

Optical and Magnetic Properties of Copper(II) compounds.

Katia Júlia de Almeida



Department of Theoretical Chemistry
School of Biotechnology
Royal Institute of Technology
Stockholm, Sweden 2007

Copyright ©2007 by Katia Júlia de Almeida

ISBN 978-91-7415-014-8

Printed by Universitetservice US AB, Stockholm 2008

Abstract

This thesis encloses quantum chemical calculations and applications of a response function formalism recently implemented within the framework of density functional theory. The optical and magnetic properties of copper(II) molecular systems are the main goal of this work. In this work, the visible and near-infrared electronic transitions, which have shown a key role in studies on electronic structure and structure-function relationships of copper compounds, were investigated in order to explore the correlation of the positions and intensities of these transitions with the geometrical structures and their molecular distortions. The evaluation of solvent effects on the absorption spectra were successfully achieved, providing accurate and inedit computational insight of these effects for copper(II) complexes. Electron Paramagnetic Resonance (EPR) parameters, that is, the electronic g tensor and the hyperfine coupling constants, are powerful spectroscopic properties for investigating paramagnetic systems and were thoroughly analysed in this work in different molecular systems. Relativistic corrections generated by spin-orbit interactions or by scalar relativistic effects were taken into account in all calculations. In addition, we have designed a methodology for accurate evaluation of the electronic g tensors and hyperfine coupling tensors as well as for evaluation of solvent effects on these properties. It is found that this methodology is able to provide reliable and accurate results for EPR parameters of copper(II) molecular systems. The spin polarization effects on EPR parameters of square planar copper(II) complexes were also considered, showing that these effects give rise to significant contributions to the hyperfine coupling tensor, whereas the electronic g tensor of these complexes are only marginally affected by these effects. The evaluation of the leading-order relativistic corrections to the electronic g tensors of molecules with a doublet ground state has been also taken into account in this work. As a first application of the theory, the electronic g tensors of dihalogen anion radicals X_2^- ($X=F, Cl, Br, I$) have been investigated and the obtained results indicate that the spin-orbit interaction is responsible for the parallel component of the g tensor shift, while both the leading-order scalar relativistic and spin-orbit corrections are of minor importance for the perpendicular component of the g tensor in these molecules since they effectively cancel each other. Overall, both optical and magnetic results show quantitative agreements with experiments, indicating that the methodologies employed form a practical way in study of copper(II) molecular systems including those of biological importance.

List of publications

Paper I K. J. de Almeida, Z. Rinkevicius, H. W. Hugosson, A. Cesar and H. Ågren **Modeling of EPR parameters of copper(II) aqua complexes.** *Chem. Phys.*, **332**, 176-187 (2007).

Paper II K. J. de Almeida, N. A. Murugan, Z. Rinkevicius, H. W. Hugosson, A. Cesar and H. Ågren **Conformations, structural transitions and visible near infrared absorption spectra of four-, five- and six-coordinated Cu(II) aqua complexes.** *submitted to Physical Chemistry Chemical Physics.*

Paper III K. J. de Almeida, Z. Rinkevicius, O. Vahtras, A. Cesar and H. Ågren **Modelling the visible absorption spectra of copper(II) acetylacetonate by density functional theory.** *in manuscript* .

Paper IV K. J. de Almeida, Z. Rinkevicius, O. Vahtras, A. Cesar and H. Ågren **Theoretical study of specific solvent effects on the optical and magnetic properties of copper(II) acetylacetonate.** *in manuscript*.

Paper V Z. Rinkevicius, K. J. de Almeida, O. Vahtras **Density functional restricted-unrestricted approach for nonlinear properties: Application to electron paramagnetic resonance parameters of square planar copper complexes.** *submitted to Journal of Chemical Physics.*

Paper VI K. J. de Almeida, Z. Rinkevicius, C. I. Oprea, O. Vahtras, K. Ruud and H. Ågren **Degenerate perturbation theory for electronic g tensors: leading-order relativistic effects.** *submitted to Journal of Chemical Theory and Computation.*

My contribution

- I performed most of the calculations in **papers I, II, III and IV** and wrote the manuscripts of **papers II, III and IV**
- I proposed the subject of the investigations of **papers I, II, III and IV**.
- I performed some calculations in **paper V and VI** and I participated in the preparation of the manuscripts of **papers I, V and VI**.

Acknowledgments

Firstly, I would like to express my sincere gratitude to my supervisor Prof. Hans Ågren for giving me the opportunity to carry out this project at the theoretical Chemistry Department, allowing me to do a lot by myself and always with an enthusiastic incentive. In particular, I am deeply thankful to him for giving me all the need support in many respects with kind understanding. Secondly, I would like to thank my supervisor Dr. Olav Vahtras for warm welcome and kind help in many aspects. I am really thankful to Dr. Zilvinas Rinkevicius for positive guidance and invaluable support during all work.

I wish to thank all colleagues: Kathrin Hopmann, Emil Jasson, Freddy Guimarães, Prakash C. Jha, Arul Murugan, Ying Hou, Keyan Lian, Xiaofei Li, Xin Li, Sathya Perumal, Hao Ren, Guangde Tu, Fuming Ying, Qiong Zhang and all members of Theoretical Chemistry for a great, pleaseant and warm working environment. I am very grateful to Dr. Viviane C. Felicissimo and Dr. Cornel Oprea for invaluable friendship and help in several moments. A lot of thanks to Lotta for giving me all help and support with small and big things.

I am very thankful to my family: my mother, brothers and sister for all their love. Finally, I would like to thank the most important people of my life, my dear husband, Jonas, and my kids, Gabriel and Rafael, for their constant and warm support and love, making me feel a really blessed person.

Contents

1	Introduction	1
2	Electronic Absorption Spectroscopy	5
2.1	Crystal and Ligand-Field theory	6
3	Magnetic Resonance Spectroscopy	9
3.1	The EPR spin Hamiltonian	11
4	Calculations of Paramagnetic Properties	15
4.1	The electronic g tensors	15
4.1.1	The electronic g tensor: Theoretical evaluation	17
4.1.2	The relativistic corrections to g tensors	19
4.2	The hyperfine coupling constants	20
4.2.1	The hyperfine coupling constants: Theoretical evaluation	21
4.2.2	Spin polarization effects in g tensors and hyperfine coupling constants	23
5	Computational Methods	27
5.1	Density Functional Theory	27
5.1.1	The Kohn-Sham approach	28
5.1.2	Exchange-correlation functionals	32
5.2	Response Theory	33
5.2.1	Linear response function	35
5.2.2	Quadratic response function	36

5.3	Solvent models	36
5.3.1	Dielectric continuum models	37
5.3.2	Discrete models	39
6	Summary of Papers	43

Chapter 1

Introduction

Copper molecular complexes have attracted increasing interest in chemistry and biochemistry due to their importance in biological systems.^{1,2} A broad range of chemical processes, including electron transfer, reversible dioxygen binding and nitrogen oxide transformations, is mediated by copper ions in active sites of protein and enzymes.²⁻⁴ The copper centers play a key role in several catalytic processes such as methane hydroxylation and dioxygen activation.^{2,4,5} Approximately one-half of all known protein crystal structures in the protein data banks contains metal ion cofactors, which are essential for charge neutralization, structures and functions.⁶ Among the non-heme metalloproteins, those containing copper are one of the most studied groups. Thorough knowledge of the electronic structure of copper systems is essential for understanding their stability, reactivity and function-structure relationships.^{7,8} In this regard, spectroscopy techniques are most important tools in elucidating the electronic and molecular structure of matter and they can provide useful and valuable information in studies of copper compounds and also in design of proteins with specific, predictable structures and functions.^{9,10}

The optical absorption and electron paramagnetic resonance (EPR) spectroscopies have a prominent position in investigations of the electronic environment of copper systems.¹²⁻¹⁶ Copper(II) complexes manifest the so-called Jahn-Teller distortion with d^9 electronic configuration of the metal cation with one unpaired electron and a nuclear spin $3/2$. This distortion causes the lability and plasticity of copper(II) compounds and leads to various coordination arrangements and extremely fast ligand exchange reactions.¹⁷ A thoroughgoing analysis of optical and magnetic parameters can give rise to important information about the local structure of the metal element and the densities of paramagnetic centers.¹⁸ While the $d \rightarrow d$ electronic transitions are extremely sensitive indicators of the d^9 configuration of copper(II) complexes, the total spin multiplicity of the ground state, the ligand-field

strength and the covalency of the metal-ligand chemical bonds, the electronic g tensor and hyperfine coupling constants are parameters that are all strongly dependent on the coordination environment of the transition metal ion.^{11,16} In particular, the EPR technique is quite selective in studies of active sites of proteins and enzymes, which contain metal ions in open-shell configurations. The active site is responsible for the paramagnetism while the remaining part of these systems is diamagnetic and therefore EPR silent. The EPR measurements, in this case, yield not only information about the *geometric* structure of the active site under investigation but are also sensitive to the details of its electronic structure, thus providing an experimental means of studying the electronic contribution to reactivity of copper systems.¹¹

The analysis of experimental optical and magnetic spectra is difficult to accomplish in most cases.¹⁹⁻²¹ Measurements are usually carried out in solution or solid phases. The absorption spectra are not well resolved in isotropic media and the alignment of molecules in the unit cell of crystal compounds is, in some cases, unfavorable for polarization measurements.^{19,20} Magnetic resonance experiments often show significant broadening of spectra due to the low symmetry of the molecular systems investigated and the different types of interactions (dipolar, exchange, etc) in paramagnetic systems. Furthermore, the extraction of useful information from spectra is a non-trivial task. Several means can be used to improve the resolution of powder EPR spectra and to increase the signal to noise ratio. For instance, the registration in a wide range of temperatures at different microwave power levels and the use of isotopes with non-zero nuclear spin.²¹ Ligand-field theory and its variants like the angular overlap model have provided a standard qualitative picture for analysing optical and magnetic spectra of the divalent copper complexes.²² While these approaches are semi-empirical in nature, they provide a most convenient framework in which experiments can be expressed and summarized.

The evaluation of optical and magnetic resonance parameters by quantum chemistry methods offers a possibility to reliably connect the optical and EPR spectra to geometrical and electronic molecular structure, with the help of spectral parameters.¹¹ Quantum chemical theory has matured to an extent that it can significantly enhance the information that can be extracted from spectra, thereby widening the interpretative and analytical power of the respective spectroscopic methods.²³ However, the application of rigorous first-principles approaches to transition metal electronic and magnetic spectra has been found to be surprisingly difficult, at least compared to the success that *ab initio* quantum chemistry has for a long time enjoyed in organic and main group chemistry.²⁴ During the past 10-15 years, significant progress has been made in the field of transition metal quantum chemical approaches.^{15,16} This is, first of all, due to the success of density functional theory (DFT). Recent advances of DFT, together with the enormous increase in available computer power,

have allowed applications to transition metal compounds of significant size even on low-cost personal computers.²⁵ Furthermore, relativistic effects, which are of substantial magnitude for metal systems can be dealt with in studies that aim at high accuracy. DFT methods can be applied to the calculation of excitation spectra within the linear response formalism.²⁶ Among a variety of DFT methods available for the evaluation of the electronic g tensors and hyperfine coupling constants, the approaches based on the restricted Kohn-Sham formalism clearly stand out as the most suitable ones for investigations of transition metal compounds, since they allow to avoid the spin contamination common in methods based on the unrestricted Kohn-Sham formalism.^{27,28} In addition, the spin-orbit contribution, which is the most important contribution, especially for EPR parameters, can be evaluated when transition metals are taken into account.

This thesis concerns applications of recently developed and implemented DFT methods for the evaluation of spin Hamiltonian parameters and optical spectra in copper complexes. The introductory chapters present an overview of different approaches employed in this work. These chapters intend to provide a general view about the formalism and advantages and disadvantages of methodologies employed in this thesis. Chapter 2 is concerned with a general view of the electronic absorption spectrum. In chapter 3, the basic fundamentals of EPR properties will be described, while in chapter 4 a short background is presented about the development of DFT methods employed in this work to compute the EPR parameters. The chapter V is dedicated to the computational tools which were used in this work to determine the absorption spectra and magnetic properties of copper compounds. The final chapter presents a survey of results obtained in this thesis.

Chapter 2

Electronic Absorption Spectroscopy

The absorption spectrum of a chemical species is a display of the fractional amount of radiation absorbed at each frequency (or wavelength) as a function of frequency (or wavelength). When a molecule interacts with an external electromagnetic field at proper frequency, it absorbs the energy and is transferred into an excited state. An electric dipole transition with the absorption of radiation can only occur between certain pairs of energy levels. The restrictions defining the pairs of energy levels between which such transitions can occur are called electron dipole selection rules.²⁹ These rules, which can be explained in terms of symmetry of the wave-functions, are true only in the first approximation. The forbidden transitions are often observed, but give rise to much less intense absorption than allowed transitions.

The transition probability for the one-photon absorption can be evaluated by the oscillator strength. If a molecular system transits from an initial state i to a final state f after absorbing a photon, then the oscillator strength is,

$$W_{if} = \frac{2}{3} \hbar \omega_{if} \mu_{if}^2, \quad (2.1)$$

where $\hbar \omega_{if}$ is the transition energy and $\vec{\mu}_{if} = \langle \Psi_i | \hat{\vec{\mu}} | \Psi_f \rangle$ is the corresponding electric transition dipole moment.

For an allowed electronic transition $|\vec{\mu}_{if}| \neq 0$ and the symmetry requirement for this is

$$\Gamma(\Psi_i) \times \Gamma(\vec{\mu}) \times \Gamma(\Psi_f) = A, \quad (2.2)$$

for a transition between non-degenerated states. The symbol A stands for the totally symmetric species of the point group concerned. In a general case, the product of ground and excited states should have the same symmetry, at least, of one of components of the tran-

sition moment operator. This is the general selection rule for a transition between two electronic states.

In particular, the selection rules governing transitions between electronic energy levels of transition metal complexes are: (1) $\Delta S = 0$, the spin rule; and (2) $\Delta l = +/- 1$, the orbital rule (Laporte). The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin. The second rule says that if the molecule has a center of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given sub-shell) are forbidden. The relaxation of these rules can, however, occur through spin-orbit coupling, which gives rise to weak spin forbidden bands, or by means of vibronic coupling. Finally, π -acceptor and π -donor ligands can mix with the d -orbitals so that transitions are no longer purely $d - d$.

Regarding the mono-nuclear coordination compounds, five types of electronic transitions have been found to take place: (1) $d - d$ transitions which involve an electronic excitation within the partially filled d -orbitals of metal ions. These transitions fall into the visible and near infrared region of the spectrum and are very good indicators of the d^n configuration of the complexes; (2) the ligand-to-metal charge transfer (LMCT) transitions that occur from filled ligand based orbitals to the partially occupied metal d -shell. In most cases these transitions fall into the visible region of the spectrum if the oxidation state of the metal is high and the coordinating ligands are "soft" in the chemical sense; (3) metal-to-ligand charge transfer (MLCT) transitions which involve promotion of electrons from mainly metal d -based orbitals to low lying empty ligand orbitals. Such transitions are typically observed in the visible region of the spectrum if the oxidation state of the metal is low and the ligand contains low-lying empty π^* -orbitals; (4) intra-ligand transitions which involve electronic excitations between mainly ligand based orbitals on the same ligand, and, (5) ligand-to-ligand charge transfer transitions in which an electron is moved from one ligand to another in the excited state.³⁰ The present work will be confined exclusively to the first type of electronic transitions. The interpretation of $d - d$ spectra has been a domain of ligand-field theory (LFT)²² and its variants like the angular overlap model³¹ for a long time. A brief view of the crystal- and ligand-field theory will be presented in the next section.

