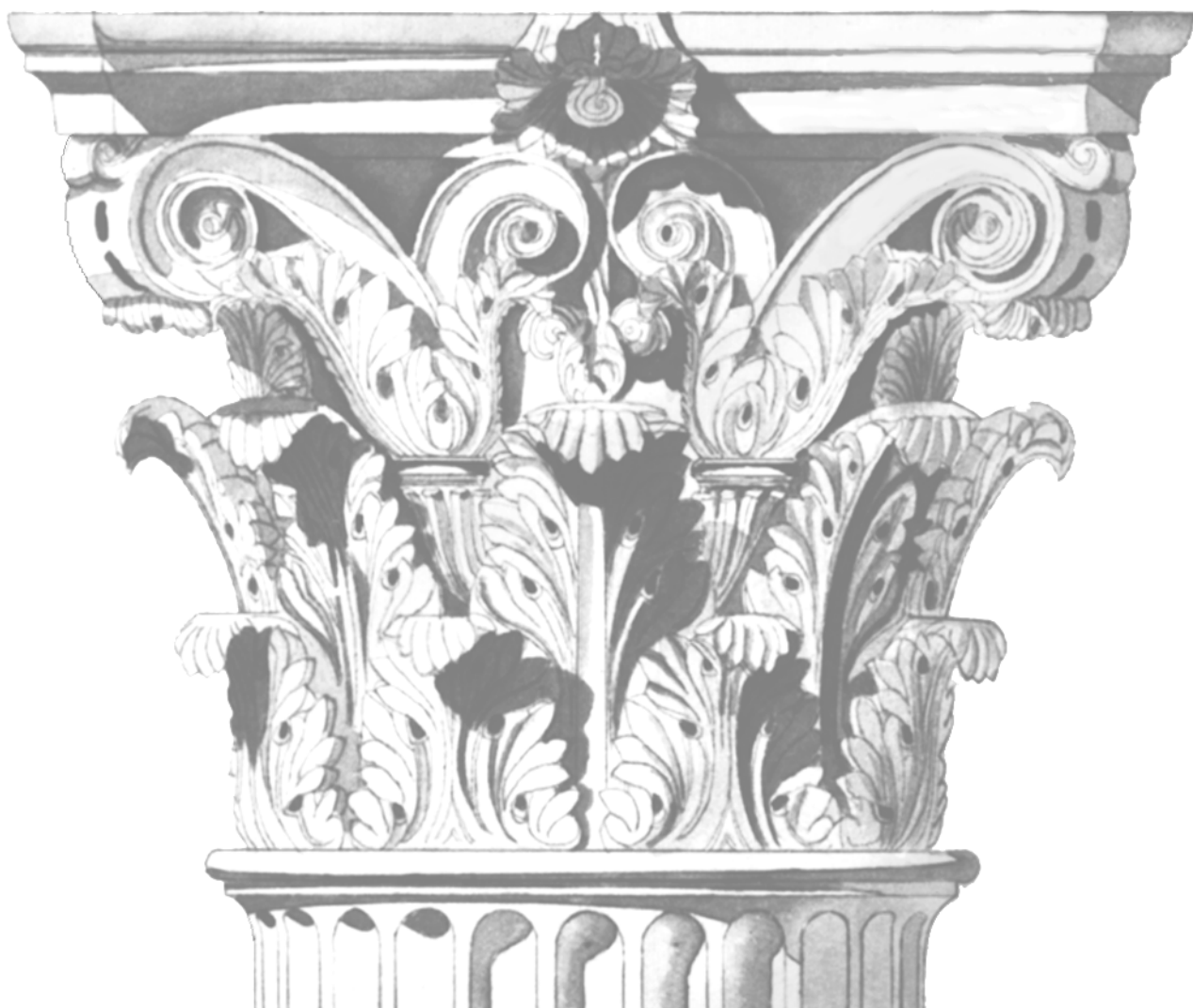


**BREIT-PAULI HAMILTONIAN
AND MOLECULAR MAGNETIC
RESONANCE PROPERTIES**

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University of Oulu

OULU 2004



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Academic Dissertation to be presented with the assent of the Faculty of Science, University of Oulu, for public discussion in Kuusamonsali (Auditorium YB210), Linnanmaa, on October 2nd, 2004, at 12 noon.

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Abstract

In this thesis, the theory of static magnetic resonance spectral parameters of nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectroscopy is investigated in terms of the molecular Breit-Pauli Hamiltonian, which is obtained from the relativistic Dirac equation via the Foldy-Wouthuysen transformation. A leading-order perturbational relativistic theory of NMR nuclear shielding and spin-spin coupling tensors, and ESR electronic g -tensor, is presented. In addition, the possibility of external magnetic-field dependency of NMR parameters is discussed.

Various first-principles methods of electronic structure theory and the role of one-electron basis sets and their performance in magnetic resonance properties in terms of their completeness profiles are discussed. The presented leading-order perturbational relativistic theories of NMR nuclear shielding tensors and ESR electronic g -tensors, as well as the theory of the magnetic-field dependent NMR shielding and quadrupole coupling are evaluated using first-principles wave function and density-functional theories.

Keywords: Breit-Pauli Hamiltonian, ESR, first-principles studies, g -tensor, indirect spin-spin coupling, magnetic-field dependence, NMR, nuclear shielding, quadrupole coupling, relativistic effects, spin Hamiltonian

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact solution of these laws leads to equations much too complicated to be soluble."

Paul Dirac 1929

Acknowledgments

This work was carried out during April 2002–May 2004 in two locations. It was started in the Department of Physical Sciences, University of Oulu, and completed in the Department of Chemistry, University of Helsinki. I had an opportunity to work in excellent environment in both places and I am grateful to the staff of these Departments, especially to Profs. Jukka Jokisaari (Oulu), Pekka Pyykkö (Helsinki), Lauri Halonen (Helsinki), and Markku Räsänen (Helsinki). The work was financially supported by the Academy of Finland, Jenny and Antti Wihuri Fund, Magnus Ehrnrooth Fund, Vilho, Yrjö, and Kalle Väisälä Foundation, Tauno Tönninki Fund, as well as the Chancellor of the University of Helsinki. The computational resources were partially provided by CSC (Espoo, Finland).

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I express my gratitude to my parents, Virpi Ylilehto and Ahti Manninen for a continuous support and a good, educated home to grow up in, which yielded my enthusiasm towards sciences that I have had since childhood.

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Very special thanks to my fiancée Minna.

Helsinki, August 2004

Pekka Manninen

List of original papers

This thesis consists of an introductory part and the following six papers which will be referred to in the text by the following Roman numbers.

- I Vaara J, Manninen P & Lantto P (2004) Perturbational and ECP calculation of relativistic effects in NMR shielding and spin-spin coupling. In: Kaupp M, Bühl M & Malkin VG (eds) Calculation of NMR and EPR Parameters: Theory and Applications, Wiley-VCH, Weinheim.
- II Manninen P, Lantto P, Vaara J & Ruud K (2003) Perturbational *ab initio* calculations of relativistic contributions to nuclear magnetic resonance shielding tensors. *Journal of Chemical Physics* 119: 2623.
- III Manninen P, Vaara J & Ruud K (2004) Perturbational relativistic theory of electron spin resonance *g*-tensor. *Journal of Chemical Physics* 121: 1258.
- IV Vaara J, Manninen P & Lounila J (2003) Magnetic field dependence of nuclear magnetic shielding in closed-shell atomic systems. *Chemical Physics Letters* 372: 750.
- V Manninen P & Vaara J (2004) Magnetic-field dependence of ^{59}Co nuclear magnetic shielding in Co(III) complexes. *Physical Review A* 69: 022503.
- VI Manninen P, Vaara J & Pyykkö P (2004) Magnetic field-induced quadrupole coupling in the nuclear magnetic resonance of noble gas atoms and molecules. *Physical Review A*, *accepted for publication*.

Paper I is a theoretical survey of all leading-order relativistic contributions to NMR nuclear shielding and spin-spin coupling tensors. Papers II and III are theoretical and *ab initio* studies on the effects of special relativity on NMR shielding tensors and ESR *g*-tensors using the Breit-Pauli Hamiltonian and perturbation theory. Papers IV–VI contain theoretical and first-principles studies on the external magnetic-field dependence of NMR parameters.

The author performed part of the calculations in Papers I and IV, and all calculations in the other papers. The theoretical work as well as the completion of all the papers were carried out as teamwork. The first versions of every paper except Papers I and IV were written by the author.

Abbreviations

AO	atomic orbital
B3LYP	three-parameter hybrid Becke-Lee-Yang-Parr exchange-correlation functional
BLYP	exchange-correlation functional with LYP correlation and Becke exchange
CAS	complete active space
CBS	complete basis set (limit)
cc	(with lower case letters) correlation-consistent
CC	(with capital letters) coupled cluster (method)
CCD	coupled cluster with double excitations
CCSD	coupled cluster with single and double excitations
CCSD(T)	CCSD with non-iterative triple excitations
CGTO	contracted Gaussian type orbital
CI	configuration interaction (method)
CISD	configuration interaction with single and double excitations
DCB	Dirac-Coulomb-Breit (Hamiltonian)
DF	Dirac-Fock (method)
DFT	density-functional theory
ECP	effective core potential
EFG	electric field gradient
ESR	electron spin resonance (spectroscopy)
FCI	full configuration interaction
FW	Foldy-Wouthyusen (transformation)
GIAO	gauge-including atomic orbital
GTO	Gaussian type orbital
HF	Hartree-Fock (theory)
IGLO	individual gauge for localised orbitals
LCAO	linear combination of atomic orbitals
LORG	localised orbitals/local origins

LDA	local density approximation
LYP	Lee-Yang-Parr correlation functional
MCSCF	multiconfigurational self-consistent field (method)
MO	molecular orbital
MP _{<i>n</i>}	<i>n</i> th order Møller-Plesset many-body perturbation theory
NMR	nuclear magnetic resonance (spectroscopy)
NON	natural occupation number
NR	non-relativistic
PT	perturbation theory
RAS	restricted active space
SCF	self-consistent field
SO	spin-orbit
SR	scalar relativistic

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List of original papers

Abbreviations

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1 Introduction

Besides experimentally, molecular properties can be investigated by computational methods. This thesis is concerned with the magnetic properties of molecules, of which the parameters of nuclear magnetic resonance (NMR) [1, 2] and electron spin resonance (ESR) [1, 3] spectroscopy are usually of interest. In magnetic resonance spectroscopy, transitions are observed between Zeeman energy levels. The use of NMR and ESR spectroscopy in the research of the structure of matter is based on the sensitivity of the spectral parameters to the prevailing microscopic state. NMR is mostly applied to closed-shell molecules and ESR to open-shell species. They can both be applied to the structural research of matter in solid, liquid, as well as gaseous form. NMR is applied widely in physics, chemistry, biochemistry, materials science, biology and medicine. ESR is used for studying radicals formed during chemical reactions or by radiation, many *d*-metal complexes, and molecules in triplet states.

In first-principles studies, the parametrisation of models is not based upon experimental results. These methods provide results that are at best quantitatively accurate and complementary to experimental methods. In the first-principles studies, the methods of quantum chemistry [4, 5] are used to solve the Schrödinger and/or Dirac equations, which are applied to the electronic cloud of the investigated atomic or molecular system. Magnetic response properties can be obtained from the approximate solutions of these equations by using perturbation theory. Of NMR parameters, the nuclear shielding tensor [6, 7], the indirect spin-spin coupling tensor [8], and the nuclear quadrupole coupling tensor [9], as well as the electronic *g*-tensor and the hyperfine coupling tensor [10, 11] among ESR parameters are usually of interest. In the first-principles studies of magnetic resonance parameters, isolated molecules at their rigid equilibrium geometries are often considered using the non-relativistic formulation of quantum mechanics. These approximations are major sources of error, as the experiments are carried out in the liquid or solid phase and at finite temperature. If heavy elements are present, the non-relativistic treatment fails. In addition, the standard assumptions made in the derivation of the effective magnetic resonance spin Hamiltonians are not necessarily guaranteed to be adequate at the field strengths that are involved in modern magnetic resonance spectroscopy.

In this thesis, the author aims i) to map the effects of the theory of special relativity on magnetic resonance observables, to develop computational modelling methods for these, and ii) to study higher than leading-order effects in the perturbation theory of mag-

netic resonance observables, in this case the external magnetic-field dependence of NMR parameters. The effects of special relativity on the molecular magnetic properties are a consequence of the strong contribution they obtain from the core region of the electronic cloud of the atom, where the speed of the electrons is no longer small compared to the speed of light. The magnetic resonance parameters of heavy elements cannot be reliably calculated without the inclusion of the effects of special relativity, and therefore it is necessary to develop relativistic computational methods for NMR or ESR studies of e.g. metal complexes. The role of the first-principles methods is especially apparent in the study of compounds containing the heaviest elements, since their experimental study is often difficult and dangerous due their radioactivity and chemical toxicity. The magnetic properties of molecules, on the other hand, provide an excellent framework for studying relativistic quantum mechanics and the manifestation of the most fundamental effects of nature on the scale of molecules. For example, the effects of electroweak interactions [12, 13] and quantum electrodynamics [14] may be observable in parameters of magnetic resonance spectroscopy.

This thesis consists of an introductory part, which describes the theoretical methodologies used, and Papers I–VI, which are reprinted in Chapter 6. In Chapter 2, an introduction to relativistic molecular quantum mechanics and a description of the Breit-Pauli Hamiltonian [4, 15, 16] can be found. The methods of modern electronic structure calculations applied in this work are described in Chapter 3, as are the basic concepts of the spectral parameters of magnetic resonance spectroscopies (Chapter 4). The summary of the thesis is given in Chapter 5.

