the Schrödinger equation. The unique form of this equation is defined by the molecular Hamiltonian. The usual non-relativistic Hamiltonian includes the kinetic energy contribution, electron-electron interaction, nuclear-nuclear and electron-nuclear interactions and is widely used in quantum-chemical calculations. However, it cannot properly describe a molecular system influenced by internal and external electromagnetic fields. Instead of the usual field-free spinless non-relativistic Hamiltonian more complicated ones are required. Here we shortly discuss the Breit-Pauli Hamiltonian designed to account for external and nuclear electromagnetic fields, electron spin and relativistic effects [53].

The simplest scheme of construction of the Breit-Pauli Hamiltonian for a system of two electrons is shown in Figure 5.1. The sum of two one-electron Dirac Hamiltonians and an interaction term that is usually the Coulomb repulsion is used as a starting point. The resulting Hamiltonian is correct to zero order in the fine structure constant, α, and does not describe the relativistic interactions caused by spin and orbital motion. The Breit operator added in the next step gives us the Breit Hamiltonian corrected to the second order of α. The corresponding Breit equation for two electrons is the analogue to the Dirac equation for one electron. It can be reduced to the non-relativistic Pauli-type equation through the Foldy-Wouthuysen transformation and the resulting Hamiltonian here is called the Breit-Pauli Hamiltonian [54, 55]. It also can be extended to many electron system if all interactions are considered as additive and involving only two electrons.

The hypothetical situation when a system contains only electrons has been considered above. Real molecules are more complicated and electromagnetic fields experienced by electrons can not only be external but also internal caused by a nuclei. Nuclei can be treated as static sources of electromagnetic fields that allow one to simply extend the Breit-Pauli Hamiltonian mentioned above to the nuclei with the assumption that particles can have masses, charges, spins and magnetogyric ratios different from the electronic ones. Of course, some of the terms needed for the description of molecular properties could be absent, but at the moment there is no unambiguous and rigorous procedure for constructing a molecular Hamiltonian for particles other than electrons, except on a phenomenological basis.
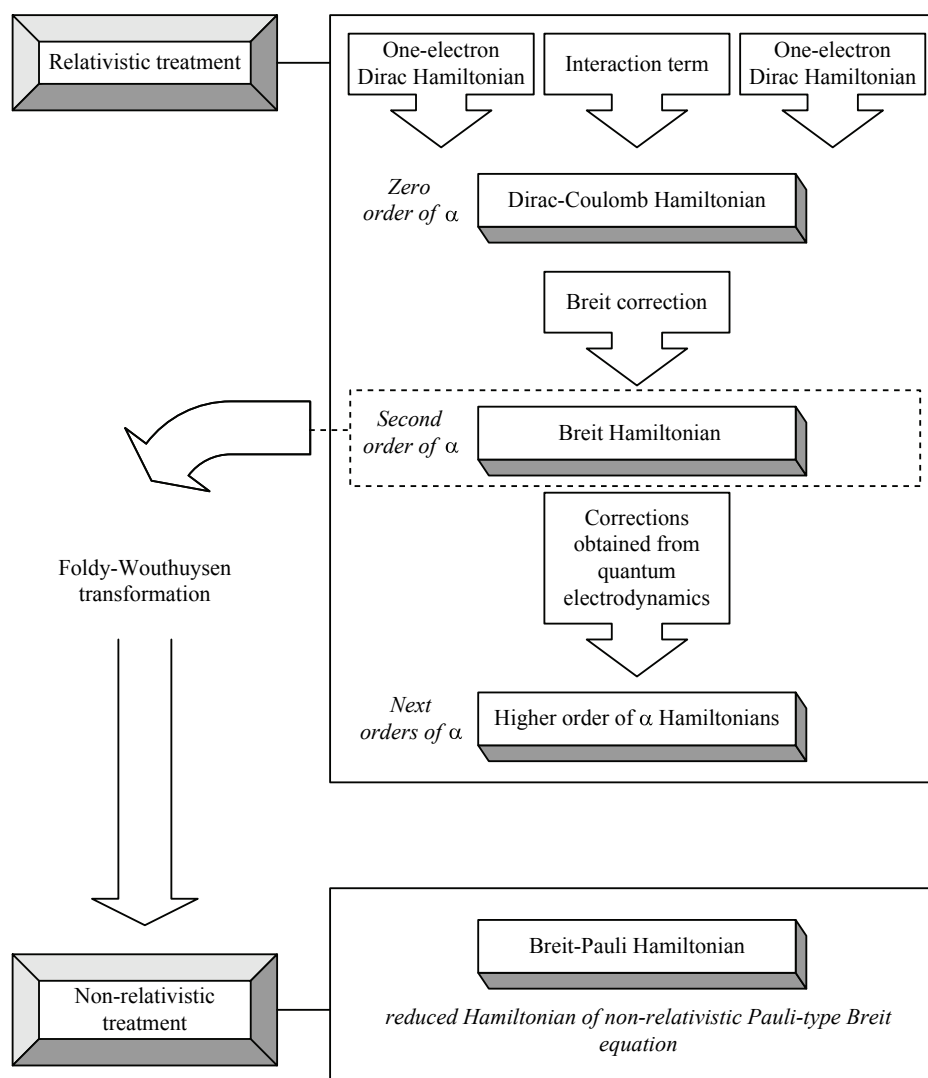
Figure 5.1: The methodology of Breit-Pauli Hamiltonian.