2.1 Crystal and Ligand-Field theory

Crystal-field theory, which was firstly proposed by Hans Bethe in 1929,³² is often used to interpret chemical bonds and to assign electronic spectra of coordination metal complexes. This theory is based strictly on the electrostatic interaction between ligands and metal ions. Subsequent modifications, which were suggested after 1935 by Van Vleck,³³ include the

covalent character in chemical interactions. The modified versions are known as ligand-field theory.³¹ During 20 years, these theories were applied exclusively to solid state physics, and only after 1950, chemists started to use these theories in studies of metal complexes.

In crystal and ligand-field theories, the ligands are considered as negative charge points, which interact with the electrons of the five d -orbitals of the transition metal. In the absence of magnetic interaction, the d -orbitals are degenerate in energy, but when the ligands get symmetrically closer to the metal ion, the degeneracy is totally or partially removed, resulting in an energetic separation of orbitals, which corresponds to the essence of these theories. In the particular case of six point charges arranged octahedrally on the cartesian axes, the five d -orbitals are perturbed and must be classified according to the O_h point group. In this case, as shown in Fig. 2.1 (a), the set of five d -orbitals are differently affected by the presence of ligands, breaking down into doubly degenerate e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}), and a triply degenerate set of orbitals (d_{xy} , d_{xz} and d_{yz}), which transform according to the t_{2g} irreducible representation of the symmetry point group. Since the d_{z^2} and $d_{x^2-y^2}$ orbitals have much of their electron density along the metal ligand bonds, their electrons experience more repulsion by the ligand electrons than those in the d_{xy} , d_{xz} and d_{yz} orbitals. The result is that the e_g orbitals are pushed up in energy while the t_{2g} orbitals are pushed down. The energy difference between these sets of orbitals is defined by the Δ_o parameter, denominated by $10Dq$. This amount is typically such that promotion of an electron from the t_{2g} to the e_g orbital leads to an absorption in the visible region of the spectrum.

Additional molecular distortions can occur in an octahedral complex. For instance, the tetrahedral distortion, which occurs in the presence of a ligand-field where the axial ligands along the z axis are moved away from metal ion (See Fig. 2.1 (b)). This distortion is often expected to take place in copper(II) complexes as it is favored by the Jahn-Teller effect which stabilizes the total energy of the molecular system. The Jahn-Teller effect is the well-known $E \otimes e$ problem,¹⁷ which occurs in non-linear systems where an unpaired electron is localized in degenerate orbitals. The tetrahedral distortion takes place to decrease the molecular symmetry and also to remove the degeneracy of orbitals, thus causing the energetic stabilization of the system. In tetragonally distorted systems, the d -orbitals with z component are stabilized in energy when axial ligands get further to the metal ion, resulting in splittings of the d -orbital as observed in Fig. 2.1 (b). The determination of the orbital splittings, which is a matter of particular interest, can *a priori* be obtained through the experimental spectrum. However, the poor resolution usually observed in an isotropic spectra does not allow for an accurate determination of these parameters. Quantum chemistry calculations arise, therefore, as a useful and robust tool to provide information about the splittings of $d-d$ orbitals and hence the degree of molecular distortion associated with these parameters.

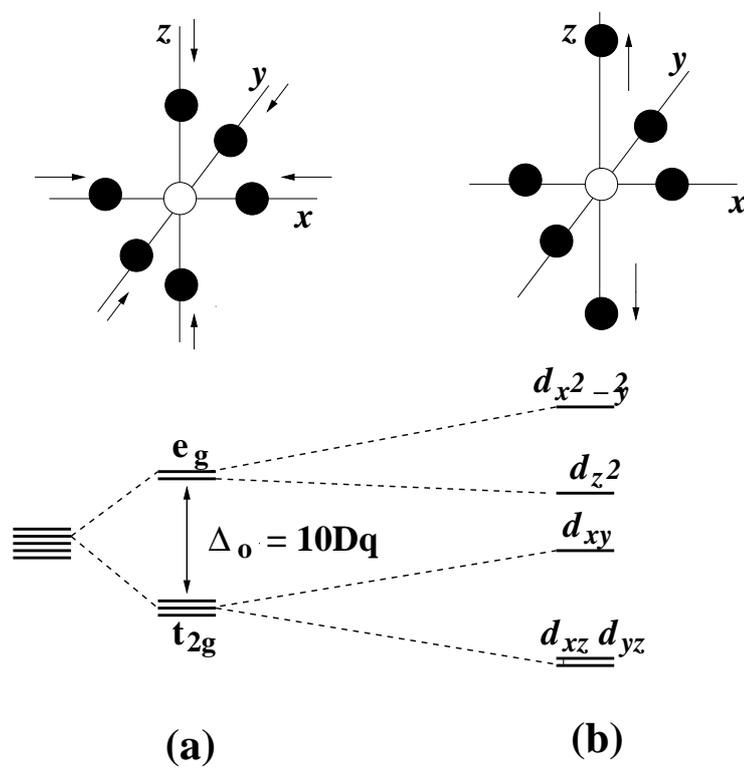


Figure 2.1: Splitting of d -orbitals in different ligand-fields.

Chapter 3

Magnetic Resonance Spectroscopy

Electron paramagnetic resonance (EPR), also known as electron spin resonance (ESR) (and electron magnetic resonance (EMR)), is a branch of magnetic resonance spectroscopy which deals with paramagnetic ions or molecules (or occasionally atoms, or "centers" in non molecular solids) with at least one unpaired electron spin. A molecule with a net electronic spin different from zero has an associated magnetic moment, which will interact with a magnetic field applied. The result of this interaction, for a state with the spin angular momentum $S = 1/2$, is a splitting (Zeeman effect) of the two spin states, corresponding to the spin $M_s = \pm 1/2$, by an amount proportional to the field strength as shown in Fig. 3.1. Typical EPR experiments detect the conditions under which a molecule undergoes transitions between these levels caused by a high-frequency oscillating magnetic field perpendicular to the steady field. When the resonance condition is met (red line in Fig. 3.1), energy absorption occurs, giving rise to the spectrum reported in the lower part of the figure Fig. 3.1. The frequencies at which the magnetic transitions occur give information about the separations between the quantized levels and can be interpreted in terms of the electronic structure of the system under study.^{34,35} Furthermore, important physical and chemical properties of a given system can be obtained by analysing magnetic transitions since many of the spin-dependent properties of a paramagnetic molecule are determined by its spin density distribution, which in turn gives information about the molecular structure. Several molecules have ground states or accessible excited states in which $S \neq 0$. Consequently, they can be observed by EPR in the gas phase, solid, liquid or trapped in relatively inert matrices.

Due to the high electron magnetic moments, the transition frequencies are correspondingly high. In a magnetic induction of 1 T, the frequency is 28 GHz which lies in the microwave range with characteristic relaxation time $\tau = 10^{-4} - 10^{-8}$ s. The large magnetic moment of the electron and the high frequencies required lead to higher sensitivities in electron than in

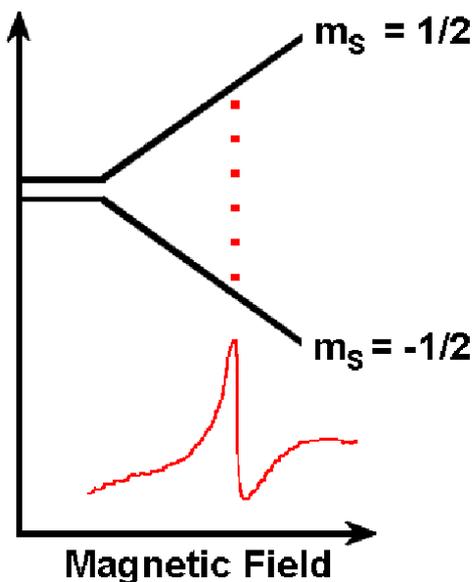


Figure 3.1: Splitting of magnetic levels.

nuclear resonance. The magnetic energy levels probed by EPR spectroscopy, which suffer a variety of electrostatic and magnetic interactions, are in general quite complex and very small differences ($< 1 \text{ cm}^{-1}$, 10^{-5} eV) are usually observed, much smaller than chemically relevant energy differences ($\approx 0.1 \text{ eV}$). The EPR spectrum of a paramagnetic center may thus be quite complex, exhibiting a larger number of lines. To interpret the spectra, one needs to take many small interactions into account. Because of the complexity of this task, the EPR spectra are parametrized in terms of an effective spin Hamiltonian, which contains some parameters that are adjustable to experiments.^{34,35,38} The effective spin Hamiltonian is an important intermediate in the interpretation of most ESR experiments and is essentially a model which allows experimental data to be summarized in terms of a rather limited number of parameters.

3.1 The EPR spin Hamiltonian

The spin Hamiltonian can be conceptually described by effective operators acting on effective spin state functions to divulge state energies, thus conveniently and intuitively relating observed peaks to their physical origin. Spin Hamiltonians are essential to understanding experimental magnetic spectroscopy, providing a formalism in which spectral data are systematically gathered. Equally, spin Hamiltonians are important to the theoretical development of quantum mechanical methods concerning resonance effects. However, the effective spin Hamiltonians should not be confused with quantum mechanical spin Hamiltonians. The expressions for experimental data and theoretical predictions are often not similar to each other, reflecting the different means by which quantification of the Hamiltonian is accomplished. While the quantum spin Hamiltonian entails a set of "quantum mechanical" operators, representing relevant physical effects which affect the transition energies, the effective spin Hamiltonians are composed of parametric matrices fitted to observed data, which describe the relationship between the system's state variables and its experimentally observed transitions. Nevertheless, both forms do represent identical physical effects and thus have a one-to-one correspondence.^{23,36}

The spin Hamiltonian approach contains operators for effective spin and magnetic interaction parameters, which occur in sets commonly called tensors, although some of them may not actually transform properly as tensors. Only static phenomena, which consist in determination of transition energies, and the corresponding line intensities and amplitudes, are taken into account in the spin Hamiltonian approach.^{34,38} The following form of the EPR spin Hamiltonian is often employed,

$$\hat{\mathcal{H}}_{\text{ESR}} = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \sum_N \mathbf{S} \cdot \mathbf{A}_N \cdot \mathbf{I}_N + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad (3.1)$$

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

The first term in Eq. 3.1 details the so-called electronic Zeeman effect that describes the coupling between the effective electronic spin moment and the static magnetic field. It governs the position of peaks (or split peak patterns) within EPR spectra. The electronic g tensor describes the influence on the unpaired electron spin density by the local chemical environment, which is quantified by the observed deviations from the free-electron g -factor, g_e (2.00231930). The second term represents a tensor coupling of the two angular momentum vectors and the \mathbf{A} parameter is denominated as the hyperfine coupling tensor. The source of this splitting is the magnetic interaction between the electron and nuclear spins. This

term manifests itself in EPR spectra as their hyperfine structure which be analysed from linewidths. Finally, the third term corresponds to high spin paramagnetism (only for systems with $\mathbf{S} > \frac{1}{2}$) arising from the magnetic dipolar interaction between the multiple unpaired electrons in the system and therefore is not present in copper(II) systems. This term give rise to so-called fine structure and the corresponding parameter is named the zero-field splitting tensor \mathbf{D} .

Although most molecules studied via EPR have non-zero nuclear magnetic moment, the magnetic dipole associated with a spinning nucleus is only the order of 1/2000 the strength of an electron spin magnetic dipole. Thus chemical shifts and nuclear spin-spin coupling interactions are typically found on a different energy scale compared to those of the electronic interaction.^{36,37} Therefore, it is quite reasonable to neglect this terms in the EPR spin Hamiltonian. In general, the spin Hamiltonian is constructed to describe all interactions among various magnetic dipoles that can change during a magnetic resonance experiment. However, it is not possible to define uniquely a spin Hamiltonian for all EPR spectra since it depends on the specific experimental condition in which the spectrum is recovered.

Considering as an example a system in solution with only an unpaired electron ($S = \frac{1}{2}$) and magnetic nuclear spin of $I = \frac{1}{2}$,^{34,35} where only isotropic tensor components can be evaluated, the EPR spin Hamiltonian of this system, for which a magnetic field \mathbf{B} defines the z -axis of the laboratory reference system, can be rewritten by using the definitions of the shift operators as

$$\hat{\mathcal{H}}_{\text{EPR}}^{\text{iso}} = g\mu_B B S_z + A \left[\frac{1}{2}(S_+ I_- + S_- I_+) + S_z I_z \right]. \quad (3.2)$$

Analogously, the first term describe the Zeeman effects, while the second one defines the hyperfine coupling interaction between the electronic and nuclear spin operators. The expressions for the relative energies of splitted states can be obtained as we use a basis of the simple product functions $|m_S, m_I\rangle = |S, m_S\rangle |I, m_I\rangle$, where the m_S and m_I are the electronic \mathbf{S} and nuclear \mathbf{I} spin projections along the z direction, in which the static magnetic field is oriented. The energy levels are obtained as eigenvalues of Hamiltonian operator Eq. 3.2:

$$E_1 = \frac{1}{2}g\mu_B B + \frac{1}{4}A \quad (3.3)$$

$$E_2 = \frac{1}{2}g\mu_B B \sqrt{1 + \left(\frac{A}{g\mu_B B}\right)^2} - \frac{1}{4}A \quad (3.4)$$

$$E_3 = -\frac{1}{2}g\mu_B B \sqrt{1 + \left(\frac{A}{g\mu_B B}\right)^2} - \frac{1}{4}A \quad (3.5)$$

$$E_4 = -\frac{1}{2}g\mu_B B + \frac{1}{4}A. \quad (3.6)$$

where the E_1 and E_4 corresponds the energies of $|\alpha, \alpha\rangle$ and $|\beta, \beta\rangle$ states which are not coupled with any other state by off-diagonal. By diagonalization of the spin Hamiltonian,

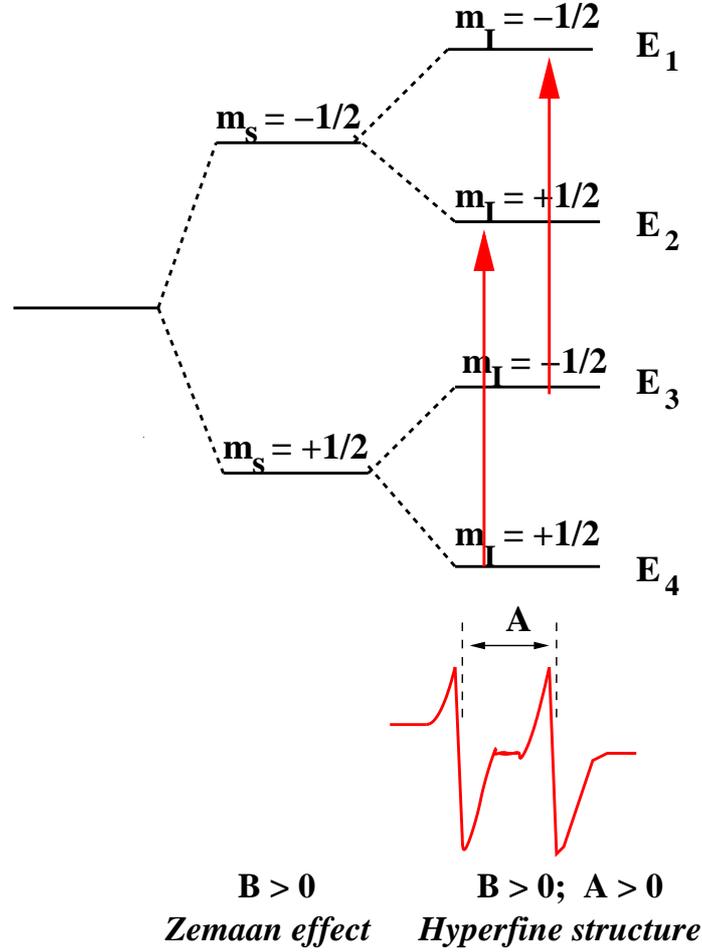


Figure 3.2: Magnetic energy levels and allowed transitions in a $S = \frac{1}{2}$ and $I = \frac{1}{2}$ system.

there are two allowed ESR transitions ($\Delta m_I = 0$ and $\Delta m_S = 1$), for which their frequencies are computed using the Eq.3.3 - 3.6,

$$E_1 - E_3 = g\mu_B B + \frac{1}{2}A \quad (3.7)$$

$$E_2 - E_4 = g\mu_B B - \frac{1}{2}A \quad (3.8)$$

$$(3.9)$$

and are thus eigenstates of $\hat{\mathcal{H}}_{\text{EPR}}$. The splitting observed in EPR spectrum is shown in

Fig. 3.2. From there, we can see that the initially degenerate states with $m_S = \pm 1$ are split by the Zeeman effect into two levels, which are further split into sub-levels of different m_I by the hyperfine interaction. The allowed transitions in EPR spectroscopy are those between states with different m_S , obeying the selection rule $\Delta m_S = \pm 1$. Thus the EPR spectrum of this system consists of two peaks separated by the hyperfine coupling constant A , as displayed in the lower part of the Fig. 3.2.