In Papers I and II, the effects of special relativity on the nuclear magnetic shielding and spin-spin coupling tensors are investigated using a scheme based on the quasi-relativistic Breit-Pauli Hamiltonian and perturbation theory. This approach is appealing especially as it provides an extrapolation scheme between the non-relativistic and “fully relativistic” regimes, but also due to its moderate computational cost. This allows the inclusion of electron correlation, which is important for these properties. An analogous approach is applied in Paper III to the electronic g -tensor of ESR spectroscopy. In these studies, *ab initio* multiconfigurational self-consistent field methods and analytical linear and non-linear response theories have been used. Paper I is a chapter of a textbook in which a systematic theoretical treatment of the perturbational inclusion of special relativity in NMR shielding and spin-spin coupling tensors is carried out, and model calculations with a comparison to the inclusion of special relativity via the effective core potential method are presented. Paper II is probably the most profound numerical analysis of this property in this framework, but a few contributions left unconsidered still prevent it from being a complete leading-order study.

Papers IV–VI consider the possibility of magnetic-field dependence of NMR observables. In Paper IV, an analytical response theory formulation of field-dependent shielding, originally proposed by Ramsey [17], is demonstrated with rigorous *ab initio* calculations, using high-quality basis sets for halogen and alkali metal ions as well as noble gases up to the fifth row. The field-dependence was found to be too small for being observable in these systems. Paper V presents a generalisation of this formulation to molecules of arbitrary symmetry, and density-functional theory calculations in two Co(III) complexes, in which this phenomenon was previously experimentally claimed [18]. A qualitative agreement with the experimental result was found. The same approach is again applied

in Paper VI on a different NMR observable, the quadrupole coupling. Paper VI presents *ab initio* and density-functional theory calculations for noble gas atoms and molecules possessing octahedral or tetrahedral symmetry, where the field-independent quadrupole coupling vanishes. The results indicate the possibility of experimental observation in certain group(IV) tetrahalides.

2 Breit-Pauli Hamiltonian

In this Chapter, a brief description of relativistic one- and many-body quantum mechanics is given. In addition, the Chapter discusses the Breit-Pauli Hamiltonian, which is obtained through a Foldy-Wouthuysen transformation of the Dirac-Coulomb-Breit Hamiltonian, and its expansion in the presence of magnetic fields [15, 16].

2.1 Dirac equation

The straightforward relativistic analogue for the non-relativistic (NR) Schrödinger equation, $H\psi = i\partial\psi/\partial t$,¹ using a relativistic energy-momentum relation, $E^2 = p^2c^2 + m^2c^4$, is the Klein-Gordon equation

$$-\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \nabla^2\right)\psi = m^2c^2\psi. \quad (2.1)$$

The problem with the Klein-Gordon equation lies with the negative energy solutions that involve a negative probability density. To avoid these, Paul Dirac suggested a form of an equation [19, 20] that is linear in both $\partial/\partial t$ and ∇ as

$$H^{\text{Dirac}}\psi = (c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta mc^2)\psi, \quad (2.2)$$

where the factors α_i ($i = 1, 2, 3$) and β are defined by demanding that the relativistic energy-momentum relation be satisfied. A comparison of Eq. (2.2) with the energy-momentum relation shows that α_i and β anticommute and that $\alpha_i^2 = \beta^2 = \mathbf{1}$. α_i and β are $N \times N$ matrices, with $N = 4$ being the lowest dimension that satisfies the equation. The equation can be written also in terms of larger N . The representation of α and β is not unambiguous. The Dirac-Pauli representation

$$\alpha_i = \begin{pmatrix} 0 & \sigma_i \\ \sigma_i & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} \mathbf{1} & 0 \\ 0 & -\mathbf{1} \end{pmatrix}, \quad (2.3)$$

¹A SI-based atomic unit system, where $\hbar = m_e = 4\pi\epsilon_0 = e = 1$, $c = 1/\alpha \approx 137$, α being the dimensionless fine structure constant, is used throughout the thesis unless otherwise noted.

where σ_i are the Pauli spin matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (2.4)$$

is the most commonly used. The Dirac equation can be shown to be Lorentz covariant and describe spin-half particles. The solution of the Dirac equation is a four-component Dirac spinor. The solution also contains negative energy solutions, but with a positive probability density. They were interpreted as positrons, electrons with opposite charge. The positrons were experimentally observed a few years later [21]. The Dirac spinor can be divided into

$$\psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}, \quad (2.5)$$

where ψ_+ and ψ_- are the large- and small-component solutions. The solutions with large ψ_+ correspond mainly to the positive energy i.e. electronic solutions, whereas solutions with large ψ_- correspond to the positronic states.²

The substitution $p_\mu \rightarrow \pi_\mu = p_\mu - qA_\mu/c$, where A_μ is the 4-vector potential ($\mathbf{A}, -i\phi$), yields the Dirac equation for a particle with charge q in the presence of an electromagnetic field. For a constant magnetic field, the scalar potential $\phi = 0$ and this equation in terms of large and small components becomes

$$\begin{pmatrix} mc^2 & c\vec{\sigma} \cdot \boldsymbol{\pi} \\ c\vec{\sigma} \cdot \boldsymbol{\pi} & -mc^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = E \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}. \quad (2.6)$$

2.1.1 Relativistic Hamiltonians for many-particle systems

As the essence of chemistry is a many-body quantum mechanical problem, it would be tempting to introduce a way of treating interacting electrons within the Dirac picture and hence obtain a proper description for the problem. The easiest way to construct a relativistic Hamiltonian for a many-electron system would be to include the potential terms that describe nucleus-electron and electron-electron Coulombic interactions,

$$H^{\text{DC}} = \sum_i \left(H_i^{\text{Dirac}} + \sum_K \frac{Z_K}{r_{iK}} \right) + \frac{1}{2} \sum'_{i,j} \frac{1}{r_{ij}}, \quad (2.7)$$

where r_{ij} denotes the distance between electrons i and j and $\mathbf{r}_{iK} = \mathbf{r}_i - \mathbf{R}_K$ is the location of i with respect to the nucleus K . The potentials of this Dirac-Coulomb Hamiltonian affect instantly, and hence H^{DC} is not Lorentz covariant. The Bethe-Salpeter equation [23, 24], which is essentially a generalisation of the Dirac equation for two particles, transforms properly under the Lorentz transformation. It is an integro-differential equation, which at least in principle can be made accurate to an arbitrarily high order. The

²The non-relativistic limit ($c \rightarrow \infty$) of the Dirac equation, often referred to as the Lévy-Leblond equation [22], is a Galilei-invariant four-component equation that describes spin one-half particles. It describes correctly also the interaction between the electron spin and an external magnetic field, with the gyromagnetic ratio equalling to 2.

solution of the resulting equation is problematic, and it features different time variables for the two particles. This is essential for the covariance but makes physical interpretation more difficult.

An approximate relativistic many-electron Hamiltonian can be constructed from the Dirac Hamiltonian by adding the Breit term [25]

$$H_{ij}^{\text{Breit}} = -\frac{1}{r_{ij}} \left[\alpha_i \cdot \alpha_j - \frac{(\alpha_i \cdot \mathbf{r}_{ij})(\alpha_j \cdot \mathbf{r}_{ij})}{2r_{ij}^2} \right] \quad (2.8)$$

that consists of the leading terms in the series obtained from the Bethe-Salpeter equation. It describes other pairwise additive interactions than the standard Coulomb interaction of electrons i and j , the first being the magnetic Gaunt term [26], and the second being a term that describes retardation, i.e. the finite speed of interaction. With this term, the Dirac-Coulomb-Breit Hamiltonian is written as

$$H^{\text{DCB}} = \sum_i H_i^{\text{Dirac}} + \sum_{i,K} \frac{1}{r_{iK}} + \frac{1}{2} \sum'_{i,j} \frac{1}{r_{ij}} + \frac{1}{2} \sum'_{i,j} H_{ij}^{\text{Breit}}. \quad (2.9)$$

It implicitly includes all relativistic effects on the kinetic energy as well as spin-orbit (SO) interaction. This Hamiltonian is, however, not Lorentz covariant, and it treats the effects of quantum electrodynamics perturbationally up to $\mathcal{O}(\alpha^2)$. Practical quantum chemistry with H^{DCB} is computationally too expensive for many purposes.

In addition, there are some theoretical defects in the Dirac-Coulomb-Breit Hamiltonian, such as the Brown-Ravenhall disease [27], or the continuum dissolution, in which any bound multi-particle state is degenerate with a state containing negative energy continuum solutions. Another problem is related to the self-consistent field solution of the four-component equations [the Dirac-Fock(-Breit) method], in which solutions are obtained that not always are true upper bounds to the exact solution [28]. This is called the finite basis set disease. It can be at least partially treated using kinetic balance [29], which, however, leads to very large basis sets. These problems have kept applications of true chemical interest largely, but not completely, beyond the reach of rigorous four-component methods.

2.2 Foldy-Wouthuysen transformation

Since chemistry is only concerned with the positive energy solutions of the Dirac equation, it would be useful to decouple the positive and negative energy components of (2.5) to give a two-component equation for the positive energy solutions, which could be used in the same manner as NR equations. There are several ways to reduce H^{DCB} into two-component form. Such approximate Hamiltonians are usually called quasi-relativistic Hamiltonians.

For an electron in potential V , when the zero-level of energy is chosen to be $+mc^2$, Eq. (2.6) is written as

$$\begin{pmatrix} V & c\vec{\sigma} \cdot \boldsymbol{\pi} \\ c\vec{\sigma} \cdot \boldsymbol{\pi} & V - 2mc^2 \end{pmatrix} \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = E \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}.$$

Elimination of the small component (ESC) gives

$$\psi_- = \frac{c\vec{\sigma} \cdot \boldsymbol{\pi}}{2c^2 + E - V} \psi_+ = \frac{1}{2c} \left(1 + \frac{E - V}{2c^2} \right)^{-1} \vec{\sigma} \cdot \boldsymbol{\pi} \psi_+ \equiv \bar{X} \psi_+,$$

and therefore

$$H^{\text{ESC}} \psi_+ \equiv V \psi_+ + c\vec{\sigma} \cdot \boldsymbol{\pi} \bar{X} \psi_+ = E \psi_+. \quad (2.10)$$

The Hamiltonian H^{ESC} is dependent on the energy E and operates on the unnormalised large component. In the normalised ESC approach [30], a normalised two-component wave function is generated, which affects the sc. picture change [31].

Foldy and Wouthuysen [32] introduced a systematic procedure, the Foldy-Wouthuysen (FW) transformation, for decoupling the large and small components to a successively higher order of c^{-1} by finding a unitary transformation that block-diagonalises the four-component Hamiltonian. For a positive-energy two-component effective Hamiltonian, the transformation matrices

$$U = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} X^\dagger \\ -\frac{1}{\sqrt{1+X^\dagger X}} X & \frac{1}{\sqrt{1+X^\dagger X}} \end{pmatrix}, \quad (2.11)$$

$$U^{-1} = U^\dagger = \begin{pmatrix} \frac{1}{\sqrt{1+X^\dagger X}} & -X^\dagger \frac{1}{\sqrt{1+X^\dagger X}} \\ X \frac{1}{\sqrt{1+X^\dagger X}} & \frac{1}{\sqrt{1+X^\dagger X}} \end{pmatrix} \quad (2.12)$$

generate the desired two-component FW wave function

$$\begin{pmatrix} \phi \\ 0 \end{pmatrix} = U \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix}. \quad (2.13)$$

When the energy-dependent \bar{X} in Eq. (2.10) is expanded with respect to $(E - V)/2c^2$ to the lowest order, $X \approx (1/2c^2)c\vec{\sigma} \cdot \mathbf{p}$ is obtained, and to order c^{-2} in the absence of electromagnetic fields

$$U = \begin{pmatrix} 1 - \frac{p^2}{8c^2} & \frac{c\vec{\sigma} \cdot \mathbf{p}}{2c^2} \\ -\frac{c\vec{\sigma} \cdot \mathbf{p}}{2c^2} & 1 - \frac{p^2}{8c^2} \end{pmatrix}. \quad (2.14)$$

This, used with the FW transformation, gives rise to the Pauli Hamiltonian [33] (writing α instead of c^{-1}),

$$H^{\text{Pauli}} = V + \frac{p^2}{2} - \frac{1}{8}\alpha^2(p^4 - \nabla^2 V) + \frac{1}{4}\alpha^2 \vec{\sigma} \cdot (\nabla V \times \mathbf{p}). \quad (2.15)$$

Here the first two terms correspond to the NR Hamiltonian. The third and the fourth term represent, respectively, the mass-velocity (mv) and Darwin (Dar) corrections that are often called the scalar relativistic (SR) corrections. The last term is the SO coupling term.