The approximate nature of the Breit-Pauli Hamiltonian does not allow for its application in direct electronic structure calculations because some of its terms are divergent. But the Breit-Pauli Hamiltonian provides a good way for evaluating different molecular properties in the framework of perturbation theory. All terms included in the Hamiltonian can be identified on the basis of the nature of the physical interactions. Following this classification one can get: kinetic energy contributions, Coulomb interactions, external electric interactions, Zeeman interactions, spin-orbit interactions, orbit-orbit interactions, spin-spin interactions and interactions of order α^4. We should notice here that the Hamiltonian itself is only correct to second order. A detailed formulation of each of the terms in the Breit-Pauli Hamiltonian is beyond the scope of this thesis. Let us consider only the most important terms for calculations of electronic g-tensors,

hyperfine coupling constants and nuclear shieldings, which are the main goal of this thesis.

- *The Zeeman interaction.* The orbital Zeeman effect contributes to the electronic g-tensor and nuclear shielding in the second order of perturbation theory. The mass-velocity correction to the electronic Zeeman term contributes to the electronic g-tensor in the first order.

- *Spin-orbit interaction.* The one-electron and two-electron spin-orbit operators contribute to the electronic g-tensor and give a main relativistic correction to the nuclear shielding constant. The paramagnetic spin-orbit operator is important for the nuclear shielding.

- *Spin-spin interaction.* The electron-nuclear spin-spin interaction term is the main contribution to the hyperfine coupling constant.

- *Diamagnetic interactions.* One and two-electron gauge corrections contribute to the electronic g-tensor in the first order of perturbation theory. A diamagnetic contribution is also important in calculations of nuclear shielding using Ramsey's expression. Electron-nuclear and nuclear-nuclear spin-spin diamagnetic interaction terms are important for hyperfine coupling constants in the first order of perturbation theory.

A detailed formulation of these operators is presented in next chapters where the evaluation of magnetic resonance parameters is described.

5.3   Electronic g-tensors, theoretical evaluation

The interaction of spin magnetic moments with the static external field is accounted for by the electronic Zeeman term in the EPR spin Hamiltonian:

$$\mathcal{H}_{ZE} = \mu_B \mathbf{S}^T \mathbf{g} \mathbf{B} \tag{5.1}$$

It is defined by the g-tensor, which consists of two contributions, the first one arises from the g-factor of the free electron, g_e=2.0023, while the second one reflects the interaction of the unpaired electron with the local environment in the molecule and, therefore, is a unique feature of each studied system. In order to separate the free electron contribution one can write the g-tensor in the form:

$$\mathbf{g} = g_e \mathbf{1} + \Delta \mathbf{g} \tag{5.2}$$

The g-tensors can be measured experimentally, but due to the difficulties in the interpretation of experimental spectra, theoretical evaluations are very helpful, not only for the correct extraction of g-values from completed measurements, but also for predicting the outcome of future experiments.

   The electronic g-tensor of a molecule can according to Eq. 5.1 be defined as a second order derivative of the molecular electronic energy with respect to the external magnetic field and electronic spin:

$$\mathbf{g} = \frac{1}{\mu_B} \frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{S}}\bigg|_{\mathbf{B}=0, \mathbf{S}=0} \tag{5.3}$$

The g_e term defining the free electron g-factor arises in a trivial way. Since the ordinary Zeeman operator has no spatial dependence for a uniform field, it can be directly included into the electronic Zeeman operator of the spin Hamiltonian. Additional corrections to the g-tensor are obtained in the first and second order of perturbation theory using Eq. 5.3 as expectation values of the corresponding Breit-Pauli Hamiltonian operators [56, 57]. Three of them, the mass-velocity correction to the electronic Zeeman effect, $\Delta\mathbf{g}_{\mathrm{RMC}}$, the one-electron gauge correction to the electronic Zeeman effect, $\Delta\mathbf{g}_{\mathrm{GC(1e)}}$ and the two-electron gauge correction to the electronic Zeeman effect, $\Delta\mathbf{g}_{\mathrm{GC(2e)}}$, contribute to first order. Their Cartesian ab components are:

$$\Delta\mathbf{g}_{\mathrm{RMC}}^{ab} = -\frac{\alpha^2}{S}\langle 0|\sum_i p_i^2 s_{z,i}|0\rangle \delta^{ab} \tag{5.4}$$

$$\Delta\mathbf{g}_{\mathrm{GC(1e)}}^{ab} = \frac{\alpha^2}{4S}\langle 0|\sum_i \sum_N \frac{Z}{r_{iN}^3}[(\mathbf{r}_{iN}\cdot\mathbf{r}_{iO})\delta^{ab} - \mathbf{r}_{iO}^a\mathbf{r}_{iN}^b]s_{z,i}|0\rangle \tag{5.5}$$

$$\Delta\mathbf{g}_{\mathrm{GC(2e)}}^{ab} = \frac{\alpha^2}{4S}\langle 0|\sum_i \sum_{i\neq j} \frac{1}{r_{ij}^3}[\mathbf{r}_{ij}\cdot(2\mathbf{r}_{jO}-\mathbf{r}_{iO})\delta^{ab} - (2\mathbf{r}_{jO}^a - \mathbf{r}_{iO}^a)\mathbf{r}_{ij}^b]s_{z,i}|0\rangle \tag{5.6}$$