The hyperfine interaction was included in the Hamiltonian (Eq. 3.2) with a positive sign, also in calculating energies and their differences. In practice A can have either sign but one cannot learn the sign from the ESR spectrum. To see this, it is important to consider Eq. 3.7 and 3.8 for the transition energies. Changing the sign of A we will give the same expressions, thus showing that the spectrum is always a set of equally spaced line (of equal intensity) regardless whether A is positive or negative. Nevertheless, the sign of the coupling constant is of substantial interest and importance since knowing it one can assign the m_I values to the lines in the EPR spectrum.

In the next chapter a general view of available methodologies for calculation of EPR properties is given together with a short background about the development of DFT methods, specifically for the electronic g tensor and hyperfine coupling constants, performed recently in our research laboratory.

Chapter 4

Calculations of Paramagnetic Properties

The quality of the interpretation of EPR spectra can be enhanced with the incorporation of quantum chemical modelling of paramagnetic molecular parameters. This procedure can also overcome the ambiguity caused by the use of empirical relationships in the effective spin Hamiltonian. Several approaches to evaluate the electronic g tensors and hyperfine coupling constants have been developed and presented in the literature in the last years.^{39–42} Nowadays, theoretical evaluation of EPR parameters is commonly used, becoming increasingly prominent due to its improved applicability in studies of larger systems, including those of biological importance. This statement holds mainly for DFT methods, which have given rise to a satisfactory accuracy in prediction of magnetic properties for a wide range of molecular systems involving radical and transition metal centers.^{43–45,47} In this chapter, a general overview of DFT methods employed in this thesis will be given with focus on calculations of the electronic g tensors and hyperfine coupling constants of the copper(II) systems, which is one of the main goals of this thesis.

4.1 The electronic g tensors

The first calculations of the electronic g tensors with quantum chemical methods were carried out in the beginning of the last decade by Grein and co-workers.⁴⁸ These works used truncated sum-over-states procedures for evaluation of electronic g tensors with restricted open-shell Hartree-Fock (ROHF) and multireference configuration interaction (MR-CI) wave functions. After these pioneering works a large amount of approaches for evaluation of the electronic g tensors have been developed. The methods vary from robust *ab initio* approaches such as

multi-configurational self consistent field (MCSCF) response theory to various methodologies based on density functional theory (DFT).^{49–51} DFT Techniques have proven successful in gaining a qualitative understanding of the experimental results. Although some unresolved problems still remain, the density functional calculations of EPR g tensors are clearly entering the age of maturity.

Basically, two distinct methods, well-known as one and two-component approaches, exist for theoretical evaluation of the electronic g tensors.²³ In one-component methods, due to the small energy scale of the EPR transitions, the magnetic field and the spin-orbit (SO) coupling are treated as perturbations leading to a second-order g tensor expression. The Breit-Pauli Hamiltonian operators are used in this method within the framework of perturbation theory.⁵² In the two-component approach, the spin-orbit coupling is treated in the self-consistent DFT calculations by using relativistic DFT methods. The SO interactions are included in the two-component Kohn-Sham equations and the g tensors, in this approach, are calculated as a first derivative of the energy, i.e. as a first order property.

Initially, two-component DFT methods of the electronic g tensors were restricted to molecules with doublet ground states as they exploited the Kramer’s doublet symmetry in the determination of the g tensor components. Recently, this restriction was lifted by means of the implementation of a spin-polarized Douglas-Kroll Kohn-Sham formalism, where molecules of arbitrary ground states can be treated. However, the relatively large computational costs of two-component methods still prohibit their applicability to large systems. On the other hand, the one-component methods have been exploited only at the *ab initio* theory level due to the lack of DFT implementations capable of treating arbitrary perturbations beyond second order. In all practical DFT calculations, the terms which require knowledge of the two-electron density matrix, not available in the Kohn-Sham DFT formalism, are either neglected, or treated approximately. Very recently, Rinkevicius and co-workers extended the spin-restricted open-shell density functional response theory from the linear to the quadratic level which allows to compute relativistic corrections to the electronic g tensors using perturbation theory at the DFT level for the first time. In the present thesis a non-relativistic evaluation of the g tensor is taken into account in all calculations of the copper(II) molecular systems under investigation by using a one-component method in which the spin restricted density functional response theory approach is applied.^{53,54} In addition, the leading-order relativistic corrections to the g tensor have been developed in this work with a initial application to dihalogen anion radicals X_2^- ($X=F, Cl, Br$ and I). A brief description of these methods will be given in the next section.

4.1.1 The electronic g tensor: Theoretical evaluation

The form of the electronic the g tensor (See Eq. 3.2) in the EPR spin-Hamiltonian allows one to treat this property as a second derivative of the molecular electronic energy E with respect the to external magnetic field \mathbf{B} and the effective electronic spin \mathbf{S} of a paramagnetic system under investigation.

$$\mathbf{g} = \frac{1}{\mu_B} \frac{\partial^2 E}{\partial \mathbf{S} \partial \mathbf{B}} \Big|_{\mathbf{S}=\mathbf{0}, \mathbf{B}=\mathbf{0}}. \quad (4.1)$$

The corresponding electronic g tensor shift can be analogously written as

$$\Delta \mathbf{g} = \frac{1}{\mu_B} \frac{\partial^2 E}{\partial \mathbf{S} \partial \mathbf{B}} \Big|_{\mathbf{S}=\mathbf{0}, \mathbf{B}=\mathbf{0}} - g_e \mathbf{1}. \quad (4.2)$$

where the g_e is the free electron g -factor and $\Delta \mathbf{g}$ carries all information about the interactions between the unpaired electron and local chemical environment of molecular system. By using first and second order perturbation theory for the system described by the Breit-Pauli Hamiltonian in which all spin- and external field-dependent operators are treated as perturbations, the following non-relativistic electronic g tensor of a molecule can be computed as

$$\mathbf{g} = g_e \mathbf{1} + \Delta \mathbf{g}_{\text{RMC}} + \Delta \mathbf{g}_{\text{GC}(1e)} + \Delta \mathbf{g}_{\text{GC}(2e)} + \Delta \mathbf{g}_{\text{SO/OZ}(1e)} + \Delta \mathbf{g}_{\text{SO/OZ}(2e)} \quad (4.3)$$

where the first three terms contributing to the g tensor shift denote the relativistic mass-velocity correction ($\Delta \mathbf{g}_{\text{RMC}}$), one- ($\Delta \mathbf{g}_{\text{GC}(1e)}$) and two-electron ($\Delta \mathbf{g}_{\text{GC}(2e)}$) gauge corrections to the electronic Zeeman effect. The remaining two terms are the so-called one- and two-electron spin-orbit contributions to $\Delta \mathbf{g}$. In this work, the term "non-relativistic g tensor" denotes the g tensor composed of the free-electron g factor, $g_e \approx 2.0023$, and g tensor shifts of order $\mathcal{O}(\alpha^2)$, $\vec{g}_{NR} = g_e \mathbf{1} + \Delta g(\mathcal{O}(\alpha^2))$, where the last term therefore corresponds to

$$\Delta g(\mathcal{O}(\alpha^2)) = \Delta \mathbf{g}_{\text{RMC}} + \Delta \mathbf{g}_{\text{GC}(1e)} + \Delta \mathbf{g}_{\text{GC}(2e)} + \Delta \mathbf{g}_{\text{SO/OZ}(1e)} + \Delta \mathbf{g}_{\text{SO/OZ}(2e)}. \quad (4.4)$$

The $\Delta \mathbf{g}_{\text{RMC}}$ and $\Delta \mathbf{g}_{\text{GC}(1e/2e)}$ terms are defined within the framework of first order perturbation theory and are evaluated as the expected value of corresponding Breit-Pauli Hamiltonian operators^{58,59}

$$\Delta \mathbf{g}_{\text{RMC}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \langle 0 | \hat{H}_{\text{RMC}} | 0 \rangle \quad (4.5)$$

$$\Delta \mathbf{g}_{\text{GC}(1e/2e)} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \langle 0 | \hat{H}_{\text{GC}(1e/2e)} | 0 \rangle \quad (4.6)$$

where the mass-velocity correction to the electron Zeeman operator is defined as

$$\hat{H}_{\text{RMC}} = \frac{\alpha^2}{2} \sum_i \mathbf{s}_i \cdot \mathbf{B} \nabla_i^2 \quad (4.7)$$

and the one- and two-electron spin-orbit gauge corrections are defined as

$$\hat{H}_{\text{GC}(1e)} = \frac{\alpha^2}{4} \sum_N Z_N \sum_i \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iO} \cdot \mathbf{r}_{iN}) - \mathbf{r}_{iO} \mathbf{r}_{iN}}{r_{iN}^3} \cdot \mathbf{B}, \quad (4.8)$$

$$\hat{H}_{\text{GC}(2e)} = -\frac{\alpha^2}{4} \sum_{i \neq j} \mathbf{s}_i + 2\mathbf{s}_j \cdot \frac{\mathbf{1}(\mathbf{r}_{iO} \cdot \mathbf{r}_{iN}) - \mathbf{r}_{iO} \mathbf{r}_{iN}}{r_{iN}^3} \mathbf{B} \quad (4.9)$$

The treatment of the gauge corrections, which is related the dependence of some magnetic operators on the choice of the origin of the coordinate system, often poses a problem for theoretical predictions of magnetic properties. However the computation of the first-order one-electron contributions to Δg is not a difficult task and only the evaluation of the two-electron gauge correction is more complex, requiring the construction of the two-particle density matrix. In the present thesis, only the first-order contribution has been evaluated since the two-electron correction is a rather small contribution, specially for copper compounds where the spin-orbit correction is the dominating contribution to Δg . The remaining two terms in the expression for the g tensor shift, $\Delta g_{\text{OZ}/\text{SO}(1e)}$ and $\Delta g_{\text{OZ}/\text{SO}(2e)}$, refer to SO corrections. An accurate evaluation of these contributions is of major importance for reliable calculations. These terms can be evaluated using second-order perturbation theory by combining the orbital Zeeman operator and the one/two-electron spin-orbit operators.

$$\Delta \mathbf{g}_{\text{OZ}/\text{SO}(1e)} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \langle \langle \hat{H}_{\text{OZ}}; \hat{H}_{\text{SO}(1e)} \rangle \rangle_0, \quad (4.10)$$

$$\Delta \mathbf{g}_{\text{OZ}/\text{SO}(2e)} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \langle \langle \hat{H}_{\text{OZ}}; \hat{H}_{\text{SO}(2e)} \rangle \rangle_0, \quad (4.11)$$

In these definitions of $\Delta g_{\text{OZ}/\text{SO}(1e)}$ and $\Delta g_{\text{OZ}/\text{SO}(2e)}$, we have introduced the linear response function defined as

$$\Delta \mathbf{g}_{\text{OZ}/\text{SO}(\text{AMFI})} = \frac{1}{S} \langle \langle \hat{\mathcal{L}}_O; \hat{H}_{\text{SO}(\text{AMFI})} \rangle \rangle_0, \quad (4.12)$$

involving the electron angular momentum operator, $\hat{\mathcal{L}}_O$, and an effective one SO operator, $\hat{H}_{\text{SO}(\text{AMFI})}$. Here, we assumed that the linear response function is computed for the ground state of the molecule with maximum spin projection, $S = M_S$. The linear response function

used in the above definition of $\Delta\mathbf{g}_{\text{OZ/SO(AMFI)}}$ can be written in the spectral representation for two arbitrary operators \hat{H}_1 and \hat{H}_2 as

$$\langle\langle\hat{H}_1; \hat{H}_2\rangle\rangle_0 = \sum_{m>0} \frac{\langle 0|\hat{H}_1|m\rangle\langle m|\hat{H}_2|0\rangle + \langle 0|\hat{H}_2|m\rangle\langle m|\hat{H}_1|0\rangle}{E_0 - E_m}, \quad (4.13)$$

where E_0 and E_m are energies of the ground $|0\rangle$ and excited states $|m\rangle$, respectively, and the sum runs over all single excited states of the molecule. The spin-orbit contribution to the electronic g tensor shift involves the evaluation of matrix elements of the one- and two-electron SO operators and is therefore the most computationally expensive part of evaluation of Δg . However, as is well established, the computation of two-electron operators in DFT is not a trivial task, but it can not be neglected, as this contribution along with its one-electron counterpart dominate the electronic g tensor shift of most molecules composed of transition metals and main group elements. The atomic mean field (AMFI) approximation for the spin-operators was then employed as an alternative way to overcome this difficulty and still obtain accurate SO matrix elements.⁵⁵ In this case, an effective one-electron spin-orbit operator in which the spin-orbit interaction screening effect of $\hat{H}_{\text{SO}(2e)}$ is accounted for in an approximative manner. This approach would not only allow us to simplify the evaluation of the matrix elements, but also to resolve the conceptual difficulty in the implementation of the $\Delta\vec{g}_{\text{SO}}$ term in density functional theory, as the formation of the two-particle density matrix, which is required for the computation of the two-electron part, can be avoided. In the AMFI approximation, the one-electron SO operator matrix elements are evaluated in the ordinary way and the two-electron SO operator matrix elements are computed according to the procedure developed by Schimmelpfennig.⁵⁶ Finally, the calculations of the g tensors have been performed by using the spin-restricted density functional response formalism, which is free from the spin contamination problems appearing in spin-unrestricted DFT approaches.

4.1.2 The relativistic corrections to g tensors

The leading-order relativistic corrections to the electronic g tensor is derived from degenerate perturbation theory (DPT) by applying the same procedure as for the ordinary $\mathcal{O}(\alpha^2)$ contributions to Δg , although one in this case needs to go beyond the second order DPT in order to retrieve all main contributions to the g tensor shift. The relativistic g tensor in this method is defined as

$$g = g_{\text{NR}} + \Delta g(\mathcal{O}(\alpha^4)) = g_e 1 + \Delta g(\mathcal{O}(\alpha^2)) + \Delta g(\mathcal{O}(\alpha^4)), \quad (4.14)$$

and includes the non-relativistic g tensor corrected by $\Delta g(\mathcal{O}(\alpha^4))$, which contains all leading-order relativistic corrections.