A two-component quasi-relativistic Hamiltonian for many-electron systems with the inclusion of the Breit term, i.e. the Breit-Pauli Hamiltonian, is gained from the Dirac-Coulomb-Breit Hamiltonian (2.9) for two-electron systems through the FW transformation and a generalisation to N electrons [4, 15, 16]. Omitting terms that describe the

motion of the nuclei, the electronic part is written as

$$H^{\text{BP}} = \sum_i h_i + \frac{1}{2} \sum_{i,j}' h_{ij}, \quad (2.16)$$

where the one-electron part is in the presence of electromagnetic fields

$$h_i = - \sum_K \frac{Z_K}{r_{iK}} \quad (2.17)$$

$$+ \frac{1}{2} (\pi_i^2 + i \vec{\sigma}_i \cdot \pi_i \times \pi_i) \quad (2.18)$$

$$- \frac{1}{8} \alpha^2 (\pi_i^2 + i \vec{\sigma}_i \cdot \pi_i \times \pi_i)^2 \quad (2.19)$$

$$+ \frac{1}{4} \alpha^2 \sum_K \frac{Z_K}{r_{iK}^3} \vec{\sigma}_i \cdot (\mathbf{r}_{iK} \times \pi_i) \quad (2.20)$$

$$+ \frac{\pi}{2} \alpha^2 \sum_K Z_K \delta(\mathbf{r}_{iK}). \quad (2.21)$$

Eq. (2.17) is the non-relativistic nuclear attraction potential, (2.18) describes non-relativistic kinematics and spin Zeeman interaction, term (2.19) is a relativistic correction to (2.18), (2.20) is the one-electron relativistic spin-orbit term, and (2.21) represents the one-electron Darwin effect. The two-electron part of the Breit-Pauli Hamiltonian consists of

$$h_{ij} = \frac{1}{r_{ij}} \quad (2.22)$$

$$- \frac{1}{4} \alpha^2 \frac{\vec{\sigma}_i \cdot (\mathbf{r}_{ij} \times \pi_i) - \vec{\sigma}_j \cdot (\mathbf{r}_{ij} \times \pi_j)}{r_{ij}^3} \quad (2.23)$$

$$- \pi \alpha^2 \delta(\mathbf{r}_{ij}) \quad (2.24)$$

$$- \frac{1}{2} \alpha^2 \left[\pi_i \cdot \frac{\pi_j}{r_{ij}} + \frac{(\pi_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \pi_j)}{r_{ij}^3} \right] \quad (2.25)$$

$$- \frac{1}{2} \alpha^2 \frac{\vec{\sigma}_i \cdot (\mathbf{r}_{ij} \times \pi_j) - \vec{\sigma}_j \cdot (\mathbf{r}_{ij} \times \pi_i)}{r_{ij}^3} \quad (2.26)$$

$$- \frac{1}{4} \alpha^2 \left[\frac{8\pi}{3} \delta(\mathbf{r}_{ij}) (\vec{\sigma}_i \cdot \vec{\sigma}_j) - \frac{(\vec{\sigma}_i \cdot \vec{\sigma}_j)}{r_{ij}^3} + \frac{3(\vec{\sigma}_i \cdot \mathbf{r}_{ij})(\vec{\sigma}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right] \quad (2.27)$$

Here (2.22) is the Coulomb repulsion between the electrons, (2.23) the two-electron spin-same orbit term, (2.24) the two-electron Darwin term, (2.25) the orbit-orbit interaction, (2.26) the spin-other orbit interaction, and (2.27) the electronic spin-spin interaction.

The cornerstone of this thesis, an approximate electronic Hamiltonian for a molecule carrying a point-like nuclear magnetic dipole $\vec{\mu}_K = \gamma_K \mathbf{I}_K$, where γ_K is the nuclear gyromagnetic ratio and \mathbf{I}_K the nuclear spin, in external magnetic field \mathbf{B}_0 , is obtained by making a substitution $\pi \rightarrow \mathbf{p} + \mathbf{A}$ into H^{BP} . This substitution and the corresponding expansion

is presented in detail in Paper I. In this treatment, the vector potential \mathbf{A} is expanded as a sum $\mathbf{A} = \mathbf{A}_0 + \mathbf{A}_K + \mathbf{A}_L$, where \mathbf{A}_0 is the vector potential corresponding to \mathbf{B}_0 in the Coulomb gauge $\nabla \cdot \mathbf{A} = 0$, and

$$\mathbf{A}_0(\mathbf{r}_i) = \frac{1}{2} \mathbf{B}_0 \times \mathbf{r}_{iO} \quad (2.28)$$

$$\mathbf{A}_K(\mathbf{r}_i) = \alpha^2 \gamma_K \frac{\mathbf{I}_K \times \mathbf{r}_{iK}}{r_{iK}^3} \quad (2.29)$$

are the fields caused by the point-like magnetic dipole moments of nuclei K and L . In Eq. (2.28), $\mathbf{r}_{iO} = \mathbf{r}_i - \mathbf{R}_O$, where O refers to the gauge origin. The terms containing a third or higher power in B_0 or a second or higher power in I_K or I_L are omitted. Explicit forms and physical interpretations of the obtained terms are presented in Tables 2.1, 2.2 and 2.3.

From the one-electron part, (2.18) is expanded as

$$\frac{1}{2} \sum_i \pi_i^2 \approx h^{\text{KE}} + h_{B_0}^{\text{OZ}} + h_K^{\text{PSO}} + h_L^{\text{PSO}} + h_{B_0^2}^{\text{SUSC}} + h_{KB_0}^{\text{DS}} + h_{LB_0}^{\text{DS}} + h_{KL}^{\text{DSO}} \quad (2.30)$$

for the NR kinematics. The NR spin Zeeman term becomes

$$\frac{1}{2} \mathbf{i} \sum_i \vec{\sigma}_i \cdot (\boldsymbol{\pi}_i \times \boldsymbol{\pi}_i) = \frac{1}{2} \sum_i \vec{\sigma}_i \cdot \mathbf{B}_i = h_{B_0}^{\text{SZ}} + h_K^{\text{FC}} + h_L^{\text{FC}} + h_K^{\text{SD}} + h_L^{\text{SD}}. \quad (2.31)$$

Some text books, e.g. [16, 34], consider these terms, especially the Fermi contact interaction h^{FC} , as relativistic effects similarly to the other terms that arise from the reduction from the Dirac equation to (Breit-)Pauli form, such as the Darwin term. However, according to the analysis by Kutzelnigg [35], these hyperfine interactions (and the spin Zeeman interaction) are not relativistic effects, but they are straightforwardly derived from the NR Lévy-Leblond equation. In (2.19), π_i^2 and $\mathbf{i} \vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i$ do not commute when spatially non-uniform nuclear dipole fields are present, and thus the term is first expanded as

$$\begin{aligned} H_{\text{kin}}^{\text{R}} &= -\frac{1}{8} \alpha^2 \sum_i \pi_i^4 - \frac{1}{8} \alpha^2 \mathbf{i} \sum_i [\pi_i^2, \vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i]_+ \\ &\quad + \frac{1}{8} \alpha^2 \sum_i (\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i)^2, \end{aligned} \quad (2.32)$$

where the anticommutator of the operators A and B is denoted as $[A, B]_+ = AB + BA$. Expanding the first term gives rise to

$$\begin{aligned} -\frac{1}{8} \alpha^2 \sum_i \pi_i^4 &\approx h^{\text{mv}} + h_{B_0}^{\text{OZ-KE}} + h_K^{\text{PSO-KE}} + h_L^{\text{PSO-KE}} + h_{KB_0}^{\text{DS-KE}} + h_{LB_0}^{\text{DS-KE}} \\ &\quad + h_{KL}^{\text{DSO-KE}} + h_{KB_0}^{\text{PSO-OZ}} + h_{LB_0}^{\text{PSO-OZ}} + h_{KL}^{\text{PSO-PSO}} + h_{B_0^2}^{\text{SUSC-KE}} \end{aligned} \quad (2.33)$$

and the electron-spin dependent second term in Eq. (2.32) becomes

$$\begin{aligned} -\frac{1}{8} \alpha^2 \mathbf{i} \sum_i [\pi_i^2, \vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i]_+ &= -\frac{1}{8} \alpha^2 \sum_i [\pi_i^2, \vec{\sigma}_i \cdot \mathbf{B}_i]_+ \\ &\approx h_{B_0}^{\text{SZ-KE}} + h_K^{\text{FC-KE}} + h_L^{\text{FC-KE}} + h_K^{\text{SD-KE}} + h_L^{\text{SD-KE}}. \end{aligned} \quad (2.34)$$

The last term to arise from $H_{\text{kin}}^{\text{R}}$ is

$$\begin{aligned} \frac{1}{8}\alpha^2 \sum_i (\vec{\sigma}_i \cdot \boldsymbol{\pi}_i \times \boldsymbol{\pi}_i)^2 &= -\frac{1}{8}\alpha^2 \sum_i (\vec{\sigma}_i \cdot \mathbf{B}_i)^2 \\ &\approx h_{KB_0}^{\text{con}} + h_{LB_0}^{\text{con}} + h_{KB_0}^{\text{dip}} + h_{LB_0}^{\text{dip}} + h_{KL}^{\text{con-dip}} + h_{KL}^{\text{dip-dip}}, \end{aligned} \quad (2.35)$$

in which the dependence on electron spin vanishes, i.e. $(\vec{\sigma}_i \cdot \mathbf{B}_i)^2 = B_i^2$, as can be seen when applying $(\vec{\sigma} \cdot \mathbf{A})(\vec{\sigma} \cdot \mathbf{B}) = \mathbf{A} \cdot \mathbf{B} + i\vec{\sigma} \cdot \mathbf{A} \times \mathbf{B}$. The corresponding ‘‘con-con’’ cross term, which is proportional to the product of the contact fields of two nuclei that do not coincide, vanishes everywhere in space. The one-electron SO term (2.20) divides into field-independent and -dependent SO interactions

$$\frac{1}{4}\alpha^2 \sum_K \frac{Z_K}{r_{iK}^3} \vec{\sigma}_i \cdot (\mathbf{r}_{iK} \times \boldsymbol{\pi}) \approx h^{\text{SO}(1)} + h_{B_0}^{\text{SO}(1)} + h_K^{\text{SO}(1)} + h_L^{\text{SO}(1)}. \quad (2.36)$$

Combining Eqs. (2.23) and (2.26) of the two-electron part gives rise to field-dependent and -independent two-electron spin-orbit interactions

$$\begin{aligned} -\frac{1}{4}\alpha^2 \frac{\vec{\sigma}_i \cdot (\mathbf{r}_{ij} \times \boldsymbol{\pi}_i) - \vec{\sigma}_j \cdot (\mathbf{r}_{ij} \times \boldsymbol{\pi}_j)}{r_{ij}^3} &\approx h^{\text{SSO}(2)} + h^{\text{SOO}(2)} + h_{B_0}^{\text{SSO}(2)} + h_{B_0}^{\text{SOO}(2)} \\ &\quad + h_K^{\text{SSO}(2)} + h_K^{\text{SOO}(2)} + h_L^{\text{SSO}(2)} + h_L^{\text{SOO}(2)}. \end{aligned} \quad (2.37)$$

From the first part of Eq. (2.25), two-electron counterparts of the operators in (2.30) appear, but they are neglected here. This term gives rise to the field-independent electron-electron orbital interaction term, listed e.g. in Ref. [16], and it is included in Table 2.2.

The terms in Tables 2.1–2.3 are classified according to their appearance in the orders of α , and further in accordance with their dependence on i) the electron spin, ii) the nuclear spin, and iii) the external magnetic field. Indices i, j are used to label electrons and K, L to label nuclei. The operators with dependence on the index K will appear in a similar form for nucleus L .

The nuclear quadrupole interaction (NQCC) listed in Table 2.1 does not arise naturally from the present treatment, in which a point-like nucleus is assumed. It arises as the leading non-trivial term from the treatment of the Coulombic Z/r_{iK} term in presence of a finite i.e. physically correct nuclear model. However, its inclusion is necessary due to its major importance in the consideration of the spectral parameters of nuclear magnetic resonance.

The operators of H^{BP} are intuitively interpretable in terms of familiar NR concepts, and provide an interpolation step between the NR and Dirac regimes. There are inherent difficulties in Hamiltonians arising from the FW-transformation, as investigated e.g. by Moss and co-workers [36–39]. Farzdel and Smith criticised the mass-velocity term [40], pointing out that for large momenta ($p > \alpha^{-1}$), the mass-velocity term is not obtained unless the expansion of the square-root operator outside its radius of convergence is used. Most of the difficulties originate from the fact that the expansions implicitly or explicitly rely on expansion $(E - V)/2c^2$, which is invalid for particles in a Coulomb potential, where there will always be a region of space close to the nucleus in which $(E - V)/2c^2 > 1$. Furthermore, several terms pose a δ -function singularity at the origin, which is absent in

Table 2.1. The $\mathcal{O}(\alpha^0)$ terms of the approximate Hamiltonian, H^{BP} , in the presence of point-like nuclear magnetic dipoles and an external magnetic field.

Label	Description	Operator
h^{KE}	Kinetic energy	$-\frac{1}{2} \sum_i \nabla_i^2$
h^{NE}	Electron-nuclear Coulomb interaction	$-\sum_{i,K} \frac{Z_K}{r_{iK}}$
h^{EE}	Electron-electron Coulomb interaction	$\frac{1}{2} \sum'_{i,j} \frac{1}{r_{ij}}$
Spin-dependence, no field-dependence		
h_K^{NQCC}	Nuclear quadrupole interaction	$-\frac{1}{2} \frac{Q_K}{I_K(2I_K-1)} \sum_i \frac{1r_{iK}^2 - 3\mathbf{r}_{iK}\mathbf{r}_{iK}}{r_{iK}^3}$
Field-dependence, no spin-dependence		
$h_{B_0}^{\text{OZ}}$	Orbital Zeeman interaction	$\frac{1}{2} \sum_i \mathbf{l}_{iO} \cdot \mathbf{B}_0$
$h_{B_0}^{\text{SUSC}}$	Diamagnetic susceptibility	$\frac{1}{8} \sum_i \mathbf{B}_0 \cdot (\mathbf{1}r_{iO}^2 - \mathbf{r}_{iO}\mathbf{r}_{iO}) \cdot \mathbf{B}_0$
Spin- and field-dependence		
$h_{B_0}^{\text{SZ}}$	Electron spin Zeeman	$\frac{1}{2} g_e \sum_i \mathbf{s}_i \cdot \mathbf{B}_0$

the Dirac Hamiltonian. These features are ostensibly problematic, as it has been demonstrated that relativistic effects originate mostly from the region close to nucleus. Numerous quantitative studies verify, however, the practical feasibility of H^{BP} for many atomic and molecular properties.