where p_i is the canonical linear momentum of electron i, $s_{z,i}$ is the z-component of the spin operator of electron i, and $\mathbf{r}_{ij}$, $\mathbf{r}_{iN}$ and $\mathbf{r}_{iO}$ are the position vectors of electron i relative to electron j, nucleus N and gauge origin O, respectively. The second order contributions arise from the one- and two-electron spin orbit and orbital Zeeman cross terms:

$$\Delta\mathbf{g}_{\mathrm{OZ/SO(1e)}}^{ab} = \frac{1}{S}\langle\langle \ell_{iO}^a; H_{\mathrm{SO(1e)}}^b\rangle\rangle_0 \tag{5.7}$$

$$\Delta\mathbf{g}_{\mathrm{OZ/SO(2e)}}^{ab} = \frac{1}{S}\langle\langle \ell_{iO}^a; H_{\mathrm{SO(2e)}}^b\rangle\rangle_0 \tag{5.8}$$

where ℓ_{iO}^a is the Cartesian a component of the angular momentum operator of electron i, and $H_{\mathrm{SO(1e)}}^b$ and $H_{\mathrm{SO(1e)}}^b$ are Cartesian b components of the one- and two-electron SO operators:

$$H_{\mathrm{SO(1e)}}^b = \frac{\alpha^2}{2}\sum_i \sum_N \frac{Z_N \ell_{iN}^b}{r_{iN}^3} s_{z,i} \tag{5.9}$$

$$H_{\mathrm{SO(2e)}}^b = -\frac{\alpha^2}{2}\sum_i \sum_{i\neq j} \frac{\ell_{ij}^b + 2\ell_{ji}^b}{r_{ij}^3} s_{z,i} \tag{5.10}$$

The determination of these response functions is the most computationally demanding part of the calculations. Their evaluation can be realized with the different methods, such as sum-over-state DFT, coupled perturbed Kohn-Sham method in unrestricted Kohn-Sham formalism, or spin restricted open shell DFT linear response theory. The last method has been chosen for the implementations and applications presented in this thesis. This approach is formally free from the spin contamination problem, but is, on the other hand, unable to account for spin-polarization effects. The last ones generally are smaller than the spin contamination effects and we consider that fact as a good reason for implementation of spin restricted open shell theory.

If all of contributions mentioned above are taken into account, we arrive at the well-known equation for determination of the g-tensor:

$$\mathbf{g} = g_e \mathbf{1} + \Delta\mathbf{g}_{\mathrm{RMC}} + \Delta\mathbf{g}_{\mathrm{GC(1e)}} + \Delta\mathbf{g}_{\mathrm{GC(2e)}} + \Delta\mathbf{g}_{\mathrm{OZ/SO(1e)}} + \Delta\mathbf{g}_{\mathrm{OZ/SO(2e)}} \qquad (5.11)$$

The presented g-tensor formulation derived from the Breit-Pauli Hamiltonian can be used for *ab initio* implementations without any approximations. However, DFT, which is one electron theory, presents a more problematic case, requiring the two-electron operators, $\Delta\mathbf{g}_{\mathrm{GC(2e)}}$ and $\Delta\mathbf{g}_{\mathrm{OZ/SO(2e)}}$, to be treated in some specific way. One should note here, that the $\Delta\mathbf{g}_{\mathrm{GC(2e)}}$ contribution is essential only if the spin-orbit contributions are small and can usually be neglected without large loss of accuracy. $\Delta\mathbf{g}_{\mathrm{OZ/SO(2e)}}$ is, on the other hand, often one of the major contributions. Therefore, the quality of the approximation made for two-electron operators is very important for the final accuracy of the calculation.

There are several methods for treating two-electron operators in the spin-orbit and gauge correction contributions, such as scaling of the nuclear charges of corresponding one-electron operators or substitution the two-electron spin-orbit operators with atomic mean field spin-orbit operators. The mean field method used in the papers presented in this thesis is additionally simplified, that is the spin-orbit integrals are only calculated for individual atoms with full atomic symmetry imposed.

The proposed methodology was used in this thesis for calculations of main group radicals and transition metal compounds. In addition, comparison with the unrestricted Kohn-Sham method was done. We found an improvement of the g-tensor values for the main group radicals in the spin contamination free restricted DFT formalism. However, for the transition metal compounds the g-values are underestimated with respect to experiment in both methods. This is an unexplored field for theoretical research. The theoretical studies of electronic g-tensors of molecular systems placed in solvent are also presented in this thesis. The Polarizable Continuum Model was chosen to account for solute-solvent interactions.

5.4 Hyperfine coupling constants

The hyperfine coupling constant, A, describes the specific interaction between magnetic moments associated with the electronic and nuclear spins. This interaction is responsible for the so-called hyperfine splitting patterns of spectral lines in EPR spectroscopy and shifts of NMR spectral lines of paramagnetic compounds due to the contact and dipolar couplings. It is accounted for in the spin Hamiltonian through the term:

$$\mathcal{H}_{HFC} = \sum_{N=1}^{N} \mathbf{S}^T \cdot \mathbf{A}_N \cdot \mathbf{I}_N \tag{5.12}$$

The hyperfine coupling tensor is usually decomposed into isotropic and anisotropic parts that differ not only by their behavior in experiments but also by their different physical origin. The isotropic part arises from experiments realized in gas phase and solution and is determined by the non-classical Fermi contact interaction between electron and nuclear spins. The anisotropic part is significant only in ordered samples, where the molecules are oriented with respect to the static external magnetic field, and is determined by the classical magnetic dipole-dipole interaction between nuclear and electron spins.