Overall, the leading relativistic corrections to the electronic g -tensor arise in perturbation theory by inclusion of scalar relativistic effects resulting in the increase of the order in c^{-1} for each term in Eq. 4.4:

$$\Delta \mathbf{g}^{\text{RMC/mv+Dar}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \left(\langle \langle \hat{H}^{\text{RMC}}; \hat{H}^{\text{mv}} \rangle \rangle_0 + \langle \langle \hat{H}^{\text{RMC}}; \hat{H}^{\text{Dar}} \rangle \rangle_0 \right) \quad (4.15)$$

$$\Delta \mathbf{g}^{\text{GC/mv+Dar}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \left(\langle \langle \hat{H}^{\text{GC}}; \hat{H}^{\text{mv}} \rangle \rangle_0 + \langle \langle \hat{H}^{\text{GC}}; \hat{H}^{\text{Dar}} \rangle \rangle_0 \right) \quad (4.16)$$

$$\begin{aligned} \Delta \mathbf{g}^{\text{SO/OZ/mv+Dar}} &= \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \left(\langle \langle \hat{H}^{\text{SO}}; \hat{H}^{\text{OZ}}, \hat{H}^{\text{mv}} \rangle \rangle_{0,0} \right. \\ &\quad \left. + \langle \langle \hat{H}^{\text{SO}}; \hat{H}^{\text{OZ}}, \hat{H}^{\text{Dar}} \rangle \rangle_{0,0} \right) \end{aligned} \quad (4.17)$$

From the enumerated terms, the last one $\Delta \mathbf{g}^{\text{SO/OZ/mv+Dar}}$ is expected to give major contributions to the total scalar relativistic correction. The evaluation of Eq. 4.17 requires the solution of a quadratic response equations which has become possible after the implementation of the spin restricted open shell quadratic response DFT (see Sec. 5.2). One more correction of fourth power in c^{-1} accounts for the coupling between the kinetic energy-corrected orbital Zeeman operator $\hat{H}^{\text{OZ-KE}}$ and the spin-orbit interaction \hat{H}^{SO} .⁵⁷

$$\Delta \mathbf{g}^{\text{OZ-KE/SO}} = \frac{1}{\mu_B} \frac{\partial^2}{\partial \mathbf{S} \partial \mathbf{B}} \langle \langle \hat{H}^{\text{OZ-KE}}; \hat{H}^{\text{SO}} \rangle \rangle_0 \quad (4.18)$$

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

$$\Delta \mathbf{g}(\mathcal{O}(c^{-4})) = \Delta \mathbf{g}^{\text{RMC/mv+Dar}} + \Delta \mathbf{g}^{\text{GC/mv+Dar}} + \Delta \mathbf{g}^{\text{SO/OZ/mv+Dar}} + \Delta \mathbf{g}^{\text{OZ-KE/SO}} \quad (4.19)$$

In this procedure only doublet states are considered in the derivation of degenerate perturbation theory terms, which involves two or more electronic spin dependent operators, and neglects the contributions arising from quartet states. The calculations of g -tensors have been performed using a spin restricted DFT quadratic response formalism, the development and implementation of which is presented in details in **paper VI**.

4.2 The hyperfine coupling constants

The presence of magnetic nuclei in a molecule leads to the so-called hyperfine splitting in EPR spectra.^{34,36} The 3 X 3 hyperfine interaction tensor \mathbf{A} can be separated into isotropic and anisotropic components, which differ by their behavior in experiments and mainly by

their different physical origin. In the first order approximation and at the nonrelativistic limit, the isotropic term is equal to the average value of the non-classical Fermi-contact interaction operator. The anisotropic part is determined by the magnetic dipole-dipole interaction between nuclear and electron spins and is essentially classical in origin, falling off with the inverse third power of the distance between the nucleus and the unpaired electrons.³⁴ For magnetic nuclei located on an at least three-fold symmetry axis, it adopts the form $(-A_{dip}, -A_{dip}, 2A_{dip})$, where A_{dip} is the so-called dipolar coupling constant. From the isotropic hyperfine coupling constant, which is directly proportional to the electron spin density at nucleus N , we can get information on the spin density distribution in a molecule. The isotropic part can be determined in experiments performed in the gas phase and solution, whereas the anisotropic components are only significant in the ordered samples where molecules are oriented by the static external field.

The Fermi contact and magnetic dipole contributions to the hyperfine coupling tensor are the first order properties and can be evaluated as expectation values over the ground state wave function within almost all standard quantum chemistry packages at *ab initio* and density functional theory (DFT) levels.⁶⁰⁻⁶³ However, some requirements such as a good description of the spin density at the positions of the nuclei, a good evaluation of spin polarization and electron correlation effects must be fulfilled in order to obtain accurate HFC results.⁵⁴ The choice of basis set with a flexible description in the core region is therefore important. On the other hand, current DFT methods can offer a reliable way to solve the remaining requirements of low computational cost. Most of these methods can provide a quite accurate prediction of HFCs of organic compounds.^{61,62} However, we are not as fortunate in the case of transition metal compounds for which the accuracy of HFCs shows significant dependence on the approach selected for the particular molecular system. Among a variety of DFT methods available for the evaluation of hyperfine coupling constants, the approaches based on the restricted Kohn-Sham formalism stand out as the most suitable ones for investigations of transition metal compounds, as they avoid the spin contamination problem quite common in methods based on the unrestricted Kohn-Sham formalism.^{53,54} In this thesis, we have selected the DFT restricted-unrestricted (RU) approach, which allows the computation of the lowest order contributions (second order in the fine structure constant) to the hyperfine coupling tensor \mathbf{A} . A brief description of this formalism will be considered in next section.

4.2.1 The hyperfine coupling constants: Theoretical evaluation

Magnetic resonance parameters are second-order properties and can be expressed as second-order derivatives of the total electronic energy with perturbations. As previously mentioned, if the first perturbation is the magnetic field strength and the second is an electronic spin,

we obtain the g tensor. On the other hand, if the perturbations are electronic and nuclear spins, the hyperfine coupling constant (HFC) can be evaluated as

$$\mathbf{A}_N = \left. \frac{\partial^2 E}{\partial \mathbf{S} \partial \mathbf{I}_N} \right|_{\mathbf{S}, \mathbf{I}_N=0} . \quad (4.20)$$

In the restricted-unrestricted (RU) approach, the hyperfine coupling is described by the Fermi-contact and magnetic dipole-dipole interaction, which are introduced as perturbations of the non-relativistic Kohn-Sham Hamiltonian \hat{H}_0 . In this case, the Hamiltonian which does not depend on the external or internal magnetic fields in the molecule can be described as

$$\hat{H} = \hat{H}_0 + x(\hat{H}_N^{\text{FC}} + \hat{H}_N^{\text{SD}}) \quad (4.21)$$

where x is the perturbation strength and \hat{H}_{FC} and \hat{H}_{SD} terms are the Fermi-contact and electronic-nuclear magnetic dipole-dipole interaction operators, respectively. \hat{H}_{FC} and \hat{H}_{dip} can be described by using the second quantized form in terms of Kohn-Sham spin-orbitals and under these conditions the energy functional $E[\rho(x), x]$ of the molecular electronic system becomes explicitly and implicitly dependent on the strength of the perturbation. Taking account of the dependence of the electron density $\rho(x)$ on the perturbation strength x one can separate the first-order derivative of the energy with respect to x into two parts

$$\frac{dE[\rho(x), x]}{dx} = \frac{\partial E[\rho(x), x]}{\partial x} + \int \frac{\delta E[\rho(x), x]}{\delta \rho(x)} \frac{\partial \rho(x)}{\partial x} d\mathbf{r} . \quad (4.22)$$

These two terms contribute to the HFC tensor \mathbf{A} of nucleus N , where the first term is computed as an expectation value of the Breit-Pauli Fermi contact \hat{H}_{FC} or spin-dipolar \hat{H}_{SD} operator in the limit $x \rightarrow 0$ and using Kohn-Sham orbitals of the unperturbed system,

$$\left. \frac{\partial E[\rho(x), x]}{\partial x} \right|_{x=0} = \langle 0 | \hat{H}_N^{\text{FC}} | 0 \rangle + \langle 0 | \hat{H}_N^{\text{SD}} | 0 \rangle \quad (4.23)$$

The second term vanishes in the unrestricted case, with the singlet and triplet rotations of the Kohn-Sham spin-orbitals in the optimization process of $E[\rho(x), x]$. Accounting for spin-polarization effects, two terms are computed as a triplet linear response function of \hat{H}_{FC} or \hat{H}_{dip} operator coupled with the restricted Kohn-Sham Hamiltonian \hat{H}_0^R of unperturbed molecular system.⁵⁴ This leads to the following expressions

$$\mathbf{A}_{FC} = \langle 0 | \hat{H}_{FC} | 0 \rangle + \langle\langle \hat{H}_{FC}; \hat{H}_0 \rangle\rangle_0 , \quad (4.24)$$

$$\mathbf{A}_{dip} = \langle 0 | \hat{H}^{dip} | 0 \rangle + \langle\langle \hat{H}^{dip}; \hat{H}_0 \rangle\rangle_0 . \quad (4.25)$$

The RU approach described above for hyperfine coupling constants performs very well for organic compounds, but unfortunately it has limited applicability in the case of transition

metal compounds since it neglects higher order spin-orbit contributions important for transition metal compounds. The respective spin-orbit contributions \mathbf{A}_{SO} can be evaluated as a linear response function between the one- and two-electron spin-orbit operators $\hat{H}_{SO(\text{AMFI})}$ ⁴⁵ and the nuclear spin electron orbit interaction operator $\hat{\mathcal{L}}_N$,

$$\mathbf{A}_{SO} = -\frac{1}{S} \langle\langle \hat{\mathcal{L}}_N; \hat{H}_{SO(\text{AMFI})} \rangle\rangle_0 . \quad (4.26)$$

The major difference between this and our method is the use of restricted linear response theory in the present calculations, rather than the unrestricted coupled-perturbed Kohn-Sham method. The AMFI approximation for the spin-orbit interaction operator is also used in this work in calculations of the hyperfine constants. This approach was previously proved to give compatible results with the full SO operators for EPR parameters. Therefore, summarizing the above equations, the hyperfine coupling tensor of copper systems was evaluated in this work in the following way:

$$\mathbf{A} = \mathbf{1}A_{FC} + \mathbf{A}^{dip} + \mathbf{A}_{SO} . \quad (4.27)$$

The outlined hyperfine coupling constant approach ensures that all important contributions encountered for transition metal compounds are accounted for and that a correct physical picture of the hyperfine interaction is reproduced.

4.2.2 Spin polarization effects in g tensors and hyperfine coupling constants

Spin contamination is a problem frequently found in calculations of energetics and properties of transition metal (TM) complexes by using spin unrestricted Kohn-Sham theory.⁴⁶ In the evaluation of the electronic g tensors and hyperfine coupling tensors of TM complexes, the deficient description of excited states by ordinary exchange–correlation functionals in combination with spin contamination is one of the major sources of errors, which prevents a reliable prediction of these EPR spin Hamiltonian parameters by DFT. An alternative methodology, namely the density functional restricted-unrestricted (DFTRU) approach based on a spin restricted Kohn-Sham theory, described in details in **paper V**, was developed to solve the spin contamination problem and at the same time account for the spin polarization effects using a so-called restricted-unrestricted technique.

The DFTRU corrections to the electronic g tensor can be done by taking into account the expressions for the electronic g tensor in the spin restricted Kohn-Sham theory, which at the non-relativistic limit reads

$$\mathbf{g} = g_e \mathbf{1} + \Delta \mathbf{g}_{\text{RMC}} + \Delta \mathbf{g}_{\text{GC}} + \Delta \mathbf{g}_{\text{SO/OZ}} , \quad (4.28)$$

where $\Delta\mathbf{g}_{\text{RMC}}$ and $\Delta\mathbf{g}_{\text{GC}}$ are the diamagnetic mass-velocity and gauge correction to the spin Zeeman effect. According to the DFTRU approach, the spin polarization contributions to $\Delta\mathbf{g}_{\text{RMC}}$, $\Delta\mathbf{g}_{\text{GC}}$ are given by two linear response functions

$$\Delta\mathbf{g}_{\text{RMC}}^{\text{RU}} = \frac{1}{\mu_B} \frac{\partial^2 \langle \langle \hat{H}_0; \hat{H}_{\text{RMC}} \rangle \rangle_0}{\partial \vec{B} \partial \vec{S}} \Big|_{\vec{B}=\vec{0}, \vec{S}=\vec{0}} \quad \text{and} \quad \Delta\mathbf{g}_{\text{GC}}^{\text{RU}} = \frac{1}{\mu_B} \frac{\partial^2 \langle \langle \hat{H}_0; \hat{H}_{\text{GC}(1e)} + \hat{H}_{\text{GC}(2e)} \rangle \rangle_0}{\partial \vec{B} \partial \vec{S}} \Big|_{\vec{B}=\vec{0}, \vec{S}=\vec{0}} \quad (4.29)$$

while in the case of $\Delta\vec{g}_{\text{SO/OZ}}$ the spin polarization contribution is of more complex nature and is defined as a sum of quadratic and linear response functions

$$\Delta\mathbf{g}_{\text{SO/OZ}}^{\text{RU}} = \frac{1}{\mu_B} \frac{\partial^2 (\langle \langle \hat{H}_0; \hat{H}_{\text{OZ}}, \hat{H}_{\text{SO}(1e)} + \hat{H}_{\text{SO}(2e)} \rangle \rangle_{0,0} + \langle \langle \hat{H}_{\text{OZ}}; \hat{H}_{\text{SO}(1e)} + \hat{H}_{\text{SO}(2e)} \rangle \rangle_0)}{\partial \vec{B} \partial \vec{S}} \Big|_{\vec{B}=\vec{0}, \vec{S}=\vec{0}} \quad (4.30)$$

Adding up all above listed contributions to $\Delta\mathbf{g}$, we obtain the final expression for evaluation of the electronic g tensor

$$\mathbf{g} = g_e \mathbf{1} + \Delta\mathbf{g}_{\text{RMC}} + \Delta\mathbf{g}_{\text{RMC}}^{\text{RU}} + \Delta\mathbf{g}_{\text{GC}} + \Delta\mathbf{g}_{\text{GC}}^{\text{RU}} + \Delta\mathbf{g}_{\text{SO/OZ}} + \Delta\mathbf{g}_{\text{SO/OZ}}^{\text{RU}} , \quad (4.31)$$

which differs from formulas used in spin restricted Kohn-Sham theory by additional spin polarization corrections appearing for each g tensor shift contribution. These new contributions to the electronic g tensor, namely $\Delta\vec{g}_{\text{RMC}}^{\text{RU}}$, $\Delta\mathbf{g}_{\text{GC}}^{\text{RU}}$ and $\Delta\mathbf{g}_{\text{SO/OZ}}^{\text{RU}}$, not only exemplify the essence of the spin polarization treatment in the DFTRU approach, but also provides a pathway for improvement of the g tensor by attenuating the $\Delta\mathbf{g}$ obtained in the spin restricted Kohn-Sham theory.