Other difficulties arise also with regard to the self-consistent treatment of FW transformed Hamiltonians, as the eigenvalue equation $H^{\text{Pauli}}\Psi = E\Psi$ yields a continuous eigenvalue spectrum without lower bound due to the mass-velocity and SO operators, unless the operator is not restricted to the solution space of the NR Hamiltonian [41]. Due to difficulties in the iterative solution of FW transformed Hamiltonians, perturbation theory has to be applied. In some cases, e.g. with the heaviest nuclei, the relativistic effects may be so large that a perturbation theoretical approach is inadequate.

Table 2.2. Partial listing of $\mathcal{O}(\alpha^2)$ terms of the approximate Hamiltonian.

Label	Description	Operator
Scalar relativistic corrections		
h^{mv}	Mass-velocity term	$-\frac{1}{8}\alpha^2\sum_i\nabla_i^4$
$h^{\text{Dar}}(1)$	Electron-nuclear Darwin term	$\frac{\pi}{2}\alpha^2\sum_{i,K}Z_K\delta(\mathbf{r}_{iK})$
$h^{\text{Dar}}(2)$	Electron-electron Darwin term	$-\frac{\pi}{2}\alpha^2\sum'_{i,j}\delta(\mathbf{r}_{ij})$
h^{OO}	Electron-electron orbital interaction	$\frac{1}{4}\alpha^2\sum'_{i,j}\frac{\nabla_i\nabla_j}{r_{ij}} - \frac{(\nabla_i\nabla_j)(\mathbf{r}_{ij}\cdot\nabla_j)}{r_{ij}^3}$
Spin-dependence, no field-dependence		
<i>Electron spin</i>		
$h^{\text{SO}}(1)$	Spin-orbit interaction	$\frac{1}{4}\alpha^2g_e\sum_{i,K}\frac{Z_K}{r_{iK}^3}\mathbf{s}_i\cdot\mathbf{l}_{iK}$
$h^{\text{SSO}}(2)$	Electron-electron spin-orbit interaction	$-\frac{1}{4}\alpha^2g_e\sum_{i,j}\mathbf{s}_i\cdot\frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\text{SOO}}(2)$	Electron-electron spin-other-orbit interaction	$-\frac{1}{2}\alpha^2g_e\sum'_{i,j}\mathbf{s}_i\cdot\frac{\mathbf{l}_{ij}}{r_{ij}^3}$
$h^{\text{SSD}}(2)$	Spin-spin dipolar interaction	$\frac{1}{4}\alpha^2g_e^2\sum'_{i,j}\frac{r_{ij}^2(\mathbf{s}_i\cdot\mathbf{s}_j) - (\mathbf{s}_i\cdot\mathbf{r}_{ij})(\mathbf{r}_{ij}\cdot\mathbf{s}_j)}{r_{ij}^5}$
$h^{\text{SSC}}(2)$	Spin-spin contact interaction	$-\frac{\pi g_e^2}{3}\alpha^2\sum'_{i,j}\mathbf{s}_i\cdot\mathbf{s}_j\delta(\mathbf{r}_{ij})$
<i>Nuclear spin</i>		
h_K^{PSO}	Orbital hyperfine interaction	$\alpha^2\gamma_K\sum_i\mathbf{l}_K\cdot\frac{\mathbf{l}_{iK}}{r_{iK}^3}$
<i>Electron and nuclear spins</i>		
h_K^{SD}	Dipolar hyperfine interaction	$\frac{1}{2}\alpha^2g_e\gamma_K\sum_i\mathbf{s}_i\cdot\frac{3\mathbf{r}_{iK}\mathbf{r}_{iK} - \mathbf{l}_{iK}^2}{r_{iK}^5}\cdot\mathbf{l}_K$
h_K^{FC}	Fermi contact hyperfine interaction	$\frac{4\pi}{3}\alpha^2g_e\gamma_K\sum_i\delta(\mathbf{r}_{iK})\mathbf{s}_i\cdot\mathbf{l}_K$

(Table 2.2 continued)

Field-dependence, no spin-dependence		
$h_{B_0}^{\text{OZ-KE}}$	Orbital Zeeman kinetic energy correction	$\frac{1}{4}\alpha^2 \sum_l \mathbf{l}_{lO} \cdot \mathbf{B}_0 \nabla_l^2$
$h_{B_0}^{\text{SUSC-KE}}$	Diamagnetic susceptibility kinetic energy correction	$\frac{1}{32}\alpha^2 \sum_l \mathbf{B}_0 \cdot [\nabla_l^2 (\mathbf{1}_{lO} r_{lO}^2 - \mathbf{r}_{lO} \mathbf{r}_{lO})]_+ \cdot \mathbf{B}_0$
Spin- and field-dependence		
<i>Electron spin</i>		
$h_{B_0}^{\text{SZ-KE}}$	Electron spin Zeeman kinetic energy correction	$\frac{1}{4}\alpha^2 g_e \sum_i \mathbf{s}_i \cdot \mathbf{B}_0 \nabla_i^2$
$h_{B_0}^{\text{SO}(1)}$	Spin-orbit Zeeman gauge correction	$\frac{1}{8}\alpha^2 g_e \sum_N Z_N \sum_i \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iO} \cdot \mathbf{r}_{iN}) - \mathbf{r}_{iO} \mathbf{r}_{iN}}{r_{iN}^3} \cdot \mathbf{B}_0$
$h_{B_0}^{\text{SSO}(2)}$	Electron-electron spin-orbit Zeeman gauge correction	$-\frac{1}{8}\alpha^2 g_e \sum'_{i,j} \mathbf{s}_i \cdot \frac{\mathbf{1}(\mathbf{r}_{iO} \cdot \mathbf{r}_{ij}) - \mathbf{r}_{iO} \mathbf{r}_{ij}}{r_{ij}^3} \cdot \mathbf{B}_0$
$h_{B_0}^{\text{SOO}(2)}$	Spin-other-orbit Zeeman gauge correction	$-\frac{1}{4}\alpha^2 g_e \sum'_{i,j} \mathbf{s}_j \cdot \frac{\mathbf{1}(\mathbf{r}_{iO} \cdot \mathbf{r}_{ij}) - \mathbf{r}_{iO} \mathbf{r}_{ij}}{r_{ij}^3} \cdot \mathbf{B}_0$
<i>Nuclear spin</i>		
$h_{KB_0}^{\text{DS}}$	Electron nuclear Zeeman modification	$\frac{1}{2}\alpha^2 \gamma_K \sum_l \mathbf{I}_K \cdot \frac{\mathbf{1}(\mathbf{r}_{lO} \cdot \mathbf{r}_{lK}) - \mathbf{r}_{lO} \mathbf{r}_{lK}}{r_{lK}^3} \cdot \mathbf{B}_0$
$h_{KB_0}^{\text{PSO-OZ}}$	Orbital hyperfine-orbital Zeeman interaction	$\frac{1}{4}\alpha^2 \gamma_K \sum_i \mathbf{I}_K \cdot \left[\frac{\mathbf{l}_{iK}}{r_{iK}^3}, \mathbf{1}_{iO} \right]_+ \cdot \mathbf{B}_0$

Table 2.3. Partial listing of $\mathcal{O}(\alpha^4)$ and $\mathcal{O}(\alpha^6)$ terms of the approximate Hamiltonian.

Label	Description	Operator
Spin-dependence, no field-dependence		
<i>Nuclear spin</i>		
$h_K^{\text{PSO-KE}}$	Kinetic energy correction of the orbital hyperfine interaction	$\frac{1}{4} \alpha^4 \gamma_K \sum_i \mathbf{I}_K \cdot \left[\nabla_i^2, \frac{\mathbf{I}_K}{r_{iK}} \right]_+$
h_{KL}^{DSO}	Electron coupled nuclear spin-spin interaction	$\frac{1}{2} \alpha^4 \gamma_K \gamma_L \sum_i \mathbf{I}_K \cdot \frac{1(\mathbf{r}_{iK} \cdot \mathbf{r}_{iL}) - \mathbf{r}_{iK} \mathbf{r}_{iL}}{r_{iK}^3 r_{iL}^3} \cdot \mathbf{I}_L$
$h_{KL}^{\text{DSO-KE}}$	Kinetic energy correction of the electron coupled nuclear spin-spin interaction	$\frac{1}{8} \alpha^6 \gamma_K \gamma_L \sum_i \mathbf{I}_K \cdot \left[\nabla_i^2, \frac{1(\mathbf{r}_{iK} \cdot \mathbf{r}_{iL}) - \mathbf{r}_{iK} \mathbf{r}_{iL}}{r_{iK}^3 r_{iL}^3} \right]_+ \cdot \mathbf{I}_L$
$h_{KL}^{\text{PSO-PSO}}$	Orbital hyperfine coupled nuclear spin-spin interaction	$\frac{1}{2} \alpha^6 \gamma_K \gamma_L \sum_i \mathbf{I}_K \cdot \left[\frac{\mathbf{I}_K}{r_{iK}}, \frac{\mathbf{I}_L}{r_{iL}} \right]_+ \cdot \mathbf{I}_L$
$h_{KL}^{\text{con-dip}}$	Contact hyperfine coupled nuclear spin-spin interaction	$-\frac{2\pi}{3} \alpha^6 \gamma_K \gamma_L \sum_i \mathbf{I}_K \cdot \left[\delta(\mathbf{r}_{iK}) \frac{3\mathbf{r}_{iL} \mathbf{r}_{iL} - 1r_{iL}^2}{r_{iL}^5} + \delta(\mathbf{r}_{iL}) \frac{3\mathbf{r}_{iK} \mathbf{r}_{iK} - 1r_{iK}^2}{r_{iK}^5} \right] \cdot \mathbf{I}_L$
$h_{KL}^{\text{dip-dip}}$	Dipolar hyperfine coupled nuclear spin-spin interaction	$-\frac{1}{4} \alpha^6 \gamma_K \gamma_L \sum_i \mathbf{I}_K \cdot \frac{1}{r_{iK}^3 r_{iL}^3} \left[9\mathbf{r}_{iK} \mathbf{r}_{iL} (\mathbf{r}_{iK} \cdot \mathbf{r}_{iL}) - 3\mathbf{r}_{iK} \mathbf{r}_{iL} (r_{iK}^2 + r_{iL}^2) + 1(r_{iK}^2 r_{iL}^2) \right] \cdot \mathbf{I}_L$
<i>Electron and nuclear spins</i>		
$h_K^{\text{SD-KE}}$	Kinetic energy correction of the dipolar hyperfine interaction	$\frac{1}{8} \alpha^4 g_e \gamma_K \sum_i \mathbf{s}_i \cdot \left[\nabla_i^2, \frac{3\mathbf{r}_{iK} \mathbf{r}_{iK} - 1r_{iK}^2}{r_{iK}^5} \right]_+ \cdot \mathbf{I}_K$
$h_K^{\text{FC-KE}}$	Kinetic energy correction of the Fermi contact interaction	$\frac{\pi}{3} \alpha^4 g_e \gamma_K \sum_i \mathbf{s}_i \cdot \left[\nabla_i^2, \delta(\mathbf{r}_{iK}) \right]_+ \cdot \mathbf{I}_K$
$h_K^{\text{SO(1)}}$	Spin-orbit hyperfine correction	$\frac{1}{4} \alpha^4 g_e \gamma_K \sum_N \sum_i \mathbf{s}_i \cdot \frac{1(\mathbf{r}_{iK} \cdot \mathbf{r}_{iN}) - \mathbf{r}_{iK} \mathbf{r}_{iN}}{r_{iK}^3 r_{iN}^3} \cdot \mathbf{I}_K$
$h_K^{\text{SSO(2)}}$	Spin-same-orbit hyperfine correction	$-\frac{1}{4} \alpha^4 g_e \gamma_K \sum_i \mathbf{s}_i \cdot \frac{1(\mathbf{r}_{iK} \cdot \mathbf{r}_{ij}) - \mathbf{r}_{iK} \mathbf{r}_{ij}}{r_{iK}^3 r_{ij}^3} \cdot \mathbf{I}_K$
$h_K^{\text{SOO(2)}}$	Spin-other-orbit hyperfine correction	$-\frac{1}{2} \alpha^4 g_e \gamma_K \sum_i \mathbf{s}_i \cdot \frac{1(\mathbf{r}_{iK} \cdot \mathbf{r}_{ij}) - \mathbf{r}_{iK} \mathbf{r}_{ij}}{r_{iK}^3 r_{ij}^3} \cdot \mathbf{I}_K$
Spin- and field-dependence		
<i>Nuclear spin</i>		
$h_{KB_0}^{\text{DS-KE}}$	Kinetic energy correction of the electron nuclear Zeeman modification	$\frac{1}{8} \alpha^4 \gamma_K \sum_i \mathbf{I}_K \cdot \left[\nabla_i^2, \frac{1(\mathbf{r}_{i0} \cdot \mathbf{r}_{iK}) - \mathbf{r}_{i0} \mathbf{r}_{iK}}{r_{iK}^3} \right]_+ \cdot \mathbf{B}_0$
$h_{KB_0}^{\text{con}}$	Nuclear spin Zeeman contact hyperfine interaction	$-\frac{2\pi}{3} \alpha^4 \gamma_K \sum_i \delta(\mathbf{r}_{iK}) \mathbf{I}_K \cdot \mathbf{B}_0$
$h_{KB_0}^{\text{dip}}$	Nuclear spin Zeeman dipolar hyperfine interaction	$-\frac{1}{4} \alpha^4 \gamma_K \sum_i \mathbf{I}_K \cdot \frac{3\mathbf{r}_{iK} \mathbf{r}_{iK} - 1r_{iK}^2}{r_{iK}^5} \cdot \mathbf{B}_0$

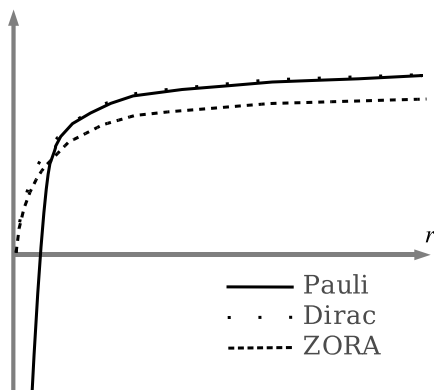


Figure 2.1. A schematic illustration of the behaviour of ZORA and Pauli approximations with respect to the Dirac equation. Drawn after Ref. [31].