The hyperfine coupling tensor can be defined as the second order derivative of the molecular electronic energy with respect to the electronic and nuclear spins:

$$\mathbf{A} = \frac{\partial^2 E}{\partial \mathbf{I} \partial \mathbf{S}}\bigg|_{\mathbf{I}=0,\mathbf{S}=0} \tag{5.13}$$

The contributions to the hyperfine coupling tensor can be obtained as expectation values of the corresponding Breit-Pauli Hamiltonian operators in the framework of first and second order perturbation theory. The Fermi contact, $\mathbf{A}_{FC}$, dipolar or magnetic dipole - dipole interaction, $\mathbf{A}_{SD}$, one-electron spin orbit, $\mathbf{A}_{HC-SO(1e)}$, two-electron spin - spin orbit, $\mathbf{A}_{HC-SSO(2e)}$, and two-electron spin other - orbit, $\mathbf{A}_{HC-SOO(2e)}$ contributions arise in the first order [58, 59].

The Cartesian ab components of the first order contributions can be written in the following form:

$$\mathbf{A}_{FC}^{ab} = \alpha^2 \frac{4\pi g_e g_N \mu_N}{3S} \langle 0| \sum_i \delta(\mathbf{r}_{iN}) s_{z,i} |0\rangle \delta^{ab} \tag{5.14}$$

$$\mathbf{A}_{SD}^{ab} = \alpha^2 \frac{g_e g_N \mu_N}{2S} \langle 0| \sum_i \frac{1}{r_{iN}^5} [3\mathbf{r}_{iN}^a \mathbf{r}_{iN}^b - \mathbf{r}_{iN}^2 \delta^{ab}] s_{z,i} |0\rangle \tag{5.15}$$

$$\mathbf{A}_{HC-SO(1e)}^{ab} = \alpha^4 \frac{g_e g_N \mu_N}{4S} \langle 0| \sum_i \sum_M \frac{Z_M}{r_{iN}^3 r_{iM}^3} [(\mathbf{r}_{iN} \cdot \mathbf{r}_{iM})\delta^{ab} - \mathbf{r}_{iN}^a \mathbf{r}_{iM}^b] s_{z,i} |0\rangle \tag{5.16}$$

$$\mathbf{A}_{HC-SSO(2e)}^{ab} + \mathbf{A}_{HC-SOO(2e)}^{ab} = \tag{5.17}$$

$$\alpha^4 \frac{g_e g_N \mu_N}{4S} \langle 0| \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^3 r_{iN}^3} [(\mathbf{r}_{iN} \cdot \mathbf{r}_{ij})\delta^{ab} - \mathbf{r}_{iN}^a \mathbf{r}_{ij}^b] \cdot (s_{z,i} + 2s_{z,j}) |0\rangle$$

where g_N is the nuclear g-tensor; μ_N - nuclear magneton; $\mathbf{r}_{ij}$, $\mathbf{r}_{iN}$, and $\mathbf{r}_{iM}$ are positions vectors of electron i relative to electron j and nuclei N and M, respectively; $s_{z,i}$ and $s_{z,j}$ are the z components of the spin operator of electrons i and j.

The second order contributions are defined as the cross terms between corresponding one- and two-electron spin orbit operators and the paramagnetic spin orbit operators:

$$\mathbf{A}^{ab}_{PSO/SO(1e)} \;=\; \alpha^4 \frac{g_e g_N \mu_N}{4S} \left\langle\!\!\left\langle \sum_i \frac{\ell^a_{iN}}{r^3_{iN}}; \sum_i \sum_M \frac{Z_M \ell^b_{iM}}{r^3_{iM}} s_{z,i} \right\rangle\!\!\right\rangle_0 \tag{5.18}$$

$$\mathbf{A}^{ab}_{PSO/SO(2e)} \;=\; \alpha^4 \frac{g_e g_N \mu_N}{4S} \left\langle\!\!\left\langle \sum_i \frac{\ell^a_{iN}}{r^3_{iN}}; \sum_i \sum_{j\neq i} \frac{\ell^b_{ij}}{r^3_{ij}} \cdot \left(s_{z,i} + 2s_{z,j}\right) \right\rangle\!\!\right\rangle_0 \tag{5.19}$$

where ℓ^a_{iN} and ℓ^a_{iM} are the Cartesian a components of the angular momentum operator of electron i; ℓ^b_{ij} is the corresponding b component for electron i.

The hyperfine coupling tensor is the sum of all of these contributions:

$$\begin{aligned} \mathbf{A} = \mathbf{A}_{FC} + \mathbf{A}_{SD} \;&+\; \mathbf{A}_{HC-SO(1e)} + \mathbf{A}_{HC-SSO(2e)} + \mathbf{A}_{HC-SOO(2e)} \\ &+\; \mathbf{A}_{SO(1e)/PSO} + \mathbf{A}_{SO(2e)/PSO} \end{aligned} \tag{5.20}$$

In practice, for free radicals only first order Fermi contact and dipolar contributions are significant. If transition metal compounds with relatively large spin orbit and other relativistic effects are considered, additional contributions describing the interaction between electronic angular momenta with magnetic dipole moments of the nuclei must be included.