In analogy to the electronic g tensor case, the following DFTRU scheme for evaluation of hyperfine coupling tensors in transition metal complexes

$$\mathbf{A}_N = \mathbf{A}_N^{\text{FC}} + \mathbf{A}_N^{\text{FC-RU}} + \mathbf{A}_N^{\text{SD}} + \mathbf{A}_N^{\text{SD-RU}} + \mathbf{A}_N^{\text{SO}} + \mathbf{A}_N^{\text{SO-RU}} , \quad (4.32)$$

where all terms are defined as

$$\mathbf{A}_N^{\text{FC}} = \frac{\partial^2 \langle \hat{H}_{\text{FC}} \rangle}{\partial \vec{I}_N \partial \vec{S}} \Big|_{\vec{I}_N=\vec{0}, \vec{S}=\vec{0}} \quad \text{and} \quad \mathbf{A}_N^{\text{FC-RU}} = \frac{\partial^2 \langle \langle \hat{H}_0; \hat{H}_{\text{FC}} \rangle \rangle_0}{\partial \vec{I}_N \partial \vec{S}} \Big|_{\vec{I}_N=\vec{0}, \vec{S}=\vec{0}} , \quad (4.33)$$

the traceless dipolar contributions are obtained as

$$\mathbf{A}_N^{\text{SD}} = \frac{\partial^2 \langle \hat{H}_{\text{SD}} \rangle}{\partial \vec{I}_N \partial \vec{S}} \Big|_{\vec{I}_N=\vec{0}, \vec{S}=\vec{0}} \quad \text{and} \quad \mathbf{A}_N^{\text{SD-RU}} = \frac{\partial^2 \langle \langle \hat{H}_0; \hat{H}_{\text{SD}} \rangle \rangle_0}{\partial \vec{I}_N \partial \vec{S}} \Big|_{\vec{I}_N=\vec{0}, \vec{S}=\vec{0}} . \quad (4.34)$$

and the spin-orbit contribution to \mathbf{A}_N can be computed as

$$\mathbf{A}_N^{\text{SO}} = \frac{\partial^2 \langle \langle \hat{H}_{\text{PSO}}; \hat{H}_{\text{SO}(1e)} + \hat{H}_{\text{SO}(2e)} \rangle \rangle_0}{\partial \vec{I}_N \partial \vec{S}} \Big|_{\vec{I}_N=\vec{0}, \vec{S}=\vec{0}} , \quad (4.35)$$

where \hat{H}_{PSO} is the orbital hyperfine interaction operator, which describes the nuclear spin interaction with orbital motion of electrons. Finally, the spin polarization correction to \vec{A}_N^{SO} is given by a sum of linear and quadratic response functions

$$\mathbf{A}_N^{\text{SO-RU}} = \frac{\partial^2 (\hat{H}_0; \hat{H}_{\text{PSO}}, \hat{H}_{\text{SO}(1e)} + \hat{H}_{\text{SO}(2e)})_{0,0} + \langle\langle \hat{H}_{\text{PSO}}; \hat{H}_{\text{SO}(1e)} + \hat{H}_{\text{SO}(2e)} \rangle\rangle_0}{\partial \vec{I}_N \partial \vec{S}} \Big|_{\vec{I}_N=\vec{0}, \vec{S}=\vec{0}} . \quad (4.36)$$

This equation includes the most important terms for description of hyperfine interaction in first row TM complexes.

Chapter 5

Computational Methods

5.1 Density Functional Theory

Density Functional Theory (DFT) has strongly influenced the evolution of quantum chemistry during the past 15 years, demonstrating a wide applicability in organic, inorganic, material and solid state chemistry as well as in biochemistry, thus serving a broad scientific community. The award of the Nobel Prize for chemistry in 1998 to one, the "protagonist" of (ab initio) wave function quantum chemistry, Professor J. A. Pople, and the founding father of DFT, professor Walter Kohn, is the highest recognition of both the impact of quantum chemistry in present-day chemical research and the role played by DFT in this evolution. DFT has proved to be a cost-effective way to include electron correlation and due to its combination of reasonable scaling with system size and good accuracy in reproducing most ground state properties, DFT is one to the most popular methods for treating large systems, including those with transition metal centers, which is one of the goals undertaken in this thesis.

The principles of Density Functional Theory (DFT) were formulated almost 40 years ago by Hohenberg and Kohn who proved that the full many-particle ground state is a unique functional of the density (ρ) that minimizes the total energy.⁶⁴ The form of the exact functional is unknown, however, and the way towards practical applications of DFT has been opened only by the Kohn and Sham's idea of constructing a noninteracting reference system having the same density as the real systems.⁶⁵ By this method, a major part of the unknown functional can be expressed exactly, leaving only a small part of the total energy to be approximated. Hartree-Fock and its descendents are based on the many-electron wavefunction, which depends on $4N$ variables, 3 spatial and 1 spin for each electron, while the DFT method solves this complex problem by using an electron density (ρ) as the basic

quantity.

$$\rho(\mathbf{r}) = N \int \dots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 ds_1 dx_2 \dots dx_N \quad (5.1)$$

where $\mathbf{x} = (\mathbf{r}, s)$ and Ψ is the wave function. The electron density (ρ) depends only on three spatial variables, independently of the number of electrons.

The energy functional of an isolated electronic molecular systems can be expressed in DFT as

$$E[\rho] = T[\rho] + V_{ee}[\rho] + V_{Ne}[\rho], \quad (5.2)$$

where the first term is the kinetic energy, $V_{ee}[\rho]$ is the electron-electron repulsion and $V_{Ne}[\rho]$ is the nuclear-electron attraction, often called the external potential, which is system dependent. The two first terms can be combined to provide the universal potential $F[\rho]$

$$F[\rho] = T[\rho] + V_{ee}[\rho] \quad (5.3)$$

By using the definition of $V_{Ne}[\rho]$, the Eq. 5.2 can be rewritten as

$$E[\rho] = F[\rho] + \int \rho(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (5.4)$$

The functionals $V_{Ne}[\rho]$ and $V_{ee}[\rho]$ are known. However, the exact determination of $F[\rho]$ is not straightforward. The individual parts of the electron-electron interaction consist of the classical Coulomb interaction (easily defined in terms of the electronic density) and the non-classical term due to exchange and electron correlation effects, whose form is unknown. Furthermore, the functional of the kinetic energy, which is of crucial importance for the quality of DFT results is also unknown in terms of the electronic density. The Kohn and Sham method, which will be briefly discussed in next section, has provided a way to overcome this problem.

5.1.1 The Kohn-Sham approach

In the Kohn-Sham scheme,⁶⁵ the density of a fictitious system is represented by that arising of non-interacting electrons. This density is taken into account to be able to describe the ground state density of a real system. The ground state wave function of such a non-interacting system can be represented by a Slater determinant.

$$\Psi_s = \frac{1}{\sqrt{N!}} \det[\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\dots\phi(\mathbf{x}_N)] \quad (5.5)$$

where the lowest state is given by the one-electron Halmiltonian

$$\hat{f}_s^{KS} = -\frac{1}{2}\nabla^2 + v_s(\mathbf{r}). \quad (5.6)$$

where no electron-electron repulsion is considered. The Kohn-Sham spin orbitals ϕ_i are determined by

$$\hat{f}_s^{KS} \phi_i(\mathbf{r}, s) = \varepsilon_i \phi_i(\mathbf{r}, s). \quad (5.7)$$

Kohn and Sham proposed that the kinetic energy $T_x[\rho]$ should be calculated exactly for the non-interacting particles. The kinetic part of such a non-interacting system is similar to the HF kinetic term. Separating the kinetic energy function in Eq. 5.3 and the electron-electron interaction we get

$$F[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho], \quad (5.8)$$

where

$$E_{xc}[\rho] = T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \quad (5.9)$$

is the so-called exchange-correlation functional. According to this equation $E_{xc}[\rho]$ will capture the missing electron-correlation due to the non-interacting nature of $T_s[\rho]$ and also the exchange part of $V_{ee}[\rho]$. The Kohn-Sham method also uses the idea of an effective potential $v_{eff}(\mathbf{r})$. One can show that the ground state density will satisfy the Euler equation in which the effective potential is defined as

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) \quad (5.10)$$

where $v_{xc}(\mathbf{r})$ is the exchange-correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})}. \quad (5.11)$$

For a given v_{eff} , $\rho(\mathbf{r})$ is obtained by solving the KS-equations

$$\hat{f}_s^{KS} \phi_i = \left[-\frac{1}{2} \nabla^2 + v_{eff}(\mathbf{r}) \right] \phi_i \quad (5.12)$$

followed by

$$\rho(\mathbf{r}) = \sum_i^N \sum_s |\phi_i(\mathbf{r}, s)|^2 \quad (5.13)$$

A trial $\rho(\mathbf{r})$ is given so that v_{eff} and, consequently, the KS-orbitals in Eq. 5.12 are determined. The problem is solved in a self-consistent method by updating the density through Eq. 5.13. KS orbitals can be expressed, like in the HF theory, in terms of a linear combination of atomic orbitals yielding the Roothaan-Hall scheme. The main difference between HF and DFT is that the former is an approximation by construction whereas DFT would be exact if the exact exchange-correlation functional (E_{xc}) was known. Since the exact E_{xc} is not known, approximations must be used and as a consequence, the development of E_{xc} functionals has been an important task for DFT. Before discussing this problem, the treatment of open-shell molecular systems in DFT, which is the topic of this thesis, will be addressed in the next section.

Open-shell systems in DFT

The Kohn-Sham energy functional for closed-shell systems is given as

$$E[\rho(\mathbf{r})] = T_s[\rho(\mathbf{r})] + J[\rho(\mathbf{r})] + E_{xc}[\rho(\mathbf{r})] + E_{Ne}[\rho(\mathbf{r})] \quad (5.14)$$

where no reference to the spin of the system is taken into account. However, in order to describe the open-shell systems, the energy of system should be considered as a function of the individual spin densities, as shown below,

$$E[\rho_\alpha, \rho_\beta] = T_s[\rho_\alpha, \rho_\beta] + J[\rho_\alpha + \rho_\beta] + E_{xc}[\rho_\alpha, \rho_\beta] + E_{Ne}[\rho_\alpha + \rho_\beta] \quad (5.15)$$

where the α and β spin densities for KS orbitals ϕ_i can be expressed as

$$\rho_\alpha(\mathbf{r}) = \sum_i n_{\alpha i} |\psi_i(\mathbf{r}, \alpha)|^2 \text{ and } \rho_\beta(\mathbf{r}) = \sum_i n_{\beta i} |\psi_i(\mathbf{r}, \beta)|^2, \quad (5.16)$$

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

Two methods are available to treat open-shell systems, the spin-restricted and unrestricted Kohn-Sham approaches, which differ only by conditions of constraint imposed in the energy functional minimization that lead to different sets of Kohn-Sham equations for spin orbitals. In the spin-restricted method, the spatial part of doubly occupied spin-orbitals is forced to be the same, while in the unrestricted calculations this restriction is lifted. In both methods, the minimization of the molecular energy functional $E[\rho_\alpha, \rho_\beta]$ is performed by means of separate constraints on the α and β densities,⁶⁶ i.e.,

$$\int \rho_\alpha(\mathbf{r}) d\mathbf{r} = N_\alpha \text{ and } \int \rho_\beta(\mathbf{r}) d\mathbf{r} = N_\beta, \quad (5.17)$$

which implies that the number of α and β electrons remains constant during the variational procedure. Therefore, in the unrestricted method, the separate sets of Kohn-Sham equations for $\psi_i(\mathbf{r}, \alpha)$ and $\psi_i(\mathbf{r}, \beta)$ spin orbitals are obtained as a result of minimization of $E[\rho_\alpha, \rho_\beta]$:

$$\hat{f}_\alpha \psi_i(\mathbf{r}, \alpha) = \left\{ -\frac{1}{2} \nabla^2 + v_{eff}^\alpha \right\} \psi_i(\mathbf{r}, \alpha) = \epsilon'_{\alpha i} \psi_i(\mathbf{r}, \alpha) \quad i = 1, 2, \dots, N_\alpha \quad (5.18)$$

$$\hat{f}_\beta \psi_i(\mathbf{r}, \beta) = \left\{ -\frac{1}{2} \nabla^2 + v_{eff}^\beta \right\} \psi_i(\mathbf{r}, \beta) = \epsilon'_{\beta i} \psi_i(\mathbf{r}, \beta) \quad i = 1, 2, \dots, N_\beta \quad (5.19)$$

where the spin dependent effective potentials are

$$v(\mathbf{r})_{eff}^\alpha = v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\mathbf{r})} \quad (5.20)$$

$$v(\mathbf{r})_{eff}^\beta = v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\mathbf{r})} \quad (5.21)$$

and $\epsilon'_{\sigma i}$ is the Lagrange multiplier for the corresponding spin-orbital $\psi_i(\mathbf{r}, \sigma)$. Equations 5.18-5.19 are coupled only by means of the electron spin densities entering the equations and the off-diagonal Lagrange multipliers do not appear. This is one of the major advantages of unrestricted Kohn-Sham theory. However, there is a price for this simple mathematical formulation of this method, namely the two Kohn-Sham matrices must be constructed and diagonalized in each iteration instead of just one effective Kohn-Sham matrix used in the spin-restricted Kohn-Sham method.

In the spin-restricted Kohn-Sham method, the spatial parts of $\psi_i(\mathbf{r}, \alpha)$ and $\psi_i(\mathbf{r}, \beta)$ spin orbitals remain the same under the minimization of $E[\rho_\alpha, \rho_\beta]$. By assuming a high spin ground state of a molecule with N_d doubly occupied orbitals and N_s singly occupied orbitals, the Kohn Sham equations under these constraints become

$$\left\{-\frac{1}{2}\nabla^2 + v_{eff}^d\right\}\psi_k(\mathbf{r}) = \sum_j \epsilon'_{kj}\psi_j(\mathbf{r}) \quad k = 1, 2, \dots, N_d \quad (5.22)$$

$$\frac{1}{2}\left\{-\frac{1}{2}\nabla^2 + v_{eff}^o\right\}\psi_m(\mathbf{r}) = \sum_j \epsilon'_{mj}\psi_j(\mathbf{r}) \quad m = 1, 2, \dots, N_s, \quad (5.23)$$

where j runs over doubly and singly occupied orbitals $j = 1, 2, \dots, N_d + N_s$. In Eq.5.22-5.23 the effective potentials are defined as

$$\begin{aligned} v(\mathbf{r})_{eff}^d &= v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{1}{2} \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\mathbf{r})} \\ &+ \frac{1}{2} \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\beta(\mathbf{r})} \end{aligned} \quad (5.24)$$

$$v(\mathbf{r})_{eff}^o = v(\mathbf{r}) + \int \frac{\rho_\alpha(\mathbf{r}') + \rho_\beta(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}[\rho_\alpha, \rho_\beta]}{\delta \rho_\alpha(\mathbf{r})}, \quad (5.25)$$

where the spin densities are given by the expressions

$$\rho_\alpha(\mathbf{r}) = \sum_{i=1}^{N_d} |\psi_i(\mathbf{r})|^2 + \sum_{j=1}^{N_s} |\psi_j(\mathbf{r})|^2 \quad \text{and} \quad \rho_\beta(\mathbf{r}) = \sum_{i=1}^{N_d} |\psi_i(\mathbf{r})|^2. \quad (5.26)$$

In the spin restricted Kohn-Sham equations, above the off-diagonal Lagrangian multipliers appear in the coupling of the equations for doubly and singly occupied orbitals and therefore the ordinary solution methods can not be applied. However, the method for handling off-diagonal Lagrange multipliers developed in restricted open shell Hartree-Fock theory can be adapted to the Kohn-Sham formalism. There are two possibilities: To solve the equations for singly and doubly occupied orbitals separately or to combine both sets of equations into the one effective with off-diagonal Lagrange multipliers absorbed into the Kohn-Sham

Hamiltonian. The second approach is more appealing from the computational point of view and has been chosen for implementation of a spin restricted Kohn-Sham method in the papers included in this thesis.