2.3 Other quasi-relativistic Hamiltonians

An alternative approach for decoupling the large and small components of the Dirac equation is the zeroth-order regular approximation (ZORA) Hamiltonian [42]. The derivation of the ZORA Hamiltonian proceeds almost in complete analogy with that of the Pauli Hamiltonian, except here the expansion is carried out with respect to $E/(2c^2 - V)$. It has similarities with the earlier Chang-Pelisser-Durand zeroth-order effective Hamiltonian [43]. ZORA contains similar relativistic corrections as are present in the Pauli Hamiltonian but in a regularised form. The inclusion of the first-order in the expansion yields FORA (first-order regular approximation). The features and differences between the Pauli and ZORA approximations are outlined in Figure 2.1, in which the x -axis is the distance r from the nucleus. The Pauli approximation breaks down near the nucleus but approaches the correct limit at large r . ZORA is bounded from below, up to $Z = 137$, and it is a good approximation for $|V| \gg |E| > 0$, i.e. where the potential dominates, but it does behave erroneously when energies and distances are large [31, 44]. This difference is due to the fact that the change of picture [45] is neglected and that the ZORA Hamiltonian does not contain all terms of the α^2 order.

There are other ideas for the regular approximation scheme. In exponential regular approximation (ERA) [46], an exponential function is added to the definition of the small component in order to correct the metrics. The idea is to remove the singularity as with ZORA, without introducing the long-range dependence into the ansatz. In modified ERA (MERA) [46], part of the relativistic contribution is omitted to avoid spin-orbit terms in the metric. In infinite-order regular approximation (IORA) [47, 48] and its MERA-type modification (MIORA) [46], the expansion may be taken to infinite order by using an unnormalised FW transformation, which results in the ZORA Hamiltonian and a non-unit metric. Filatov and Cremer [49] recently presented a scaled IORA (SIORA) method, in which an effective energy-independent relativistic Hamiltonian was obtained by a reg-

ular expansion of the exact Hamiltonian for electronic states in terms of linear energy-independent operators.

Another alternative is an approach with external field projectors. This method has been developed by Hess [50, 51] on the basis of theoretical work by Sucher [52] and Douglas and Kroll [53]. This scheme is often called the Douglas-Kroll-Hess (DKH) method. In the method, the FW transformation is carried out up to the first order in the momentum space, and the result is then split into odd and even parts. After that, the FW transformation is repeated to order n , with antihermitian matrices W_n , $U_n = \sqrt{1 + W_n^2} + W_n$. The form of the W 's is chosen to cancel certain terms. The resulting Hamiltonian is decoupled, i.e. it operates on the large and small components independently, to order $n + 1$. Already U_1 includes several relativistic phenomena. DKH is widely used in molecular calculations. It has the benefit of being bounded from below, with no unphysical states occurring. It also approaches the correct NR limit.

Yet another alternative is to apply perturbation theory straight to the Dirac equation, and to change the metrics between the large and small component, yielding direct (or Dirac) perturbation theory (DPT) [54–56]. This approach gives non-singular forms for energy and wave function to arbitrary order. However, it is computationally almost as expensive as using the four-component framework, and its implementation is considered to be difficult.

Besides in the Hamiltonian, the relativistic effects can partly be included as “artifacts” in the formally non-relativistic calculations themselves by using the relativistic effective core potential (ECP) approach (see e.g. Refs. [57] or [58] and references therein).

3 Methods of Electronic Structure Calculations

This Chapter addresses the various methods of modern electronic structure theory. The description focuses on the methods used in the applications presented in this thesis.

3.1 Wave function theories

To find an approximate solution to the n -electron Schrödinger equation, one approach would be to postulate a trial wave function as a product of n one-electron wave functions,

$$\Theta(\mathbf{x}_1, \dots, \mathbf{x}_n) = \varphi_1(\mathbf{x}_1) \cdots \varphi_n(\mathbf{x}_n). \quad (3.1)$$

This is called the Hartree product. Due to the Pauli exclusion principle, it must also be demanded that the many-electron wave function be antisymmetric with respect to the interchange of the coordinates of any two electrons. The wave function conforms to the exclusion principle if the trial function is written as

$$\Phi = CA\Theta, \quad (3.2)$$

where A is the antisymmetrisation operator, by which $A\Theta$ can be expressed as a determinant. The normalisation constant can be shown to be $C = (n!)^{-1/2}$ and

$$\Phi(\{\mathbf{x}\}) = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_2(\mathbf{x}_1) & \cdots & \varphi_k(\mathbf{x}_1) & \varphi_l(\mathbf{x}_1) & \cdots & \varphi_n(\mathbf{x}_1) \\ \varphi_1(\mathbf{x}_2) & \varphi_2(\mathbf{x}_2) & \cdots & \varphi_k(\mathbf{x}_2) & \varphi_l(\mathbf{x}_2) & \cdots & \varphi_n(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \varphi_1(\mathbf{x}_n) & \varphi_2(\mathbf{x}_n) & \cdots & \varphi_k(\mathbf{x}_n) & \varphi_l(\mathbf{x}_n) & \cdots & \varphi_n(\mathbf{x}_n) \end{vmatrix}, \quad (3.3)$$

which is referred to as the Slater determinant.

Within the Born-Oppenheimer approximation, the non-relativistic many-electron Hamiltonian is written as

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_K \frac{Z_K}{r_{iK}} + \sum_{i < j} \frac{1}{r_{ij}} \quad (3.4)$$

$$= \sum_i h(\mathbf{x}_i) + \frac{1}{2} \sum'_{i,j} g(\mathbf{x}_i, \mathbf{x}_j). \quad (3.5)$$

With the determinant wave function, the energy of the many-electron system is written as

$$\begin{aligned} E[\Phi] &= \langle \Phi | H | \Phi \rangle = \sum_k \langle \varphi_k | h | \varphi_k \rangle + \frac{1}{2} \sum_{k,l} (\langle \varphi_k \varphi_l | g | \varphi_k \varphi_l \rangle - \langle \varphi_k \varphi_l | g | \varphi_l \varphi_k \rangle) \\ &= \sum_k \langle \varphi_k | h | \varphi_k \rangle + \frac{1}{2} \sum_k \langle \varphi_k | J - K | \varphi_k \rangle. \end{aligned} \quad (3.6)$$

In the latter equality, the Coulomb and exchange operators J and K are introduced.

3.1.1 Hartree-Fock equations

The orbitals that define the wave function expressed as a Slater determinant can be determined using the variational principle. By introducing the Fock operator

$$F = h + \sum_k J_k - \sum_k K_k = h + J - K, \quad (3.7)$$

the variation of φ_k subject to the orthonormality constraint $\langle \varphi_k | \varphi_l \rangle = \delta_{kl}$ yields the general Hartree-Fock (HF) equation

$$F | \varphi_k \rangle = \sum_l \varepsilon_{lk} | \varphi_l \rangle. \quad (3.8)$$

When ε_{kl} is diagonalised by a unitary transformation in a transformed molecular orbital (MO) basis, the canonical HF equations

$$F | \varphi_k \rangle = \varepsilon_k | \varphi_k \rangle \quad (3.9)$$

are obtained. The corresponding orbitals are canonical HF orbitals, and the eigenvalues ε_k are referred to as the orbital energies.¹ The HF method does not describe the electron-electron interaction in detail, and it is thus called an uncorrelated treatment. Correlation energy is defined as the difference between the exact energy and the energy obtained by the HF method [60].

The electron spin degree of freedom can be introduced to the MO theory by defining spin-orbitals

$$\begin{aligned} \varphi^{(\alpha)}(\mathbf{x}) &= \phi^{(\alpha)}(\mathbf{r})\alpha \\ \varphi^{(\beta)}(\mathbf{x}) &= \phi^{(\beta)}(\mathbf{r})\beta, \end{aligned} \quad (3.10)$$

¹An alternative language for this standard, “first-quantisation” presentation is the formalism of the second quantisation (see [59] and references therein), where the wave functions are also expressed in terms of operators, namely the creation and annihilation operators, a_p^\dagger and a_p , respectively, operating on the vacuum state. From these operators, one is able to construct all the standard operators of the first quantisation, such as those appearing in the electronic Hamiltonian. For example, the Hartree-Fock equations would be written as $\hat{f} a_{p\sigma}^\dagger |vac\rangle = \varepsilon_p a_{p\sigma}^\dagger |vac\rangle$, where the Fock operator is written using the singlet excitation operator E as $\hat{f} = \sum_{pq} f_{pq} E_{pq}$. The eigenfunctions of \hat{f} in the basis where the Fock matrix f_{pq} is diagonal, are canonical spin-orbitals and the corresponding eigenvalues ε_p are the orbital energies.

Although the second quantisation formalism allows developing the important relationships in an elegant manner, the first quantisation notation is used throughout the work for the reasons of illustrativity and consistency with the original papers.

where ϕ are spatial orbitals, which may also depend on whether the spin part is α or β , the eigenfunctions of the operator s_z . A distinction must be made on the basis of whether the Fock operator operates on an α or a β orbital – in it, one-electron and Coulomb operators are the same as before, whereas exchange interaction is possible only between electrons with the same spin part. This straightforward inclusion of spin is known as the unrestricted Hartree-Fock theory (UHF), which does not have constraints for the total wave function. The UHF method is subject to spin-contamination, as nothing guarantees that the total spin operator S^2 satisfies the necessary relation $S^2\Psi = S(S+1)\Psi$.

When considering a singlet electronic state, perfect spin pairing, i.e. setting the spatial functions to be equal, is an important simplification. The computational requirements are then reduced because summations over $n/2$ occupied orbitals in the energy expression (3.6) are needed. This procedure is called the restricted Hartree-Fock (RHF), and it is the most commonly used Hartree-Fock type method.

In the restricted open-shell Hartree-Fock theory (ROHF), perfect spin pairing is used for n_c closed shells, while n_o open shells are treated to be singly occupied, all with the α spin.

3.1.2 Self-consistent field theory

Although the HF method clearly simplifies the original Schrödinger equation of the many-electron problem, the resulting equations are too complicated to be soluble for all but atoms and small diatomics. For practical purposes, the spatial molecular orbital $\phi(\mathbf{r})$ is expanded to a linear combination of atomic orbitals (LCAO),

$$\phi_k(\mathbf{r}) = \sum_p c_{kp} \chi_p(\mathbf{r}). \quad (3.11)$$

Although the $\chi_p(\mathbf{r})$ are referred to as the approximate atomic orbitals, they are in this basis set expansion approach hardly more than functions of the coordinates of a single electron. To find a solution for the HF equations, the energy is minimised with respect to the coefficients c_{kp} . This is performed under the orthonormality constraint $\mathbf{c}^\dagger \mathbf{S} \mathbf{c} = \mathbf{1}$, where \mathbf{S} is the overlap matrix, $S_{pq} = \langle \chi_p | \chi_q \rangle$. This is achieved in the Roothaan-Hall equations [61, 62],

$$\mathbf{F} \mathbf{c} = \mathbf{S} \mathbf{c} \boldsymbol{\varepsilon} \quad (3.12)$$

where $\boldsymbol{\varepsilon}$ is a diagonal matrix containing orbital energies. In the self-consistent field (SCF) procedure, a set of orbitals is guessed, without any particular justification. With these, the Fock operator is constructed, diagonalised and, hence, a new set of orbitals is obtained. These orbitals will replace the previous ones in the construction of the new Fock operator. This procedure is repeated until a satisfactory convergence is found, i.e. the orbitals no longer change within some threshold. At this point, the orbitals satisfy the HF equations.

There are some practical aspects to consider in the SCF procedure. The first guess for the initial orbitals should be made paying attention to rapid convergence. The extended Hückel guess is often considered the best approach. The Hückel guess, in which the guess for MOs is a linear combination of AOs, is obtained by first diagonalising the Hückel matrix and then projecting the MOs into the actual basis set. The direct inversion

of iterative subspace (DIIS) [63, 64] is the modern standard for robust and efficient SCF iteration in quantum chemical programs due to its capability of handling oscillations. In some cases, the limitations of disk storage and input/output capacity may be an issue for integral evaluation. To avoid these problems, direct and semi-direct SCF schemes [65] have been presented, in which all or part of the integrals are evaluated on-the-fly when necessary, instead of being stored. In the direct SCF procedure, the number of evaluated integrals can be efficiently reduced since insignificant integrals are neglected. This technique is called integral prescreening, and it produces major advantages in computational cost for the calculation of the energies and properties of large molecules [59].