Despite that calculations of Fermi contact and spin dipolar contributions are formally simple, there are open questions regarding the spin polarization effects. These questions are addressed in our work through the restricted- unrestricted method, which means that the wave function is calculated with a spin-restricted optimization allowing one to avoid the spin contamination problem, and relaxed in the presence of perturbation by introducing additional variables.

In the restricted-unrestricted method the Fermi contact and spin dipolar contributions are calculated not only as expectation values of the corresponding Breit-Pauli Hamiltonian operators, Eqs. 5.14 and 5.15, but additional spin polarization terms appear. These terms are computed as linear response functions and account for the relaxation of the wave function or spin density in the presence of hyperfine operators:

$$\mathbf{A}_{FC} = \langle 0|H_{FC}|0\rangle + \langle\!\langle H_{KS}; H_{FC}\rangle\!\rangle_0 \tag{5.21}$$

$$\mathbf{A}_{SD} = \langle 0|H_{SD}|0\rangle + \langle\!\langle H_{KS}; H_{SD}\rangle\!\rangle_0 \tag{5.22}$$

where H_{KS} is the unpeturbed Kohn-Sham Hamiltonian.

Originally, the response terms in Eqs. 5.21 and 5.22 were calculated as triplet response functions, neglecting the coupling between singlet and triplet orbital rotations introduced in the parameterization of the perturbed Kohn-Sham determinant; the motivation for this approximation is that the triplet excitations should play the major role in the spin polarization process. As it was shown in one of the works presented in this thesis, including the mixing of singlet and triplet orbital rotations does not essentially affect the final quality of the results.

5.5 NMR of paramagnetic molecules

5.5.1 Nuclear magnetic shielding in diamagnetic molecules

Given an external magnetic field, the local field experienced by a nucleus depends strongly on its local electronic environment in the molecule. The quantity accounting for this effect is called the nuclear shielding tensor, $\boldsymbol{\sigma}_N$. The $\boldsymbol{\sigma}_N$ tensor is presented in the spin Hamiltonian by the nuclear Zeeman term:

$$\mathcal{H} = -\sum_N \gamma_N \mathbf{B}^T \cdot (1 - \boldsymbol{\sigma}_N) \cdot \mathbf{I}_N = -\sum_N g_N \mu_N \mathbf{B}^T \cdot (1 - \boldsymbol{\sigma}_N) \cdot \mathbf{I}_N \qquad (5.23)$$

The nuclear shielding tensor of the molecule due to Eq. 5.23 can be defined as the second order derivative of the electronic energy with respect to the external magnetic field and nuclear spin:

$$\boldsymbol{\sigma} = \frac{1}{\gamma} \frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{I}} \bigg|_{\mathbf{B}=0, \mathbf{I}=0} \qquad (5.24)$$

In the framework of first and second order perturbation theory based on the Breit-Pauli Hamiltonian, two leading contributions to the nuclear shielding tensor can be calculated. The diamagnetic nuclear spin - electron orbit term arises in the first order; its Cartesian ab component reads:

$$\sigma_{N,ab}^{\text{dia}} = \frac{1}{\gamma_N} \frac{\partial^2}{\partial I_N^a \partial B^b} \langle 0 | H_{DS(N,B)} | 0 \rangle \bigg|_{\mathbf{I}_N=0, \mathbf{B}=0} \qquad (5.25)$$

$$H_{DS(N,B)} = \frac{1}{2} \alpha^2 \gamma_N \sum_i \mathbf{I}_N \cdot \frac{\mathbf{1}(\mathbf{r}_{iO} \cdot \mathbf{r}_{iN}) - \mathbf{r}_{iO}\mathbf{r}_{iN}}{r_{iN}^3} \cdot \mathbf{B} \qquad (5.26)$$

In the second order, the paramagnetic nuclear spin - electron orbit contribution is calculated as a cross term between the paramagnetic nuclear spin - electron orbit and orbital Zeeman operators.

$$\sigma_{N,ab}^{\text{para}} = \frac{1}{\gamma_N} \frac{\partial^2}{\partial I_N^a \partial B^b} \langle\langle H_{PSO(N)}; H_{OZ(B)} \rangle\rangle_0 \bigg|_{\mathbf{I}_N=0, \mathbf{B}=0} \qquad (5.27)$$

$$H_{PSO(N)} = \alpha^2 \gamma_N \sum_i \frac{\ell_{iN}}{r_{iN}^3} \cdot \mathbf{I}_N \qquad (5.28)$$

$$H_{OZ(B)} = \frac{1}{2} \sum_i \ell_{iO} \cdot \mathbf{B} \tag{5.29}$$

Thus, the nuclear shielding tensor of diamagnetic molecules, also called the orbital shielding tensor (being independent of electron spin), is given by the sum of the diamagnetic and paramagnetic contributions [60]:

$$\boldsymbol{\sigma}_N^{\mathrm{orb}} = \boldsymbol{\sigma}_N^{\mathrm{dia}} + \boldsymbol{\sigma}_N^{\mathrm{para}} \tag{5.30}$$

5.5.2   Nuclear magnetic shielding in paramagnetic molecules

Consider now how the nuclear shielding tensor can be defined in the case of paramagnetic molecules. Such systems contain unpaired electrons along with non-zero spins nuclei. The spin Hamiltonian of paramagnetic molecules, where specific nuclear spin-spin interactions are ignored, can be written in the general form [9, 61]:

$$\mathcal{H} = \mu_B \mathbf{B}^T \cdot \mathbf{g} \cdot \mathbf{S} - \sum_N g_N \mu_N \mathbf{B}^T \cdot (1 - \boldsymbol{\sigma}_N) \cdot \mathbf{I}_N + \sum_N \mathbf{S} \cdot \mathbf{A}_N \cdot \mathbf{I}_N \tag{5.31}$$

The energy levels of a paramagnetic system with unpaired electron and a single magnetic nucleus ($I = 1/2$), and with an isotropic g-tensor described by Eq. 5.31, are shown in Figure 5.2.