5.1.2 Exchange-correlation functionals

The exchange-correlation energy (E_{xc}) contains non-classical contributions to the potential energy, as well as the difference between the kinetic energy of the noninteracting reference system and that of the real interacting system. The most basic approximation to E_{xc} is the local density approximation (LDA)⁶⁶

$$E_{xc}^{LDA}[\rho_\alpha, \rho_\beta] = \int \rho(\mathbf{r}), \varepsilon_{xc}(\rho_\alpha(\mathbf{r}), \rho_\beta) d\mathbf{r} \quad (5.27)$$

where ρ_α and ρ_β are the spin densities and ε_{xc} denotes the one-particle exchange-correlation energy in a uniform electron gas, which leads to dependence of the exchange-correlation potential only on the density at the point where it is evaluated. The most common form of LDA assumes the Slater exchange term (S) together with the Vosko, Wilk and Nussair parametrization (VWN)⁶⁷ of the exact uniform electron gas model for the correlation part. To improve upon this rather crude approximation, the most widely used corrections are the so-called generalized gradient approximation (GGA) that employs not only the density but also its gradient

$$E_{xc}^{LDA}[\rho_\alpha, \rho_\beta] = \int f(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r}), \nabla\rho_\alpha, \nabla\rho_\beta). \quad (5.28)$$

This procedure improves the description of electron density in the bonding regions of the molecules, where a high variation of electronic density is expected to take place. The main correlation corrections commonly in use are by Perdew (P86),⁶⁸ by Lee, Yang and Parr (LYP),⁶⁹ and by Perdew and Wang (PW91).⁷⁰ Of the corrections to the exchange energy, the most common forms are those by Perdew and Wang (PW and PW91),^{71,72} and by Becke (B).⁷³ From the more recently introduced exchange functionals, there is the modified Perdew-Wang (mPW)⁷⁴ and the Gill 1996 (G96)⁷⁴ functionals. Recently, the so-called meta-GGA functionals have been developed,⁷⁶ in which the gradient of the electronic density is augmented by some additional parameter(s) of inhomogeneity: either the Laplacian of the density, the local kinetic energy density, or both.

Another class of functionals, often called "hybrid functionals" introduced by Becke, uses a linear combination of Hartree-Fock, LDA and B88 exchange contributions.⁷⁷ Becke's so-called three-parameter hybrid functional (B3) includes ca. 20% of exact HF exchange, while the "half-and-half" hybrid functional (BH)⁷⁸ incorporates as much as 50% exact exchange.

The most successful among these functionals is B3LYP,^{69,79} which has proved to be the most accurate functional for energetic calculations of molecular systems within the Kohn-Sham method. The B3LYP functional combines Dirac, exact Hartree-Fock exchange, and Becke exchange functionals with VWN and LYP correlation functionals in the form

$$E_{xc}^{B3LYP} = a_{xc}E_x^{LDA} + (1 - a_{xc})E_x^{HF} + a_xE_x^B + E_c^{VWN} + a_cE_c^{LYP} \quad (5.29)$$

with a_{xc} , a_x , a_c being parameters resulting from fitting to experimental results on a benchmarking set of molecules. More recently, one modified B3LYP functional with 38 % admixture of the exact Hartree-Fock exchange,^{80,81} denominated B(38HF)P86, was developed by Solomon *et. al.*. This functional was spectroscopically calibrated to improve the theoretical description of the correct balance between ionic and covalent bonding of Cu d^9 complexes. This functional as well as the B3LYP functional were used in the theoretical prediction of absorption spectra and magnetic properties of copper(II) complexes studied in this thesis.

5.2 Response Theory

Density functional response theory is the response theory applied to the Kohn-Sham method, which provides a way for formulating the time-dependent perturbation in which the approximate molecular wavefunction is parameterized and a series of response functions is introduced.⁸² The response functions describe the changes of an observable property when the system is influenced by one or several perturbing fields. In a given frequency of the oscillating field corresponding to an excitation energy, a large response in the system will occur, where the transition energy denotes a pole in the response function and the residue determines the transition matrix elements. When a molecular system is perturbed by a time dependent perturbation field, its Hamiltonian \hat{H} is written as the sum of the unperturbed Hamiltonian \hat{H}_0 and the time dependent perturbation term $\hat{V}(t)$,

$$\hat{H} = \hat{H}_0 + \hat{V}(t) \quad (5.30)$$

In the frequency domain, the perturbation operator can be written as

$$\hat{V}(t) = \int_{-\infty}^{\infty} \hat{V}^\omega \exp[(-i\omega + \varepsilon)t] d\omega \quad (5.31)$$

where ε is a small positive infinitesimal that ensures that the system is in the unperturbed state $\hat{V}(-\infty) = 0$, $t = \infty$. The perturbation operator is required to be Hermitian, which is also a condition for the frequency component of V^t .

$$(V^\omega)^\dagger = V^{(-\omega)} \quad (5.32)$$

At the finite time t and when the perturbation caused by the external field is sufficiently small, we can write the perturbed wave function as a perturbation expansion

$$\begin{aligned} |\tilde{0}(t)\rangle &= |0\rangle + \int_{-\infty}^{\infty} |0_1^{(\omega_1)}\rangle \exp[(-i\omega_1 + \varepsilon)t] d\omega_1 \\ &+ \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |0_2^{(\omega_1, \omega_2)}\rangle \exp[(-i(\omega_1 + \omega_2) + 2\varepsilon)t] d\omega_1 d\omega_2 + \dots \end{aligned} \quad (5.33)$$

where $|0_1^{(\omega_1)}\rangle$ and $|0_2^{(\omega_1, \omega_2)}\rangle$ denote terms linear and quadratic in the perturbation, respectively. The time-evolution of the expectation value of a physical operator A (molecular properties) can be written as

$$\begin{aligned} \langle \tilde{0}(t) | \hat{A} | \tilde{0}(t) \rangle &= \langle 0 | \hat{A} | 0 \rangle + \int_{-\infty}^{\infty} \langle \langle \hat{A}; \hat{V}^{\omega_1} \rangle \rangle_{\omega_1} \exp[(-i\omega_1 + \varepsilon)t] d\omega_1 \\ &+ \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \langle \langle \hat{A}; \hat{V}^{\omega_1}, \hat{V}^{\omega_2} \rangle \rangle_{\omega_1, \omega_2} \exp[(-i(\omega_1 + \omega_2) + 2\varepsilon)t] d\omega_1 d\omega_2 + \dots \end{aligned} \quad (5.34)$$

where $\langle 0 | \hat{A} | 0 \rangle$ is the expectation value of operator \hat{A} for the unperturbed system, $\langle \langle \hat{A}; \hat{V}^{\omega_1}, \dots, \hat{V}^{\omega_n} \rangle \rangle$ is the response function, which describes the response of the molecular properties. The main advantage of response theory is the actual evaluation of the response functions. Inner projection replace the sum over all excited electronic states, which is quite expensive and cannot be easily implemented in DFT. The DFT response methodology can be formulated in density matrix or second quantization formalism, for which numerically equivalent results are obtained. However, the second quantization form of DFT response equations is more practical from a computational point of view. uniform way. The basic principles of the second quantization form of DFT response, which was used in the calculations of this work, will be briefly described. The derivation of the response equations from the time dependent Kohn-Sham equation starts as

$$(\hat{H}(t) + \hat{V}(t))|\tilde{0}\rangle = i \frac{d}{dt} |\tilde{0}\rangle \quad (5.35)$$

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

$$\hat{H}(t) + \hat{V}(t) = \sum_{\sigma} \int d\tau \hat{\Psi}_{\sigma}^{\dagger}(\mathbf{r}) [f_{\sigma}(\mathbf{r}, t) + v(\mathbf{r}, t)] \hat{\Psi}_{\sigma}(\mathbf{r}, t) . \quad (5.36)$$

In Eq. 5.36 the fermion field operator $\hat{\Psi}_{\sigma}(\mathbf{r})$ is restricted to spin orbitals with equal spatial parts

$$\hat{\Psi}_{\sigma}(\mathbf{r}) = \sum_j \varphi_j(\mathbf{r}) a_{j\sigma} \quad (5.37)$$

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

$$|\tilde{0}\rangle = \exp[-\hat{\kappa}(t)] |0\rangle \quad (5.38)$$

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

$$\hat{\kappa}(t) = \sum_{rs\sigma} \kappa_{rs}(t) E_{rs}^\sigma \equiv \sum_{rs\sigma} \kappa_{rs}(t) a_{r\sigma}^\dagger a_{s\sigma} \quad (5.39)$$

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

$$\rho_\sigma(\mathbf{r}, t) = \langle \tilde{0} | \hat{\rho}_\sigma(\mathbf{r}) | \tilde{0} \rangle = \langle 0 | \exp[\hat{\kappa}(t)] \hat{\rho}_\sigma(\mathbf{r}) \exp[-\hat{\kappa}(t)] | 0 \rangle \quad (5.40)$$

where the electron spin-density operator is

$$\hat{\rho}_\sigma(\mathbf{r}) = \hat{\Psi}_\sigma^\dagger(\mathbf{r}) \hat{\Psi}_\sigma(\mathbf{r}) = \sum_{pq} \varphi_p^*(\mathbf{r}) \varphi_q(\mathbf{r}) E_{pq}^\sigma. \quad (5.41)$$

The Ehrenfest principle for a one electron operator \hat{Q} using Eq. 5.35 and Eq. 5.38 may be written as

$$\left\langle 0 \left| \left[\hat{Q}, \exp[\hat{\kappa}(t)] \left(\hat{H}(t) + \hat{V}(t) - i \frac{d}{dt} \right) \exp[-\hat{\kappa}(t)] \right] \right| 0 \right\rangle = 0. \quad (5.42)$$

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

$$\hat{\kappa}(t) = \hat{\kappa}^{(1)}(t) + \hat{\kappa}^{(2)}(t) + \dots \quad (5.43)$$

Inserting this expansion of variational parameters into Eq. 5.42 and collecting the terms at the corresponding orders one can readily identify equations for the determination of the response functions.

5.2.1 Linear response function

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

$$\left\langle 0 \left| \left[\hat{\mathbf{q}}, \left[\hat{\kappa}^\omega, \hat{H}^{(0)} \right] + \hat{H}^\omega \right] \right| 0 \right\rangle + \omega \left\langle 0 \left| \left[\hat{\mathbf{q}}, \hat{\kappa}^\omega \right] \right| 0 \right\rangle = - \left\langle 0 \left| \left[\hat{\mathbf{q}}, \hat{V}^\omega \right] \right| 0 \right\rangle \quad (5.44)$$

where the non-redundant excitation operators E_{pq}^σ have been collected in the column vector $\hat{\mathbf{q}}$. The solution of Eq. 5.44 allows one to evaluate the linear response function for an arbitrary one-electron operator \hat{A} in the presence of a perturbation \hat{V}^ω acting on the molecular system in the following way

$$\langle\langle \hat{A}; \hat{V} \rangle\rangle_\omega = \left\langle 0 \left| \left[\hat{\kappa}^\omega, \hat{A} \right] \right| 0 \right\rangle . \quad (5.45)$$

5.2.2 Quadratic response function

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

$$\begin{aligned} \left\langle 0 \left| \left[\hat{\mathbf{q}}, \hat{H}^{\omega_1, \omega_2} + 2P_{12} \left[\hat{\kappa}^{\omega_1}, \hat{H}^{\omega_2} + \hat{V}^{\omega_2} \right] + (\omega_1 + \omega_2) \hat{\kappa}^{\omega_1, \omega_2} \right. \right. \right. \\ \left. \left. \left. + P_{12} \left[\hat{\kappa}^{\omega_1}, \left[\hat{\kappa}^{\omega_2}, \hat{H}^{(0)} \right] \right] + (\omega_2 - \omega_1) \left[\hat{\kappa}^{\omega_1}, \hat{\kappa}^{\omega_2} \right] \right] \right| 0 \right\rangle = 0 \end{aligned} \quad (5.46)$$

$$\left\langle 0 \left| \left[\hat{\mathbf{q}}, \left[\hat{\kappa}^{\omega_1}, \hat{H}^{(0)} \right] + \hat{H}^{\omega_1} \right] \right| 0 \right\rangle + \omega \langle 0 | [\hat{\mathbf{q}}, \hat{\kappa}^{\omega_1}] | 0 \rangle = - \left\langle 0 \left| \left[\hat{\mathbf{q}}, \hat{V}^{\omega_1} \right] \right| 0 \right\rangle \quad (5.47)$$

$$\left\langle 0 \left| \left[\hat{\mathbf{q}}, \left[\hat{\kappa}^{\omega_2}, \hat{H}^{(0)} \right] + \hat{H}^{\omega_2} \right] \right| 0 \right\rangle + \omega \langle 0 | [\hat{\mathbf{q}}, \hat{\kappa}^{\omega_2}] | 0 \rangle = - \left\langle 0 \left| \left[\hat{\mathbf{q}}, \hat{V}^{\omega_2} \right] \right| 0 \right\rangle \quad (5.48)$$

where we introduced the symmetrization operator

$$P_{12}f(1)g(2) = \frac{f(1)g(2) + f(2)g(1)}{2} . \quad (5.49)$$

The solution of Eq. 5.48 allows one to evaluate the quadratic response function for an arbitrary one-electron operator \hat{A} in the presence of a perturbations \hat{V}^{ω_1} and \hat{V}^{ω_2} in the following way

$$\langle\langle \hat{A}; \hat{V}, \hat{V} \rangle\rangle_{\omega_1, \omega_2} = \left\langle 0 \left| \left[\hat{\kappa}^{\omega_1, \omega_2}, \hat{A} \right] + P_{12} \left[\hat{\kappa}^{\omega_1}, \left[\hat{\kappa}^{\omega_2}, \hat{A} \right] \right] \right| 0 \right\rangle . \quad (5.50)$$

5.3 Solvent models

The environment plays a key role in the determination of the properties and reactivity of substances in the condensed phase. The complexity of chemical phenomena in solution has required the development of a variety of models and computational techniques to represent molecules in solution.⁸³ These techniques differ in the level of detail used to describe the chemical system, the physical rules underlying the process of interest, and the mathematical

formulas used to describe these rules. A given theoretical model must be able to incorporate properly the nature of all the relevant features of the solvation process, so that the results can be contrasted with experiment and the quality of the model can be addressed. The final goal of theoretical models is the understanding of the chemical behavior of molecules in environments.

From the theoretical point of view, the "solvent effect" can be interpreted as the change experienced by a chemical system (the solute) on transfer from the gas phase to a dilute solution. The solvent may influence the nuclear and electronic distribution of the solute, as well as the chemical reactivity and intermolecular interactions. In the last 30 years, different methods have been developed to gain insight into these effects.⁸⁴ All these methods can broadly be grouped into two categories depending on the model used to represent the solvent: i) continuum medium, and ii) discrete particles (the microscopic level). In the former methods, the solvent is considered as a homogeneous dielectric continuum medium which reacts against the solute charge distribution generating a reaction field, which it then interacts with the solute. In the latter model, explicit solvent molecules are taken into account around of the solute for the description of the solvent effect.

The computational cost of the supermolecule approach by using quantum mechanical calculations limits the description of the solvent to a few molecules. This is mainly useful to analyse specific interactions with the solute. Alternative methods based on a microscopic description of the solvent determines the average representation of the system in solution from the ensemble of configurations collected from simulations. The classical and/or quantum mechanical treatment can be used in the description of the solute and solvent. A general description and the main characteristics of the continuum and discrete approaches for the description of solvation phenomena will be outlined in the next section.