3.1.3 Configuration interaction and coupled cluster methods

The HF method yields a finite set of spin-orbitals within a finite basis set. In general, a basis with M members leads to $2M$ different spin-orbitals, of which the n lowest in energy correspond to the HF wave function Φ_0 . Numerous different Slater determinants can be formed using also the remaining $2M - n$ spin-orbitals. The singly excited determinant, which corresponds to raising a single electron from an occupied spin-orbital φ_k to a virtual spin-orbital φ_a , is defined as [cf. (3.3)]

$$\Phi_k^a = \det|\varphi_1 \varphi_2 \cdots \varphi_a \varphi_l \cdots \varphi_n|. \quad (3.13)$$

Correspondingly, in the doubly excited determinant Φ_{kl}^{ab} two electrons have been promoted, one from φ_k to φ_a and one from φ_l to φ_b , and so forth, for multiply excited determinants. These determinants, or their linear combinations, constructed so that the spin symmetry is correct, are called configuration state functions (CSF). The CSF is an eigenfunction of all the operators that commute with the Hamiltonian. They can be interpreted as approximate excited-state wave functions or used as a linear combination with Φ_0 to improve the representation of the ground-state wave function. The exact ground-state and excited-state wave functions can be expressed as a linear combination of all possible n -electron Slater determinants arising from a complete set of spin-orbitals,

$$\Psi = C_0 \Phi_0 + \sum_{kl} C_k^l \Phi_k^l + \sum_{ka} \sum_{lb} C_{kl}^{ab} \Phi_{kl}^{ab} + \dots \quad (3.14)$$

where $\{C\}$ are expansion coefficients that are determined variationally by minimising the Rayleigh ratio, and each excited determinant appears only once in the summation. An *ab initio* approach in which the wave function is expressed as Eq. (3.14) is called the configuration interaction method (CI) [66]. In calculations which are classified as full CI (FCI), all the CSFs of the appropriate symmetry are used for a given finite basis set. The energy associated with Ψ is the exact ground-state energy for a given Hamiltonian. FCI is thus the best possible calculation in the given basis set. In truncated or limited CI calculations, the wave function is written as a sum over a finite number of determinants. However, the number of determinants in FCI grows very rapidly as the number of basis set functions grows, which makes this method inapplicable to all but the smallest systems. Limitation to Φ_0 and single and double excitations (CISD) or only to double excitations (CID) can be carried out up to systems of moderate size (less than 100 electrons). Paper III used the

CISD method to provide natural occupation numbers (NON) of the considered dihalogen anions. One of the most serious problems related to the truncated CI methods is that they lack size-extensivity, i.e. the energy of the system AB computed when subsystems A and B are infinitely far apart is not equal to the sum of energies A and B separately computed. This is due to the linear parametrisation of the CI wave function.

In the coupled cluster (CC) method [67], the wave function (3.14) is not written as a linear but as an exponential expansion, which yields size-extensivity. The CC method is in its untruncated form implicitly equivalent to the FCI. As in CI, the CC expansion can be truncated to e.g. double excitations (CCD) [68] or to single and double excitations (CCSD) [69]. The CC approach is considered a very rigorous quantum chemical method that treats well both dynamical and static correlation. CC equations can be treated also by means of perturbation theory [70]. This leads to CC2, which is a perturbational treatment of CCD; and CC3, which approximates the CCSDT. These are closely connected to Møller-Plesset perturbation theory (MP n) energies. The CCSD(T) [71] model extends CCSD with perturbational treatment of triple excitations. CCSD(T) is widely regarded as the best single-reference correlation treatment with a computational cost low enough to be applicable to chemically interesting systems. Despite their popularity and conceptual attractiveness, the CC methods were not applied in the present work, mainly because they have not been implemented in the software used for the purposes of this thesis.

In multireference CI (MRCI), a set of reference configurations is created, from which the excited determinants are formed for use in a CI calculation. Because the reference determinants are often singly or doubly excited from the HF wave function, the combined effect of including both the single and double excitations in MRCISD leads to the inclusion of the most important determinants up to quadruple excitations. Therefore, MRCISD significantly reduces the size-extensivity error encountered in CISD, and a large fraction of the exact correlation energy can be achieved with MRCI calculations with a reasonable number of determinants. The MRCI methods were not, however, employed in this work mainly due to their high computational cost and a lack of urgent need of multi-reference treatment.

3.1.4 Møller-Plesset perturbation theory

Perturbation theory provides another approach for the treatment of correlation energy. In the MP n procedure [72, 73], the Fock operator is used as the unperturbed Hamiltonian, and the difference between the exact Hamiltonian and the sum of the one-electron Fock operators is used as the perturbation operator. The first correction to ground-state energy is provided by second-order perturbation theory. This inclusion is designated as MP2, and it is perhaps the most often applied *ab initio* method for electron correlation treatment in quantum chemistry. Implementations for higher-order energy corrections, e.g. MP3 and MP4, exist widely in quantum chemical software, but they are not considered neither practical nor even very reliable.

In Papers I, II, IV and VI, MP2 theory was used to calculate NONs, and in Paper III, it was applied to geometry optimisation.

3.1.5 Multiconfigurational self-consistent field method

In the multiconfigurational self-consistent field method (MCSCF), in addition to the expansion coefficients in Eq. (3.14), the LCAO expansion (3.11) coefficients are optimised. The simultaneous optimisation makes MCSCF computationally expensive but the optimisation of orbitals partially compensates for the truncation errors in CI, and accurate results can thus be obtained by the inclusion of a relatively small number of CSFs. The complete active space self-consistent field (CASSCF) method [74] and the restricted active space self-consistent field (RASSCF) method [75, 76] provide examples of MCSCF approaches. In CASSCF, spin-orbitals are divided into three classes: inactive orbitals, the lowest energy spin-orbitals that are occupied in all the determinants; virtual orbitals, which are unoccupied in all determinants; and active orbitals that often are energetically intermediate between the first two. All possible combinations with the correct spatial and spin symmetries are allowed in the active space of a CAS wave function, hence corresponding to FCI in the active molecular orbital space. In order to reduce the number of determinants, or alternatively, to enlarge the manageable active space, RASSCF divides the active space further into subspaces, whose occupation numbers are constrained. Usually the number of subspaces is three, and the maximum number of holes in RAS1 or electrons in RAS3 is specified, while no constraints are given for RAS2. CASSCF calculations are always multi-reference, since none of the configurations that can be constructed from the occupied and virtual MOs are favoured over others. RASSCF calculations can either be multireference or single-reference, depending on whether or not the unconstrained subspace contains virtual MOs. Multireference wave functions are capable of handling static correlation effects, whereas dynamic correlation effects can be evaluated using single-reference wave functions. In general, dynamic correlation effects are difficult to treat using MCSCF methods because active spaces can seldom be chosen large enough.

The choice of the active space for MCSCF calculation is not trivial. Usually the MOs are selected according to their NONs, obtained from a preceding CI or MP_n calculation, or by chemical intuition.

In addition to HF, MCSCF is the most important first-principles method used in this thesis. The CASSCF method was applied in the response calculations of all Papers, and RASSCF was used in Papers IV and VI.

3.2 Density-functional theory

Over the last few years, density-functional theory (DFT) [5] has gained popularity in the chemical community due to its capability to treat electron correlation with low computational cost as compared to correlated, *ab initio* post-HF methods.

3.2.1 Hohenberg-Kohn theorems and Kohn-Sham equations

If n is the number of electrons, the density $\rho(\mathbf{x})$ is defined as

$$\rho(\mathbf{x}) = \int |\Psi|^2 d\mathbf{x}_1 \cdots d\mathbf{x}_n \quad (3.15)$$

where $\Psi(\mathbf{x}_1 \cdots \mathbf{x}_n)$ is the wave function of the molecule. DFT is based on two key theorems by Hohenberg and Kohn [77]. The central idea of these theorems is that if the exact electron density is known, the full Hamiltonian is known and hence the wave function and the energy are determined. Thus, the system is exactly, albeit indirectly, described. The first Hohenberg-Kohn theorem states that the electron density $\rho(\mathbf{x})$ determines the external potential $v(\mathbf{x})$. According to the second Hohenberg-Kohn theorem, any approximate density $\tilde{\rho}$ which provides $v(\mathbf{x})$, determines its own wave function $\tilde{\Psi}$.

The energy of the system of interacting electrons can be expressed as a functional of the electron density as follows

$$\begin{aligned} E[\rho] &= \int v(\mathbf{x})\rho(\mathbf{x})d\mathbf{x} + T[\rho] + V_{ee}[\rho] \\ &= \int v(\mathbf{x})\rho(\mathbf{x})d\mathbf{x} + T_s[\rho] + J[\rho] + (T[\rho] - T_s[\rho]) + (V_{ee}[\rho] - J[\rho]) \\ &\equiv \int v(\mathbf{x})\rho(\mathbf{x})d\mathbf{x} + T_s[\rho] + J[\rho] + E_{xc}[\rho]. \end{aligned} \quad (3.16)$$

In the last form, the kinetic energy and the electron-electron interaction of the initial expression are written in terms of the kinetic energy T_s of the artificial, non-interacting reference system, the Coulomb energy J , and the exchange-correlation energy functional,

$$\begin{aligned} E_{xc}[\rho] &= T[\rho] - T_s[\rho] + V_{ee}[\rho] - J[\rho] \\ v_{xc}(\mathbf{x}) &= \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{x})}, \end{aligned} \quad (3.17)$$

the latter being a functional derivative called the exchange-correlation potential. The Kohn-Sham equation [78]

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{x}) + \int \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} d\mathbf{x}' + v_{xc}(\mathbf{x}) \right] \varphi_k(\mathbf{x}) = \varepsilon_k \varphi_k(\mathbf{x}) \quad (3.18)$$

operating on Kohn-Sham spin-orbitals $\varphi_k(\mathbf{x})$ gives an exact density once the exact exchange-correlation functional has been determined. When this is compared with the HF equations, it is seen that the usual, non-local and non-multiplicative exchange term is replaced by the $v_{xc}(\mathbf{x})$ potential, which is both local and multiplicative. The Kohn-Sham methodology is immediately available for both closed- and open-shell molecules through an unrestricted formulation.

3.2.2 Exchange-correlation functional

The wave function methods can, in principle, be systematically improved from the HF description all the way to the FCI. Within the present formulation of the DFT, there is

no straightforward way in which the exchange-correlation functional $E_{xc}[\rho]$ could be systematically improved. The simplest model is uniform electron gas or local density approximation (LDA) [79–81]. In this scheme, correlation energy can be parametrised very accurately [82] using the quantum Monte Carlo (QMC) methods [83], and an analytical expression can be found for the exchange energy. However, the electronic cloud of a molecule is by no means uniform. For this reason, the LDA is usually worse than the HF method as the first approximation in problems related to chemistry. This does not hold in the strongly correlated electronic systems occurring e.g. in condensed matter physics. Paper V of this thesis applied the LDA approximation in molecular property calculations.

One of the failures of LDA exchange is its incorrect asymptotic behaviour. In the Becke exchange term [84], there is a correction term involving a gradient of the density, which causes the exchange-energy density to have the correct r^{-1} asymptotic dependence. The functionals of form

$$E_{xc} = \int F(\rho_\alpha, \rho_\beta, \nabla\rho_\alpha \cdot \nabla\rho_\alpha, \nabla\rho_\beta \cdot \nabla\rho_\beta, \nabla\rho_\alpha \cdot \nabla\rho_\beta) d\mathbf{x} \quad (3.19)$$

are commonly called generalised gradient approximations (GGA). They are all local functions. The addition of gradient corrections is natural, since a density gradient expansion is formally required to introduce the inhomogeneity of a molecular density. The Becke functional has one adjustable parameter, chosen such that the sum of the LDA and Becke exchange terms accurately reproduces the exchange energies of the six noble gas atoms. The Lee-Yang-Parr (LYP) correlation functional [85] involves the gradient and the Laplacian of the density. The advantage of this correlation functional is that it has no relation to the LDA approximation but was derived from an actual correlated wave function. A popular choice for the DFT exchange-correlation functional is to use the Dirac exchange with Becke correction, and the LYP correlation functional (BLYP). The other functionals that have gained popularity are e.g. the Perdew86-correlation functional [86] and the Perdew-Wang91 exchange-correlation functional (PW91) [87], which were derived from the properties of slowly varying electron gas, and the functional with Becke exchange and P86 correlation (BP86). In the present thesis, BP86 was used in Paper III in the calculation of non-relativistic g -tensors and in Paper IV in the geometry optimisation of group(IV) tetrahalides.

A major development in DFT has been the introduction of adiabatic connection or hybrid functionals, in which semi-empirical mixing of the non-local, exact Hartree-Fock exchange energy with local exchange-correlation energy functionals is introduced. For example, $0.8E_x^{\text{Dirac}} + 0.2E_x^{\text{HF}} + 0.72\Delta E_x^{\text{Becke88}} + 0.19E_c^{\text{LDA}} + 0.81E_c^{\text{Perdew86}}$ is the B3P86 functional [88, 89], and the very popular B3LYP functional [88, 90] consists of $0.8E_x^{\text{Dirac}} + 0.2E_x^{\text{HF}} + 0.72\Delta E_x^{\text{Becke88}} + 0.19E_c^{\text{LDA}} + 0.81E_c^{\text{LYP}}$. The latter is the most important exchange-correlation functional for the present work. It was used in the molecular property calculations of Papers V and VI.

Recently, orbital-dependent exchange-correlation functionals, the exact exchange functionals, have drawn much attention (for a review, cf. [91]). In a short time, they have proved to be successful in areas that have traditionally been difficult for DFT.

3.3 Response theory

The interaction between a molecular system and an external perturbation such as an applied magnetic or electric field can be described in terms of time-dependent perturbation theory (PT). A higher than second-order treatment, which is required e.g. by intense fields, is rather laborious in terms of traditional PT. A compact treatment can be obtained by formulating the time-dependent PT in terms of an explicit, exponential, unitary and time-dependent transformation of the reference state [92] and expressing the perturbation treatment in terms of linear and non-linear response functions [93–96]. A number of molecular properties that refer to frequency-dependent or frequency-independent perturbations, or combinations of them, can be expressed in terms of response functions. This methodology can be applied to approximate states, such as those provided by SCF, DFT, or MCSCF methods. These expressions contain explicit references to the set of the eigensolutions of the time-independent reference problem, but explicit summations over intermediate states can be avoided by using the techniques described in Ref. [95].