Suppose, that the studied paramagnetic system interacting with the external magnetic field is described by the Breit-Pauli Hamiltonian. The nuclear shielding tensor is again defined by Eq. 5.24. In addition to the orbital shielding contributions, the effects emanating from the interaction between the unpaired electron and the nuclear spins must be taken into account. Such effects are described by the hyperfine interaction operators of the Breit-Pauli Hamiltonian.

The Fermi contact and the spin dipolar operators contribute to the nuclear shielding in the first order of perturbation theory:

$$H_{FC(N)} = \alpha^2 \frac{4\pi}{3} g \gamma_N \sum_i \delta(\mathbf{r}_{iN}) \mathbf{S}_i \cdot \mathbf{I}_N \tag{5.32}$$

$$H_{SD(N)} = \alpha^2 \frac{1}{2} g \gamma_N \sum_i \mathbf{I}_N \cdot \frac{3\mathbf{r}_{iN} \cdot \mathbf{r}_{iN} - \mathbf{1} r_{iN}^2}{r_{iN}^5} \cdot \mathbf{S}_i \tag{5.33}$$

Strictly speaking, these two contributions completely describe the interaction affecting the nuclear shielding tensor in light main-group radicals. Molecular systems with large spin-orbit coupling and other relativistic effects require those other operators consistent up to fourth order in the fine-structure constant are taken into account (see section 4.5).

The corresponding nuclear shieldings can be obtained, according to Eq. 5.24, as the expectation values of the Fermi contact and spin dipolar operators. The expectation value of the electronic spin angular momentum S, when z is taken
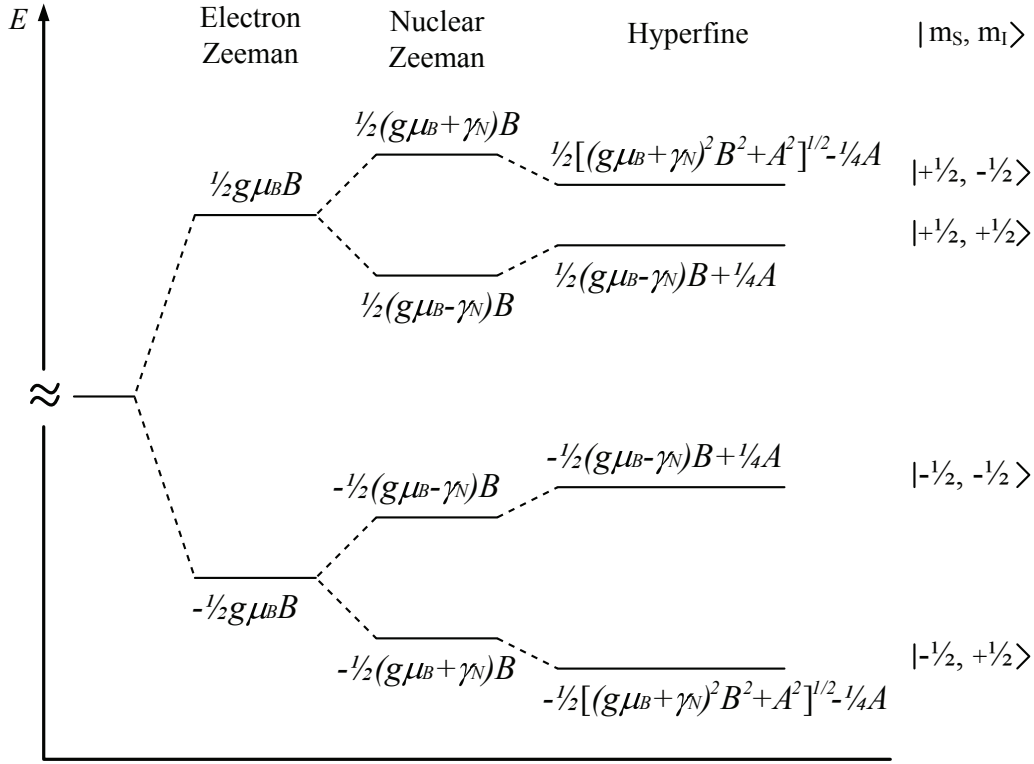
Figure 5.2: The energy levels structure of a proton-like system in an isotropic medium. The direction of the external magnetic field **B** is assumed to be along the z axis.

to be the direction of the static magnetic field B and temperature is so high that the thermal energy is large compared to the Zeeman energy, is defined in the form [62]:

$$\langle S_z \rangle = -g\mu_B \frac{S(S+1)B}{3kT} = -\frac{1}{2}g\frac{S(S+1)B}{3kT} \tag{5.34}$$