5.3.1 Dielectric continuum models

The dielectric continuum models treat the solvent environment by a homogeneous dielectric medium characterized by its dielectric constant ϵ . The solute is embedded in a cavity of certain shape and size. The solute charge distribution interacts with the medium, polarizing it and creates a reflection charge distribution on the cavity surface which will interact electrostatically with the solute leading to a net stabilization. The continuum models can be classified according to two main characteristics: i) the shape of the cavity that defines the solute/solvent interface, and ii) the description of the solute charge distribution and the solvent field. Regarding the solute/solvent interface, a large number of cavities have been used. The simplest methods define cavities of regular shape, such as spheres, ellipsoids or cylinders, while the most accurate methods use cavities adapted to the molecular shape.

The most widely used method is the polarized continuum model (PCM) model,^{85,86} in which the cavity has a realistic shape and size and is constructed by interlocking spheres. With regard to the treatment of the solute charge distribution and solvent reaction field, Tomasi and Persico⁸⁷ have categorized the different treatments in five formalisms: 1) multipole expansions, 2) apparent surface charges, 3) image charges, 4) finite difference, and 5) finite elements. The methods based on multipole expansions can be easily implemented and are probably the simplest ones.

In the PCM model, which is based on the apparent surface charge, the solvation free energy for a solvated molecule is defined as

$$\Delta G_{sol} = \Delta G_{elec} + \Delta G_{cav} + \Delta G_{disp} + \Delta G_{rep} \quad (5.51)$$

where ΔG_{elec} is the electrostatic contribution, ΔG_{cav} corresponds to the work needed to form the cavity, ΔG_{disp} denotes the short range solute-solvent interactions and ΔG_{rep} represents the short range solute-solvent repulsive forces. The electrostatic term is defined as

$$\begin{aligned} \Delta G_{sol} = \langle \Phi^{sol} | \hat{H}^0 + \hat{V}^0 | \Phi^{sol} \rangle &- \langle \Phi^0 | \hat{H}^0 | \Phi^0 \rangle - \\ &- \frac{1}{2} [\langle \Phi^{sol} | \hat{V}_R | \Phi^{sol} \rangle + \int \rho_{nuc} V_\sigma(s) ds] \end{aligned} \quad (5.52)$$

where V_R and σ_i are

$$V_R = \sum_{i=1}^M \frac{\sigma_i S_i}{|r_i - r|}, \sigma_i = -\frac{\varepsilon - 1}{4\pi\varepsilon} \left(\frac{\delta(V_\sigma + V_\rho)}{\delta n} \right)_i. \quad (5.53)$$

The cavity contribution depends only on the shape of the cavity, specifically for a spherical cavity, it can be computed as

$$G_{cav} = \sum_i^{spheres} \frac{A_i}{4\pi R_i^2} G_i^{HS}, \quad (5.54)$$

where R_i is the radius of the sphere, G_i^{HS} is the cavitation energy for a sphere of radius R_i and A_i is the area of the sphere i . The dispersion contribution (G_{disp}) is formulated as

$$\begin{aligned} G_{dis} &= \frac{1}{\pi} \int_0^\infty dw \sum_{K \neq 0} \frac{w_{0K}^M}{(w_{0K}^M)^2 + w^2} \int dr_1 \\ &x \int_\Sigma \frac{dr_2}{r_{12}} P_M(0K|r_1) \sigma_S[\varepsilon(iw), P_M(0K|r); r_2], \end{aligned} \quad (5.55)$$

where $P_M(0K|r)$ and w_{0K}^M are the transition densities and energies for solute M , respectively, σ_S is the surface charge density induced in the solvent by the electric field of the

charge distribution $P_M(0K|r)$ and $\varepsilon(iw)$ is the computed dielectric constant at imaginary frequencies. Finally, the repulsion term is given as

$$G_{rep} = \alpha \int_{\mathbf{r} \notin C} dr P(\mathbf{r}), \quad (5.56)$$

where α is a constant defined by properties of the solvent, $P(\mathbf{r})$ is the solute electron charge distribution and C is the cavity domain.

5.3.2 Discrete models

The discrete models can be divided basically in two categories depending on the treatment of the solute: i) classical methods and ii) quantum mechanical (QM) methods where in both cases, the solvent is described in terms of discrete particles.⁸⁴ In the classical discrete methods, the microscopic description of the solute and the solvent and their intermolecular interactions is evaluated by a force-field, which has different energy terms for bonded (stretching, bending, torsion) and non-bonded (electrostatic, van der Waals) interactions. These terms adopt very simple expressions, which allow an easy evaluation of the potential energy of the system. Two well-known methods, called Monte Carlo (MC) and Molecular Dynamics (MD), are included in this class of discrete models.⁸⁸ The sampling of the solute-solvent configurational space by MD is performed from the trajectories determined by integration of the equations of motion, which can be performed following the Newton, Lagrange or Hamiltonian formalisms. MC samplings are obtained from the application of Boltzmann probabilistic rules to a very large set of randomly selected configurations. In principle, MD and MC samplings should be identical for infinite simulations if the system is in equilibrium. Regarding the quantum discrete methods, they can still be grouped into two categories depending on whether a classical or QM evaluation is used in the description of the solvent. The methods which combine the QM treatment of the solute with a classical treatment of the solvent employ a classical force field to represent the solvent interaction. The total Hamiltonian of the solute-solvent system is decomposed into three terms,

$$\hat{H}^{ef} = \hat{H}^{MM} + \hat{H}^{QM} + \hat{H}^{QM/MM} \quad (5.57)$$

where, \hat{H}^{MM} is a Hamiltonian for the intramolecular solute interactions, \hat{H}^{QM} is a classical Hamiltonian for the solvent-solvent (intra and intermolecular) interactions and $\hat{H}^{QM/MM}$ is a coupling term to account for the solute-solvent interactions (QM/MM). These methods are often known as hybrid quantum mechanical /mechanical molecular (QM/MM) methods and both versions using Monte Carlo and Molecular dynamics to evaluate the classical part of the systems can be found. Finally, the second model of quantum discrete methods treats

all the molecules of the system of interest at the QM level. The hybrid Car Parrinello molecular dynamics method has been used in this thesis and will be therefore described in more detail in the next section.

Car Parrinello molecular dynamics method

The Car Parrinello molecular dynamics method uses the unified approach of molecular dynamics and Density-Functional theory. This method computes ground-state electronic properties of large disordered systems at a level of state-of-the-art electronic structure calculations and performs *ab initio* MD simulations where the only assumptions are the validity of classical mechanics to describe the ionic motion and the Born-Oppenheimer (BO) approximation to separate nuclear and electronic coordinates.⁸⁹ Following the Kohn and Sham (KS) formalism, the electron density is written in terms of occupied single-particle orthonormal orbitals,

$$n(\mathbf{r}) = \sum_i |\phi(\mathbf{r})|^2. \quad (5.58)$$

A point of the BO potential energy surface is given by the minimum with respect to the $\phi_i(\mathbf{r})$ of the energy functional,

$$E[\{\psi_i\}, \{R_I\}, \{\alpha_v\}] = \sum_i \int_{\Omega} d^3r \psi_i^*(\mathbf{r}) [-(\hbar^2/2m)\nabla^2] \psi_i(\mathbf{r}) + U[n(\mathbf{r}), \{R_I\}, \{\alpha_v\}]. \quad (5.59)$$

Here $\{R_I\}$ indicates the nuclear coordinates and $\{\alpha_v\}$ are all the possible external constraints imposed on the system, like the volume Ω , the strain $\epsilon_{\mu\nu}$, etc. The functional U contains the internuclear Coulomb repulsion and the effective electronic potential energy, including external nuclear, Hartree, and exchange and correlation contributions. A different approach is adopted concerning the convectional formulation for the minimization of the energy functional. This approach, known as "dynamical simulated annealing", is useful as a minimization procedure and allows the study of finite temperature properties. The parameters $\{\psi_i\}$, $\{R_I\}$ and $\{\alpha_v\}$ in the above energy-function equation are considered to be dependent on time. The Lagrangian

$$L = \sum_i \frac{1}{2} \mu \int_{\Omega} d^3r |\dot{\psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_v \frac{1}{2} \mu_v \dot{\alpha}_v^2 - E[\{\psi_i\}, \{R_I\}, \{\alpha_v\}]. \quad (5.60)$$

where the ψ_i is introduced, are subject to the holonomic constraints

$$\int_{\Omega} d^3r \psi_i^*(\mathbf{r}, t) \psi_j(\mathbf{r}, t) = \delta_{ij}. \quad (5.61)$$

In Eq. 5.63 the dot indicates a time derivative, M_I are the physical ionic masses, and μ and μ_v are arbitrary parameters of appropriate units. The Lagrangian in Eq. 5.63 generates a dynamics for the parameters $\{\psi_i\}$'s, $\{R_I\}$'s and $\{\alpha_v\}$'s through the equations of motion:

$$\mu\ddot{\psi}_i(\mathbf{r}, t) = -\delta E/\delta\psi_i^*(\mathbf{r}, t)\psi_j(\mathbf{r}, t) + \sum_{ik} \Lambda_{ik}\psi_k(\mathbf{r}, t) \quad (5.62)$$

$$M_I\ddot{R}_I = -\nabla_{R_I} E, \quad (5.63)$$

$$\mu_v\ddot{\alpha}_v = -(\partial E/\partial\alpha_v), \quad (5.64)$$

where Λ_{ik} are Lagrange multipliers introduced in order to satisfy the constrains in Eq. 5.64. The ion dynamics in Eqs. 5.65-5.67 may have a real physical meaning, whereas the dynamics associated with the $\{\psi_i\}$'s and the $\{\alpha_v\}$'s is fictitious and has to be considered only as a tool to perform the dynamical simulated annealing.

Chapter 6

Summary of Papers

The present thesis encloses applications of the DFT methods developed by our research group for the evaluation of visible near infrared absorption spectrum and EPR spectral parameters of copper(II) molecular systems. The subject of the first two papers is to study the first solvation shell of copper(II) ion in aqueous solution, which was described in these investigations by using different supermolecule models of water molecules around the copper(II) ion, as shown in Fig. 6.1. The EPR parameter results are investigated in **paper I**, while the visible near-infrared electronic transitions were investigated in **paper II**. The Copper(II) Acetylacetonate complex, $\text{Cu}(\text{acac})_2$ (Fig. 6.2) was investigated in **paper III** and **paper IV**. The determination and assignment of the visible electronic absorption tran-

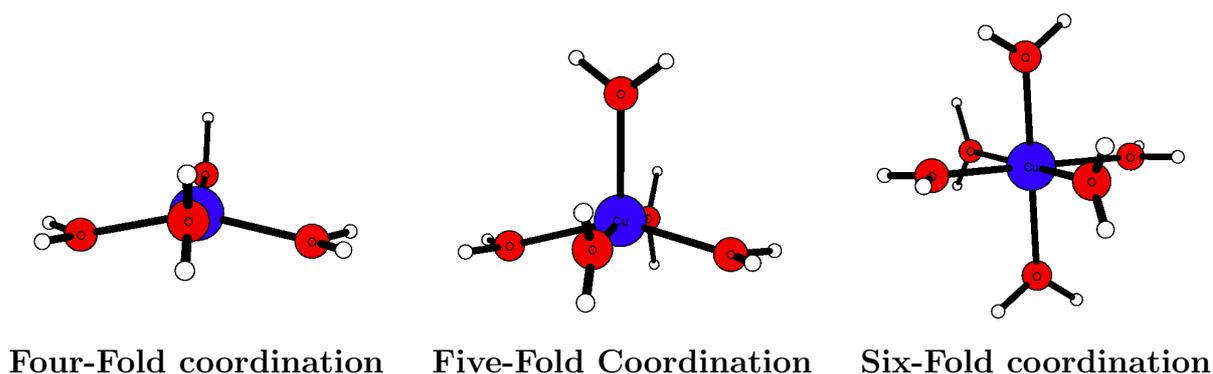


Figure 6.1: Supermolecular models of the first solvation shell of copper(II) in water.

sitions as well as the spin orbit correction for these transitions of Copper(II) Acetylacetonate was evaluated in **paper III**. The solvent effect on the optical and magnetic properties of $\text{Cu}(\text{acac})_2$ complex was studied in **paper IV** in order to evaluate the solvatochromic shift due to the closest solvent molecules around the copper(II) complexes. In **paper V**, an accurate treatment of spin polarization effects in molecular properties is presented. Finally, a new approach for the evaluation of the leading-order relativistic corrections to the electronic g tensors of molecules with a doublet ground state is presented in **paper VI**. Overall, the performance of the DFT response implementation in the calculation of optical and magnetic properties proved to be satisfactory, giving rise to accurate results for most problems investigated in this work.

In **Paper I** we report density functional theory calculations of the electronic g tensor and hyperfine coupling constants of the copper dication in sixfold- and fivefold-coordination models of the first aqueous solvation sphere. The obtained results indicate that the electronic g tensor of these copper complexes can in principle be used to elucidate the coordination environment of the hydrated copper dication. This is not found to be the case for the copper

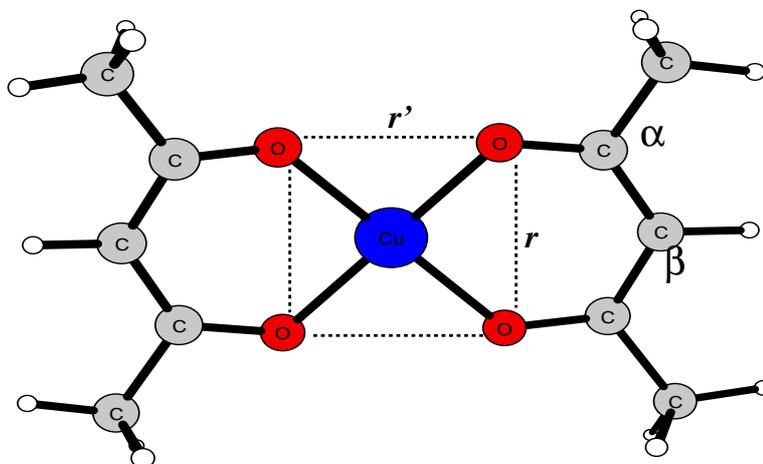


Figure 6.2: The Copper(II) Acetylacetonate complex.

hyperfine coupling constants, i.e. they can not be used for determination of the coordination of hydrated copper dications. Overall, the electronic g tensor favors the five-fold coordina-

tion of copper(II) ion in aqueous solution, while the hyperfine coupling constants contradict this finding, favoring the six-fold coordination. This can be attributed to shortcomings of the methodology which neglects vibrational and environmental effects. In addition to these results, we have designed a methodology for the accurate evaluation of the electronic g tensors and hyperfine coupling tensors in copper complexes, and demonstrate the applicability of this approach to copper dication aqua complexes.