In the present thesis, only frequency-independent properties were studied. Time-dependent PT becomes identical to time-independent PT at the limit of static perturbations. Hence, the compact and efficient response theory formulation has been used in all Papers.

3.4 One-electron basis sets

There are three general features determining the accuracy of quantum chemical methods: the choice of the Hamiltonian, electron correlation treatment (truncation of the many-particle space), and the description of the one-particle space, i.e. the basis set used. This is schematically illustrated in Fig. 3.1. Of these, the choice of the basis set is the most important factor determining the quality of a quantum chemical calculation. Insufficient basis sets yield erroneous results regardless of the level of theory, whereas with a proper basis set, at least qualitatively correct results are obtained for many problems already at the SCF level of theory and using the NR Hamiltonian.

3.4.1 Gaussian-type orbital basis set families

The most common choice for the χ , the LCAO basis functions in Eq. (3.11), is to use Gaussian type orbitals (GTO) centered on atomic nuclei,

$$\chi_p^l(r, \theta, \phi) = Y_{lm}(\theta, \phi) r^l e^{-\zeta r^2}, \quad (3.20)$$

where $Y_{lm}(\theta, \phi)$ are the spherical harmonics for angular momentum quantum number l , r the distance from the nucleus, and ζ exponents that are optimised separately for each element. GTOs are sometimes expressed in Cartesian coordinates. While physically more correct basis sets exist (e.g. Slater type orbitals, tabulated numerical AOs), the mathematical properties of GTOs, such as the Gaussian product theorem, have made them popular.

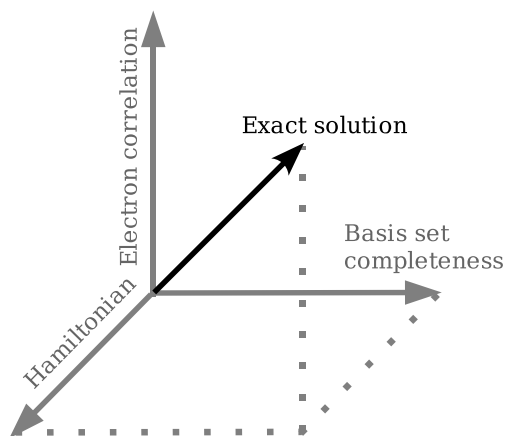


Figure 3.1. The three features determining the accuracy of a quantum chemical calculation.

Ref. [97] is a general review on basis sets.

The use of increasingly large basis sets that produce results converging to some particular value is usually regarded as a pragmatic solution to the problem of basis set incompleteness. The majority of HF and DFT applications employ contracted GTO (CGTO) sets that significantly increase efficiency. There are two different contraction schemes: segmented contraction, where each GTO contributes only to a single CGTO, and general contraction, where such a restriction is not applied. Examples of the segmented scheme include the Pople/McLean-Chandler basis set families [98, 99], the Karlsruhe basis sets [100–102], and basis sets by Huzinaga [103]. The correlation-consistent (cc) basis set families by Dunning and co-workers [104–109] are the most widely used generally contracted basis sets. The basic idea behind the correlation consistent basis sets is that functions that contribute approximately the same amount to correlation energy are grouped together in the contraction pattern. The cc basis sets provide smooth, monotonous convergence for electronic energy and for many molecular properties, especially for those originating in the valence region. The polarised valence cc-pVxZ ($x = D, T, Q, 5, 6$, corresponding to the number of contracted Gaussian type functions used to represent a Slater-type orbital) and core-valence (cc-pCVxZ) sets can be augmented with diffuse functions (aug-cc-pVxZ and aug-cc-pCVxZ). These sets have been used in studies on the basis set convergence of e.g. correlation energy [106, 110, 111] and HF energy [112]. In similar studies on harmonic frequencies [107] and electric dipole moments [113], convergence to limiting values has been observed as well. The basis sets become very large at large x , and it is not straightforward to extend the family beyond the published x values or to new elements. The atomic natural orbital (ANO) basis sets by Roos and co-workers [114, 115] provide another general contraction approach. In the basis sets, the contraction coefficients are natural orbital coefficients, which are obtained by optimising atomic energies.

An important measure of the computational cost of a considered task is its scaling

behaviour, i.e. how drastically the cost of the method increases with the size of the calculation. This is denoted as $\mathcal{O}(N^a)$, where N is the number of basis functions and a is the scaling exponent. The theories most often used in quantum chemical calculations scale formally as N^4 (HF and DFT), N^5 (MP2), N^6 (CCSD) and N^7 (CCSD(T)) ([116] and references therein). The “scaling wall” of these methods connotes that these methods rapidly become unfeasible as the size of the system of interest grows. In order to make *ab initio* methods available for very large systems such as biomolecules or those present in materials science, it is imperative to reduce the scaling exponents of the previously mentioned methods, aiming at a linear, $\mathcal{O}(N)$, scaling. In the last few years, the asymptotic linear scaling has been achieved for most parts of DFT [117], HF and MP2 [118, 119], as well as for CC methods [120, 121].

3.4.2 Basis sets and magnetic resonance properties

Magnetic properties are particularly sensitive to the quality of the basis sets due to many contributing physical phenomena arising from both the vicinity of the nucleus and from the valence region. In practice, a triple-zeta basis set with polarisation is needed at the minimum in the calculation of molecular magnetic properties. The vector potential in Eq. (2.28), which is used to include the external magnetic field in the Hamiltonian, is not uniquely defined, since the gauge origin O can be freely chosen, fulfilling the condition $\mathbf{B}_0 = \nabla \times \mathbf{A}_0(\mathbf{r}_i)$. On the contrary, all the observables should be independent of the choice of the gauge origin. For e.g. NMR shieldings, the gauge-origin dependence is often removed using the gauge-including atomic orbital (GIAO) ansatz [122–124]. GIAOs, often also referred to as the London orbitals, are basis functions with a parametrised extra spatial-dependence,

$$\omega_p^K = \exp(-i\mathbf{A}_0^K \cdot \mathbf{r})\chi_p^K, \quad (3.21)$$

where the phase factor contains the vector potential at the position of the atomic orbital, $\mathbf{A}_0^K = \mathbf{B}_0 \times (\mathbf{R}_K - \mathbf{R}_O)/2$ and χ_p^K is an atomic orbital positioned at nucleus K . The use of GIAOs makes the energy and the energy derivatives independent of the gauge origin \mathbf{R}_O . The formulation of magnetic properties in terms of GIAOs was presented in Refs. [124, 125]. GIAOs also provide rapid basis set convergence for several molecular properties [126]. In Papers II and V, the NR shielding tensors were calculated using GIAOs. Other widely used approaches include the individual gauge for localised orbitals (IGLO) method [127, 128], in which the local phase factors are attached to the MOs instead of the AOs; and the localised orbital/localised origin (LORG) method [129, 130]. In this thesis, well-tempered² basis sets [103, 131] are most often used for elements up to Ar. For heavier elements, the primitive sets by Fægri are taken and contracted and polarised similarly to the IGLO sets [131] of Kutzelnigg *et al.* This is based on the previous experience by e.g. Vaara *et al.* [132–134] and Helgaker *et al.* [135]. The IGLO basis sets have been found to provide good core-region flexibility and a contraction pattern well-suited

²The exponents are not independently optimised with respect to SCF energy but instead generated in a series of $\zeta_m = \alpha\beta^{m-1}(1 - \gamma(m/M)^\delta)$, in which the parameters α , β , γ , and δ are optimised with respect to SCF energy.

for magnetic properties with a very reasonable basis set size [135, 136]. The basis set convergence is studied in the present work by uncontracting the largest (HIV) set and adding further steep and diffuse functions. In Paper II, the addition was made to the l -values occupied in the ground state of the atom, and in the other Papers to every l -value present in the set. The new exponents were obtained by successive multiplication or division by the factor of three.

During the last few years, numerous approaches to calculating magnetic resonance parameters using highly sophisticated *ab initio* methods and flexible basis sets have been used, taking into account e.g. environmental, thermal and relativistic effects [137]. For example, Gauss *et al.* [138] were recently able to reproduce quantitative accuracy with experiment of ^{13}C shielding in various molecules by using coupled cluster CCSD and CCSD(T) wave functions, very large basis sets and including vibrational averaging. However, the predictions of the complete basis set (CBS) i.e. infinite-zeta values of NMR parameters have been fewer and appeared only recently. Kupka *et al.* performed a CBS fitting for NMR shieldings, calculating them using DFT and HF and cc-sets [139], and Vaara and Pyykkö approached the CBS limit explicitly at the Dirac-Hartree-Fock level of theory by saturating the uncontracted basis sets with steep and diffuse exponents [140].

3.4.3 NMR properties and basis-set completeness

In the following, a previously unpublished discussion on the performance of different basis set families and convergence with respect to the basis set size in indirect spin-spin couplings J_{HF} , nuclear shieldings constants σ_{F} and isotropic magnetisabilities ξ (see Chapter 4) of the hydrogen fluoride molecule at the SCF level of theory is presented. The GIAO-ansatz [125] is used for the shielding constants and the magnetisabilities. Although the basis-set convergence of these properties has been extensively discussed e.g. in Refs. [135, 141], its connection to the concept of basis-set completeness is further elaborated on here. The performance of different basis sets for a certain molecular property can be qualitatively understood with this concept, which can be measured by the completeness profiles introduced by Chong [142] as

$$Y(\alpha) = \sum_m \langle g(\alpha) | \chi_m \rangle^2. \quad (3.22)$$

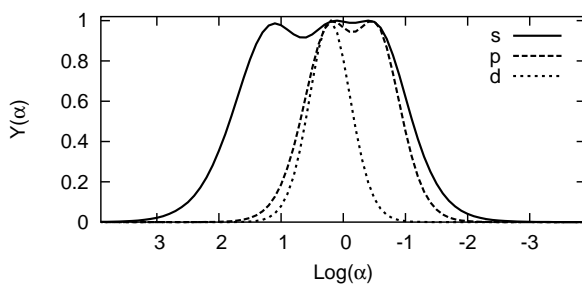
This quantity, the sum of the squares of the overlap of the orthonormalised basis $\{\chi\}$ with the probe GTO $g(\alpha)$, where α is the exponent of GTO, becomes unity for all α in a complete basis set. The completeness profile of a basis set is $Y(\alpha)$ plotted against $x = \log \alpha$. In a certain exponent interval $[\alpha_{\text{min}}, \alpha_{\text{max}}]$ this quantity is directly, but not trivially, connected to the possibility of reproducing all the physical phenomena with spatial origin at a certain distance range from the atomic nucleus.

The effect of the n -tuple valence description on completeness profiles is demonstrated in Fig. 3.2, where correlation-consistent basis sets are plotted from double to quintuple-zeta sets. The coverage area is extended at all stages, but not dramatically. The correlation consistent core-valence basis sets (cc-pCV5Z illustrated in Fig. 3.3b) extend the ideas of the original cc-pVxZ sets by including extra functions designed for core-core and core-valence correlation. The addition of extra steep functions (from cc-pV5Z to cc-pCV5Z)

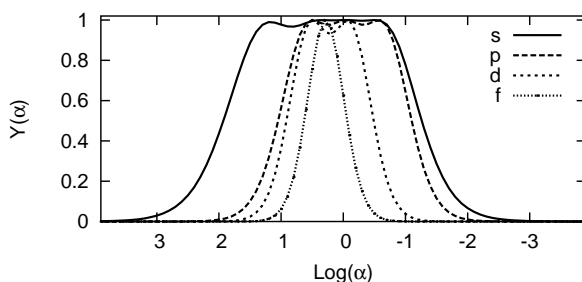
significantly expands the exponent range where s -profile becomes close to unity, and despite the pits, improves the p -space as well. The Huzinaga-Kutzelnigg-type basis sets, which are used for the present calculations in addition to the cc-sets, are visualised in Fig. 3.4. These figures demonstrate how the Huzinaga-Kutzelnigg-type basis sets remain close to unity deep into the high-exponent (with low l) area, showing why these sets perform so well on magnetic properties, especially spin-spin coupling, despite their moderately small size, as mentioned before. The last profile is the HIVu73+*ghi* set, detailed below. In the profile, s , p and d spaces remain complete much further to the steep region than the area shown.

The spin-spin coupling J_{HF} is strongly dependent on the quality of the description of the electron cloud at the vicinity of nuclei, while the shielding is sensitive to both the description of the core and valence regions, and the magnetisability is mainly a valence property. The CBS limit was studied by first completely uncontracting the HIV and successively adding steep primitives (obtained with multiplication by three from the largest existing exponent) to every l -shell, until four-decimal convergence was found in each property, and then saturating the sets with diffuse functions in a similar manner. On top of this, further $4f3g2i$ exponents for F and $4f3g2h$ for H were added, obtained from the aug-cc-pV6Z basis set. Spin-spin coupling constants, magnetic shielding constants and isotropic magnetisabilities calculated with different basis-set families are presented in Figure 3.5. The differences in the performance of the different families are notable, especially in the spin-spin coupling. The correlation-consistent basis sets (cc-pVxZ and the like) tend to converge when increasing their characteristic number x but the limiting values differ between the different subfamilies of the correlation consistent sets, and thus cannot represent an actual CBS limit. Even the largest cc-pV5Z still lacks 11% of the CBS value of J_{HF} , mostly due to the insufficient description of the high-exponent s -shell, which is known to be critical for FC contribution. The improvement in the representation of s - and p -spaces between cc-pVxZ and cc-pCVxZ sets is visible in comparison of Figs. 3.2d and 3.3b, as well as in J_{HF} calculated with cc-pCV5Z that is only 5% below the CBS value.