The contact shielding and dipolar shielding becomes, respectively:

$$\sigma_{N,ab}^{\text{con}} = \frac{1}{\gamma_N} \frac{\partial^2 \langle H_{FC(N)} \rangle}{\partial I_N^a \partial B^b}\bigg|_{\mathbf{I}_N=\mathbf{0},\mathbf{B}=\mathbf{0}} = -\frac{\pi}{\gamma_N} A_N^{\text{iso}} \delta^{ab} g \frac{S(S+1)}{3kT} \tag{5.35}$$

$$\sigma_{N,ab}^{\text{dip}} = \frac{1}{\gamma_N} \frac{\partial^2 \langle H_{SD(N)} \rangle}{\partial I_N^a \partial B^b}\bigg|_{\mathbf{I}_N=\mathbf{0},\mathbf{B}=\mathbf{0}} = -\frac{\pi}{\gamma_N} A_{N,ab}^{\text{dip}} g \frac{S(S+1)}{3kT} \tag{5.36}$$

where A_N^{iso} is the isotropic hyperfine coupling constant; $A_{N,ab}^{\text{dip}}$ is the component of the dipolar hyperfine coupling tensor; and where the notation $\langle\ \rangle$ expresses the ensemble average, reflecting that in the time-scale of an NMR experiment, only the average spin polarization is detectable [62]. The Fermi contact contribution describes the interaction of the nuclear magnetic moments with the electronic currents induced by the electron density at the nuclear positions themselves. The spin dipolar interaction can be defined as the interaction between

two magnetic dipoles going through space: one of them is localized on the nucleus, while another is formed by the electron spin density outside this nucleus. The dipolar contribution influences the anisotropy and asymmetry of the nuclear shielding. The contact contribution is isotropic.

The total nuclear shielding tensor of a paramagnetic molecule, where only the first-order temperature-dependent paramagnetic contributions are included, can be written as sum of orbital, contact and dipolar shieldings,

$$\boldsymbol{\sigma}_N = \boldsymbol{\sigma}_N^{\mathrm{orb}} + \boldsymbol{\sigma}_N^{\mathrm{con}} + \boldsymbol{\sigma}_N^{\mathrm{dip}} \tag{5.37}$$

5.5.3   Chemical shifts

The chemical shift is the central quantity provided by NMR spectra. The main requirement in the measurement of the chemical shift is to maintain the magnetic field homogeneity. If this requirement is largely satisfied, only the effects from the electronic environment of the nuclei affect the resonance frequency. This resonance frequency can be measured with respect to the resonance frequency of some reference compound [33]:

$$\delta^{\mathrm{exp}} = \frac{\nu_0 - \nu_{\mathrm{ref}}}{\nu_{\mathrm{ref}}} \tag{5.38}$$

and is usually expressed in ppm. It can also be defined in terms of nuclear shielding constants:

$$\delta^{\mathrm{exp}} = \sigma_{\mathrm{ref}} - \sigma_0 \tag{5.39}$$

Following our previous discussion, the chemical shift of a paramagnetic molecule in an isotropic environment, where $\sigma_{\mathrm{iso}} = \frac{1}{3}\mathrm{Tr}\,\boldsymbol{\sigma}$ is satisfied, can be written as:

$$\delta = \sigma_{\mathrm{iso}}^{\mathrm{ref}} - \left(\sigma_{\mathrm{iso}}^{\mathrm{orb}} + \sigma_{\mathrm{iso}}^{\mathrm{con}}\right) \tag{5.40}$$

the $\sigma_{\mathrm{iso}}^{\mathrm{ref}}$ is here the shielding constant of the resonating nucleus in the diamagnetic reference compound.

Chapter 6

Summary

Density functional theory provides a relatively fast and inexpensive way for calculations of spin Hamiltonian parameters among other theoretical methods applied in recent times. Therefore it has been systematically used in the works presented in thesis.

The implementation of *ab initio* restricted open-shell Hartree-Fock, multiconfiguration self-consistent field (MCSCF) and uncoupled sum-over-state density functional theory methods for calculations of the nuclear shielding tensors of open-shell organic molecules is presented in paper I. This work was realized with standard quantum chemistry packages, such as DALTON and deMon-NMR-EPR, with the aim to extend the closed-shell nuclear shielding code to open-shell systems, by using available code for calculations of hyperfine coupling tensors. The proposed approach, consistent to second- order in the fine structure constant, and neglecting spin-orbit coupling and orbital contributions to the magnetic susceptibility, was applied to calculations of small radicals (BH_2, CH_2^- and NH_2) at the *ab initio* level, as well as to medium size nitroxides at the DFT level. A detailed formulation for the orbital and spin-dependent fully isotropic Fermi contact and anisotropic spin-dipole contributions was presented. A quantitative (MCSCF) and qualitative (DFT) agreement with available experimental data was achieved, while the uncorrelated ROHF results were classified as unacceptable. This prompted us to use the DFT methodology for investigations of larger organic molecular systems.

The influence of hydrogen bonding in nuclear shielding tensors of nitronylnitroxides was studied in paper II. We used our previously developed formalism for calculations of NMR shieldings of hydrogen-bonded hydroxyphenyl nitronylnitroxide complexes in which water molecules were used to simulate the molecular environment of the real crystal structure. The comparison of calculated and experimental data was in good agreement for the proposed model of molecular crystals, as the signs and trends in the NMR chemical shifts were fully reproduced. In addition, it was found that the magnetic nature characterizing each type of crystal was strictly reflected in the changes of the contact contribution to the nuclear shielding tensors of these molecules. These changes

correspond to the spin delocalization pattern in the molecules and are strongly influenced by the bonding with the water molecules and by the mutual interaction of the imidazolyl and phenyl rings. The orbital part of the shielding was also found to have a relatively large magnitude in comparison with the contact term, and was dominated by the first order non-paramagnetic effects.