In **Paper II** we investigate the visible near-infrared absorption spectra of the copper(II) aqua complexes, specifically the $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$ $n=4, 5, 6$, systems. We have performed Car-Parrinello molecular dynamics simulations at ambient conditions for four-, five- and six-coordinated Cu(II) aqua complexes. The obtained results show that each Cu(II) aqua system gives rise to a particular spectral pattern for every solvation models investigated (Fig. 6.3), where both positions and intensities of the $d \rightarrow d$ electronic transitions can be used to characterize the coordination environment of the hydrated Cu(II) ion. The near infrared electronic transition plays a decisive role in characterization of the five- and six-coordinate copper(II) aqua complexes and can be used to monitor the axial bond lengths in these complexes. Based on comparisons with experimental results available, B3LYP results favor the distorted fivefold-coordination arrangement for the molecular structure of

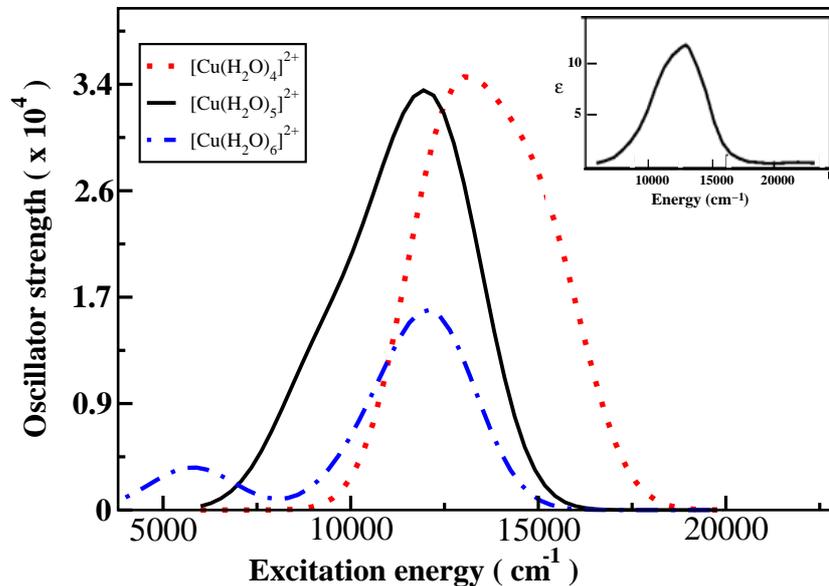


Figure 6.3: The computed visible near-infrared simulated spectra of aqua copper(II) complexes.

the Cu(II) ion in aqueous solution.

In **Paper III** we report the visible absorption spectra of the Copper(II) Acetylacetonate complex, $\text{Cu}(\text{acac})_2$. The spin-restricted open-shell density functional linear response (DFT-LR) formalism was employed to evaluate the electronic transitions in the visible region. The absorption transitions and the spin-orbit coupling effect on the splitting of d -orbitals were investigated. The B3LYP calculations provide a consistent prediction of the $3d - 3d$ excitation energies and the ordering of d -orbitals, compared to experimental data available. Our results indicate also a failure of the crystal-field theory which predicts the d -ordering of $\text{Cu}(\text{acac})_2$. The spin-orbit coupling corrections show only additional contribution to the $3d - 3d$ splittings, as compared to the ligand field effect, which proved to be the main factor to the energy splittings of the d -orbitals of $\text{Cu}(\text{acac})_2$.

In **Paper IV** solvent effects on the visible near infrared absorption spectrum and the EPR parameters of $\text{Cu}(\text{acac})_2$ were evaluated at the density functional theory level employing the supermolecule model. The effect of the solvent basicity is analysed. We observed that the supermolecule model shows to be quite efficient to describe the solvent effects on the optical and magnetic properties of the copper(II) molecular complexes. This feature is largely due to the fact that a direct and specific interaction is expected to take place in copper(II) systems, thus providing the major contribution of the solvent-solute interaction. The performance of the DFT response implementation in the calculation of optical and magnetic properties proved to be satisfactory, giving rise to accurate results for the most problems investigated in this work. The optical spectrum as well as the EPR parameters show a strong dependence on the coordination environment around the copper complex. A high solvatochromic effect is predicted for the $3d - 3d$ transitions, showing that the coordination of the solvent at the axial position of $\text{Cu}(\text{acac})_2$ is the main factor that influences the positions of the d -orbitals of $\text{Cu}(\text{acac})_2$. Compared to the electronic g tensor, the hyperfine coupling constants of the $\text{Cu}(\text{acac})_2$ complex show a more pronounced dependence on the effect of base strength.

In **Paper V**, an approach developed by our group is used to formulate new schemes for computation of the electronic g tensors and hyperfine coupling constants, which include spin polarization effects within the framework of spin restricted Kohn-Sham theory. The proposed computational schemes are used to study the spin polarization effects on electron paramagnetic resonance spin Hamiltonian parameters of square planar copper complexes. Obtained results indicate that spin polarization gives rise to sizable contributions to the hyperfine coupling tensor of copper in all investigated complexes, while the electronic g tensor of these complexes are only marginally affected by spin polarization and other factors, like choice of exchange-correlation functional or molecular structures, which have more pronounced impact on the accuracy of the results.

In **Paper VI**, we evaluate the leading-order relativistic corrections to the electronic g tensors of molecules with a doublet ground state. This approach has been implemented in the framework of spin-restricted density functional theory and is in the present paper, as a first illustration of the theory, applied to study relativistic effects on the electronic g tensors of dihalogen anion radicals X_2^- ($X=F, Cl, Br, I$). The results indicate that the spin-orbit interaction is responsible for the large parallel component of the g tensor shift of Br_2^- and I_2^- , and furthermore that both the leading-order scalar relativistic and spin-orbit corrections are of minor importance for the perpendicular component of the g tensor in these molecules since they effectively cancel each other.

Bibliography

- [1] E. I. Solomon, M. J. Baldwin, M. D. Lowery, *Chem. Rev.*, 92:521, 1992.
- [2] E. I. Solomon, U. M. Sundaram, T. E. Machonkin, *Chem. Rev.*, 96:2563, 1996.
- [3] J. P. Klinman, *Chem. Rev.*, 96:2541, 1996.
- [4] E. A. Lewis, W. B. Tolman, *Chem. Rev.*, 104:1047, 2004.
- [5] A. L. Gavrilova, B. Bosnich, *Chem. Rev.*, 104:349, 2004.
- [6] D. B. Rorabacher, *Chem. Rev.*, 104:651, 2004.
- [7] P. Frank, M. Benfatto, R. K. Szilagyi, P. D'Angelo, S. Della Longa, K. O. Hodgson, *Inorg. Chem.*, 44:19922, 2005.
- [8] E. I. Solomon, J. W. Hare, H. B. Gray, . *Proc. Natt. Acad. Sci.*, 73:1389, 1976.
- [9] E. I. Solomon, J. W. Hare, D. M. Dooley, J. H. Dawson, P. J. Stephens, H. B. Gray, *J. Am. Chem. Soc.*, 102:168, 1980.
- [10] B. G. Malmström, *Eur. J. Biochem.*, 223:711, 1994.
- [11] F. Neese. *Current Opinion in Chemical Biology*, 7:125, 2003.
- [12] L. Basumallick, R. Sarangi, S. D. George, B. Elmore, A. B. Hooper, B. Hedman, K. O. Hodgson, E. I. Solomon, *J. Am. Chem. Soc.*, 127:3531, 2005.
- [13] D. K. Garner, M. D. Vaughan, H. J. Hwang, M. G. Savelieff, S. M. Berry, J. F. Honek, Y. Lu, *J. Am. Chem. Soc.*, 128:15608, 2006.
- [14] Y. Nishida, S. Kida, *Coord. Chem. Rev.*, 27:275, 1979.
- [15] S. Sinnecker, F. Neese, *J. Comp. Chem.*, 27:1473, 2006.

- [16] F. Neese, T. Petrenko, D. Ganyushin, G. Olbrich, *Coord. Chem. Rev.*, 251:288, 2007.
- [17] I. B. Bersuker, *Chem. Rev.*, 101:1067, 2001.
- [18] P. M. Lenahan, J. F. Conley Jr., *J. Vac. Sci. Technol. B*, 16:2134, 1998
- [19] J. Ferguson, *J. Chem. Phys.*, 34:1609, 1961.
- [20] J. Ferguson, R. L. Belford, T. S. Piper, *J. Chem. Phys.*, 37:1569, 1962.
- [21] G. Jeschke, *Cur. Opn. Sol. Stat. Mat. Sci.*, 7:181, 2003.
- [22] J. E. Huheey, *Inorganic Chemistry*, 3th. Ed.; Harper/Row; New York, pp 396, 1983.
- [23] M. Kaupp, M. Bühl, V. G. Malkin, *Calculation of NMR and EPR Parameters: Theory and Applications*, Wiley-VCH, 2004.
- [24] W. J. Hehre, L. Radom, P. V. R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbital Theory* John Wiley and Sons, New York, 1986
- [25] P. Geerlings, F. De Proft, W. Langenaeker, *Chem. Rev.*, 103:1793, 2002.
- [26] Z. Rinkevicius, I. Tunell, P. Salek, P. Vahtras, H. Ågren, *J. Chem. Phys.*, 119:34, 2003.
- [27] Z. Rinkevicius, L. Telyatnyk, P. Salek, O. Vahtras, H. Ågren, *J. Chem. Phys.*, 119:34, 2003.
- [28] Z. Rinkevicius, L. Telyatnyk, P. Salek, O. Vahtras, H. Ågren, *J. Chem. Phys.*, 121:7614, 2004.
- [29] P. R. Bunker, P. Jensen, *Molecular symmetry and spectroscopy*, 2 ed. NRC Research Press, 1998.
- [30] A. Vogler and H. Kunkley, *Comments Inorg. Chem.* 9:201, 1990.
- [31] L. G. Vanquickenborne and A. Ceulemans, *Coord. Chem. Rev.*, 48:157, 1983.
- [32] H. Bethe, *Ann. Phys.*, 3:135, 1929.
- [33] J. H. Van Vleck, *J. Chem. Phys.*, 3:807, 1935.
- [34] J. E. Harriman, *Theoretical Foundations of Electron Spin Resonance*, Academic Press, New York-San Francisco-London, 1978.

- [35] J. H. Weil, J. R. Bolton, and J. E. Wertz, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*, Wiley, New York, 1994.
- [36] N. M. Atherton, *Principles of Electron Spin Resonance*, Ellis Horwood and Prentice Hall, 1993.
- [37] C. P. Poople, Jr., H. A. Farach, *Handbook of Electron Spin Resonance*, Vol. 2, Columbia, SC 29208, USA, 1999.
- [38] F. Neese and E. I. Solomon, in *Magnetoscience- From Molecules to Materials*, Vol 4, Eds. M. Drillon and J. S. Miller. Willey, 2002.
- [39] S. Patchkovskii, T. Ziegler, *J. Chem. Phys.*, 111:5730, 1999.
- [40] S. Patchkovskii, T. Ziegler, *J. Am. Chem. Soc.*, 122:3506, 2000.
- [41] E. van Lenthe, A. van der Avoird, P. E. S. Wormer, *J. Chem. Phys.*, 108:4783, 1998.
- [42] F. Neese, *J. Chem. Phys.*, 118:3939, 2003.
- [43] M. Kaupp, R. Reviakine, O. L. Malkina, A. Arbuznikov, B. Schimmelpfennig, V. G. Malkin, *J. Comput. Chem.*, 23:794, 2002.
- [44] M. Munzarova, M Kaupp, *J. Phys. Chem. A.*, 103:9966, 1999.
- [45] F. Neese, *J. Chem. Phys.*, 118:3939, 2001.
- [46] M. Kaupp, R. Reviakine, O. L. Malkina, A. Arbuznikov, B. Schimmelpfenning and V. G. Malkin, *J. Comput. Chem.*, 23:794, 2002.
- [47] P. Pyykkö *Chem. Rev.*, 88:563, 1988.
- [48] G. H. Lushington, F. Grein, *J. Chem. Phys.*, 106:3292, 1997.
- [49] O. Vahtras, B. Minaev, H. Ågren, *Chem. Phys. Lett.*, 281:186, 1997.
- [50] E. van Lenthe, P. E. S. Wormer, A. van der Avoird, *J. Chem. Phys.*, 107:2488, 1997.
- [51] F. Neese, *J. Chem. Phys.*, 115:11080, 2001.
- [52] R. McWeeny and B. T. Sutcliffe, *Methods of Molecular Quantum Mechanics*, Academic Press, London, 1969.
- [53] Z. Rinkevicius, L. Telyatnyk, P. Salek, O. Vahtras, and H. Ågren, *J. Chem. Phys.*, 119:10489, 2003.

- [54] Z. Rinkevicius, L. Telyatnyk, O. Vahtras, and H. Ågren, *J. Chem. Phys.*, 121:7614, 2004.
- [55] O. Malkina, J. Vaara, B. Schimmelpfenning, M. Munzarova, V. Malkin, M. Kaupp, *J. A. Chem. Soc.*, 122:9206, 2000.
- [56] K. Ruud, B. Schimmelpfenning, and H. Ågren, *Chem. Phys. Lett.*, 310:215, 1999.
- [57] P. Manninen, J. Vaara, and K. Ruud, *J. Chem. Phys.*, 121:1258, 2004.
- [58] G. H. Lushington, F. Grein, *Theor. Chim. Acta.*, 93:259, 1996.
- [59] G. Schreckenbach, T. Ziegler, *J. Phys. Chem. A*, 101:3388, 1996.
- [60] L. A. Eriksson, V. G. Malkin, O. I. Malkina, D. R. Salahub, *J. Chem. Phys.*, 99:9756, 1993.
- [61] R. Batra, B. Giese, M. Spichty, G. Gescheidt, K. N. Houk, *J. Phys. Chem.*, 100:18371, 1996.
- [62] M. L. Munzarova, M. Kaupp, *J. Phys. Chem. A*, 103:9966, 1999.
- [63] S. A. Perera, L. M. Salemi, R. J. Bartlett, *J. Chem. Phys.*, 106:4061, 1997.
- [64] P. Hohenberg, W. Kohn, *Phys. Rev. B*, 136:864, 1964
- [65] W. Kohn, J. J. Sham, *Phys. Rev. A*, 140:1133, 1965.
- [66] R. G. Parr and W. Yang. *Density Functional Theory of Atoms and Molecules*. Oxford University Press, New York, 1989.
- [67] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, 58:1200, 1980.
- [68] J. P. Perdew, Y. Wang, *Phys. Rev. B*, 33:8222, 1980.
- [69] C. Lee, W. Yang, G. R. Parr, *Phys. Rev. B*, 37:785, 1988.
- [70] J. P. Perdew, Y. yang, *Phys. Rev. B*, 45:13244, 1992
- [71] J. P. Perdew, Y. yang, *Phys. Rev. B*, 33:8800, 1986.
- [72] J. P. Perdew, in *Electronic Structure of Solids*, eds. P. Ziesche, H. Eschring, Akademie Verlag, Berlin, 1991.
- [73] A. D. Becke, *J. Phys. Chem.* , 38:3098, 1993.

- [74] C. Adamo, V. Barone, *J. Chem. Phys.*, 108:664, 1998.
- [75] P. M. W. Gill, R. D. Adamson, *Chem. Phys. Lett.*, 261:105, 1996.
- [76] A. V. Arbouznikov, M. Kaupp, V. G. Malkin, *Phys. Chem. Chem. Phys.*, 4:5467, 2002.
- [77] A. D. Becke, *J. Chem. Phys.* , 98:5467, 1993.
- [78] A. D. Becke, *J. Chem. Phys.* , 98:1372, 1993.
- [79] A. D. Becke, *Phys. Rev. A*, 38:3098, 1988.
- [80] E. I. Solomon, R. K. Szilagyi, G. S. DeBeer, L. Basumallick, *Chem. Rev.* , 104:419, 2004.
- [81] R. K. Szilagyi, M. Metz, E. I. Solomon, *J. Phys. Chem. A*, 106:2994, 2002.
- [82] J. Olsen, P. Jorgensen, *J. Chem. Phys.*, 82:3235, 1985.
- [83] M. Orozco, F. J. Luque, *Chem. Rev.*, 100:4187, 2000.
- [84] M. Orozco, C. Alhambra, X. Barril, *J. Mol. Model.* , 2:1, 1996.
- [85] S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* , 55:117, 1981.
- [86] M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* , 255:327, 1996.
- [87] J. Tomasi, M. Persico, *Chem. Rev.* , 94:2027, 1994.
- [88] M. P. Allen, D. J. Tildesley, *Computer Simulations of Liquids.*, Clarendon Press, Oxford, 1987.
- [89] R. Car, M. Parrinello, *Phys. Rev. Lett.*, 55:2471, 1985.