Calculations of EPR parameters, such as the electronic g-tensors and hyperfine coupling constants, were presented in the next papers. Our method based on a spin-restricted open-shell Kohn-Sham formalism, which is free of the spin contamination problem, combined with linear response theory was used for the calculation of electronic g-tensors. The atomic mean field spin-orbit operators were proposed for an approximate treatment of the two-electron spin-orbit operators in the calculations of the second-order contributions to the g-tensors.

Paper III presents test calculations with the aim to examine the performance of the proposed formalism. A group of organic radicals and transition metal compounds was investigated. The calculated results were compared with MR-CI as a reference method for organic radicals and with corresponding unrestricted calculations. Quantitative agreement with results of high level $ab\ initio$ calculations and experimental data was indicated for all organic radicals except of anions where the spin polarization plays a large role and unrestricted methods work better. The investigation of various exchange-correlation functionals indicates the best performance for the BP86 functional. The corresponding results for the transition metal compounds were systematically underestimated and showed a strong dependence on the choice of exchange-correlation functional. In this case a good performance for the BHPW91 functional was found, that gives systematically improved results for all molecules except $Ni(CO_3)H$. Contrary to previous suggestions by other authors, it was concluded that the source of this problem is not related to the spin contamination problem.

In paper IV, the previously developed formalism for the calculations of electronic g-tensors was extended by the possibility to include solvent effects treated in the framework of the polarizable continuum model (PCM). Calculations of two simple organic species, di-t-butyl nitric oxide and diphenyl nitric oxide, in protic and aprotic solvents were carried out. The quality of the results confirms the inability of PCM to properly describe the solvent effects coming from a protic environment, where hydrogen bonding plays a significant role and should be included explicitly. The BP86 functional was seen to perform better than others in this context. Among different types of optimized geometries the one optimized in vacuum gives results closest to experiment.

Paper V presents calculations of hyperfine coupling constants. The restricted-unrestricted approach previously applied only at the MCSCF level and which accounts for spin polarization was implemented and tested for the spin-restricted Kohn-Sham method. This allows for a proper description of both spin contamination and spin polarization effects that cannot be realized in the unrestricted Kohn-Sham method widely used in many quantum chemistry pack-

ages. The results of the calculations of hyperfine coupling constants for a selected set of organic radicals and transition metal compounds indicate a good performance of the restricted-unrestricted approach. This accomplishment considerably extends the ability of quantum chemical calculations of EPR spectral parameters. It was found that for organic radicals the performance of the spin-restricted and unrestricted methods is rather similar and the only advantage of the first one is the possibility to separate the spin-polarization term from the direct term related to the unpaired electron density contribution. At the same time, significant differences between unrestricted and restricted-unrestricted results were found for transition metal compounds, where spin contamination can be essential. The testing of different exchange-correlation functionals shows that B3LYP can be recommended for such type of calculations.

A generalization of the previously described restricted-unrestricted approach for calculations of hyperfine coupling tensors is presented in paper VI. The formalism was extended by accounting for the mixing between singlet and triplet excitations instead of describing the spin polarization in terms of the triplet operators only. The same set of organic radicals and transition metal compounds was used for checking the performance of the proposed method. For both classes of molecules the corresponding changes in the isotropic hyperfine coupling constants were found to have the order of a few megahertz. That indicates that only a negligibly small effect introduced the singlet excitation operators. Therefore, the previously accepted approximation was confirmed, and the simplified restricted-unrestricted approach where only triplet operators are accounted for in the response term is able to adequately describe the spin polarization effect.

Paper VII reports the calculations of electronic g-tensors and hyperfine coupling tensors for azurin model compounds including the well-known model for the blue copper active site along with five extended models containing Met13, Met44, Asn47, Thr113 and Ser118. The calculated electronic g-tensors were found to be in good correlation with experimental data. On the other hand, an agreement between the calculated hyperfine coupling tensors and a rather limited set of experimental data was not as clear. Generally, the isotropic hyperfine coupling constants of the remote nitrogens N_{ϵ_2} and hydrogens H_{ϵ_2} of both His46 and His117 are not satisfactorily reproduced causing a poor total hyperfine coupling tensor. We attributed the failure in the description of these hyperfine coupling constants to the small spin polarization contribution obtained in our work. As expected, large paramagnetic influence of the copper center on the coordinated residues was found, while far away from the metal site it starts to decrease. Surprisingly, the hyperfine couplings of the backbone nuclei of both Asn47 and Thr113 were found to be quite large and to have different mechanisms of formation. We also reported data for the total hyperfine coupling tensors of the remaining residues. The only available experimental data for backbone nitrogen of Asn47 correlate well with the calculated total hyper-

fine coupling.

The next paper, paper VIII, presents a summary of the theory and applications of spin-restricted DFT linear response theory for calculations of properties of open-shell molecules. It contains a short description of several previous works concerning an implementation of DFT linear response in the DALTON program and its performance in a wide range of applications, such as calculations of excitation energies; dynamic polarizabilities; g-tensors of transition metal radicals; g-tensors for the molecules influenced by solvent; and, finally, hyperfine-couplings of transition metal radicals.

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