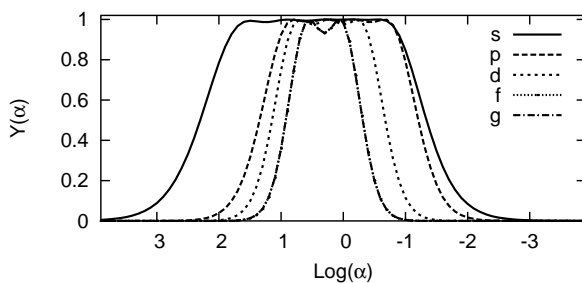
In nuclear magnetic shielding constants, which are not as dependent on the description of the high-exponent area of s -space as spin-spin couplings, all families essentially converge to CBS. Already basis sets of triple- ζ quality provide accurate shieldings. This is partly due to the GIAO ansatz. It is worth noting that the Huzinaga-type sets provide better results than the cc-sets of corresponding size, e.g. HIII (45 basis functions total) is 0.1 ppm above the CBS values, whereas cc-pVTZ (44 basis functions) differs by 1.3 ppm. Similarly to the shielding, the magnetisabilities converge to the CBS limit within all families. The effect of augmentation is significant, for example aug-cc-pVTZ differs from the CBS by 0.1% and the unaugmented set by 2.2%.



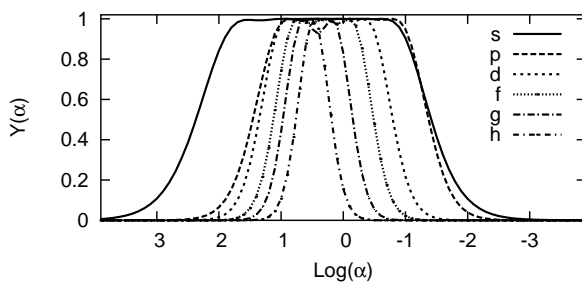
a) cc-pVDZ, [9s4p1d|3s2p1d]



b) cc-pVTZ, [10s5p2d1f|4s3p2d1f]

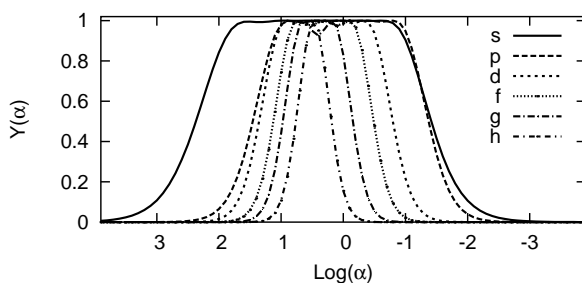


c) cc-pVQZ, [12s6p3d2f1g|5s4p5d2f1g]

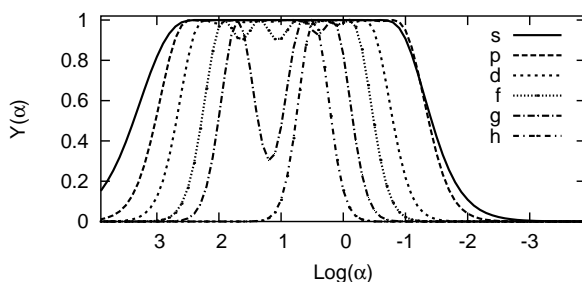


d) cc-pV5Z, [14s8p4d3f2g1h|6s5p4d3f2g1h]

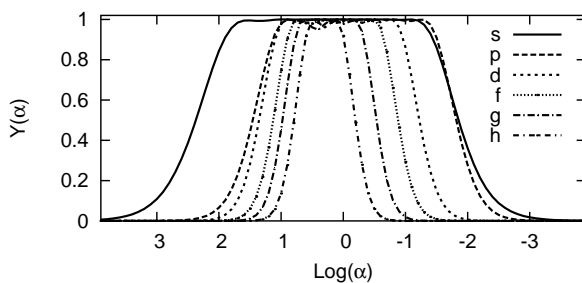
Figure 3.2. The effect of n -tuple valence description on the completeness of basis sets: completeness profiles of cc-pVXZ ($X = D, T, Q, 5$) basis sets of fluorine.



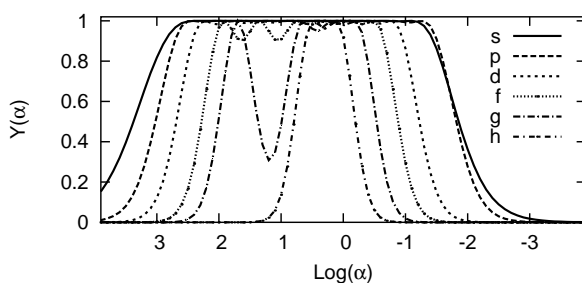
a) cc-pV5Z, [14s 8p 4d 3f 2g 1h|6s 5p 4d 3f 2g 1h]



b) cc-pCV5Z, [18s 12p 7d 5f 3g 1h|10s 9p 7d 5f 3g 1h]

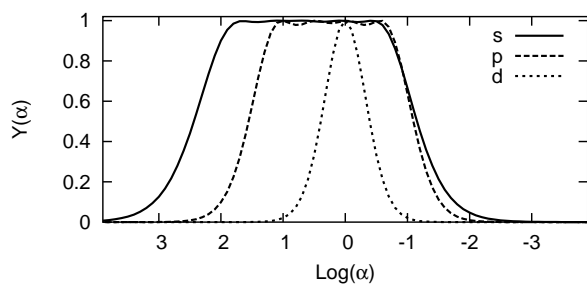


c) aug-cc-pV5Z, [15s 9p 5d 4f 3g 2h|7s 6p 5d 4f 3g 2h]

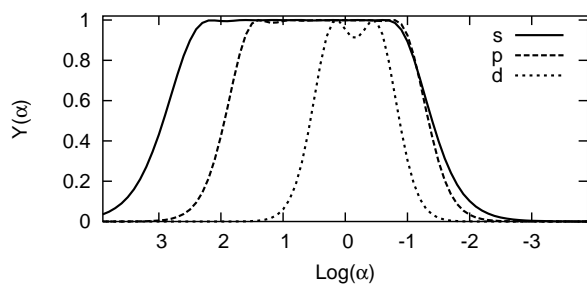


d) aug-cc-pCV5Z, [19s 13p 8d 6f 4g 2h|11s 10p 8d 6f 4g 2h]

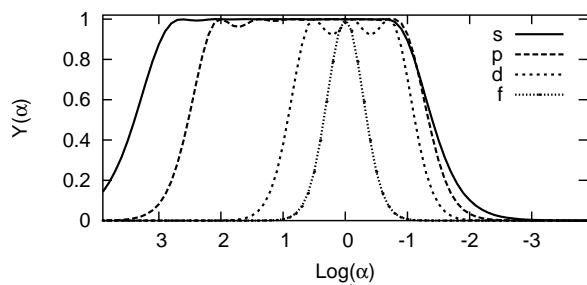
Figure 3.3. The effect of augmentation and core-polarisation on the completeness of basis sets: completeness profiles of cc-pV5Z, cc-pCV5Z, aug-cc-pV5Z, and aug-cc-pCV5Z basis sets of fluorine.



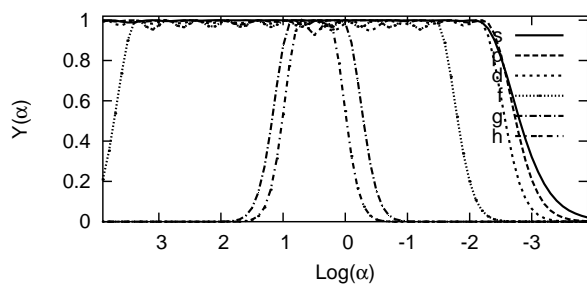
a) HII [9s5p1d|5s4p1d]



b) HIII [11s7p2d|7s6p2d]



c) HIV [11s7p3d1f|8s7p3d1f]



d) HIVu73+ghi [21s17p13d11f3g2h1i|21s17p13d11f3g2h1i]

Figure 3.4. The completeness profiles of basis sets HII, HIII, and HIV, as well as the assumed "magnetic-properties-CBS" of fluorine.

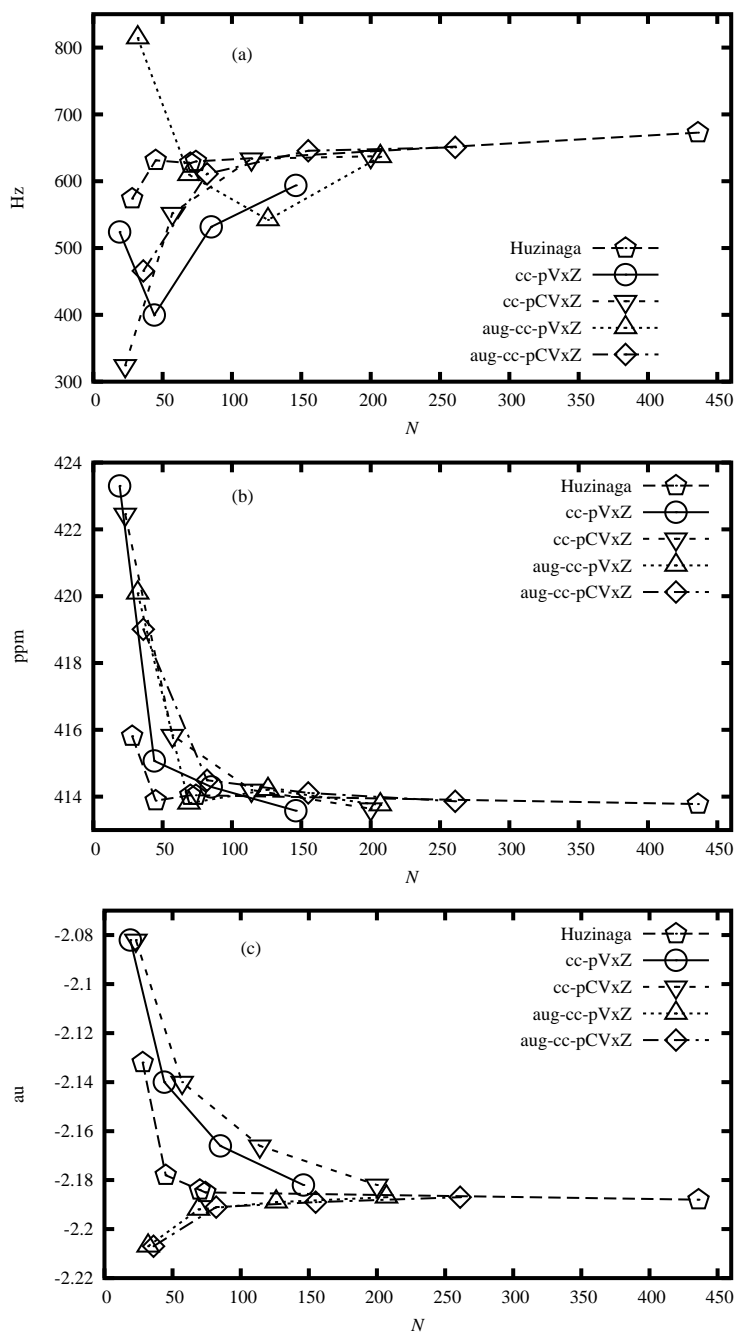


Figure 3.5. (a) Indirect spin-spin couplings J_{HF} , (b) nuclear magnetic shieldings σ_{F} , and (c) isotropic magnetisabilities in hydrogen fluoride as a function of basis-set size, calculated at the SCF level of theory with different basis set families.

3.5 Computer software for electronic structure calculations

The central software package used in the present work is the DALTON program [143]. This software is the result of mainly Scandinavian co-operation, and it is free for academic use. It was useful for the purposes of this work due to the implementation of response theory detailed in the earlier section, with user-defined perturbation operators. This enables the calculation of desired properties or phenomena, static or time-dependent, by combining different integrals that are allowed by the integral package of DALTON in different orders of the perturbation theory. This makes the program an efficient tool for the development and application of quantum chemical methods. Some one-electron integrals needed in this work were implemented in DALTON during the course of the work.

For geometry optimisations, commercial software packages GAUSSIAN 98 [144] and TURBOMOLE [145] were used because of their computational effectiveness and their great variety of available computational means. In addition, a program written by the author was used, which is capable of plotting the completeness profiles of one-electron basis sets introduced above.

4 Spectral Parameters of Magnetic Resonance

This Chapter introduces a unified treatment for NMR and ESR spectral parameters within a Breit-Pauli framework. A perturbational relativistic theory is presented for the parameters, where the leading-order relativistic corrections appear two powers higher in the fine structure constant than the non-relativistic expressions. In addition, this Chapter brings forward a theory for the magnetic-field dependence of NMR parameters, which is based on the Breit-Pauli Hamiltonian and perturbation theory.

4.1 Spin Hamiltonians and spectral parameters

Although the actual interactions that give rise to the spectra of magnetic resonance spectroscopies are complicated, they can be accounted in terms of effective spin Hamiltonians, in which the energy levels of spin subsystems are quantified and the other degrees of freedom are submerged into their numerical parameters.

4.1.1 NMR spin Hamiltonian

In NMR spectroscopy [1, 2], the applied external magnetic field \mathbf{B}_0 breaks the degeneracy of the Zeeman states of nuclei possessing nuclear spin \mathbf{I} , and radio-frequency pulses are used to induce transitions between the nuclear spin energy states. NMR spectrum is obtained by applying a Fourier transformation to the signal emitted by the spin system. The spectrum carries a large amount of information about the chemical and magnetic environment of the nuclei. In order to analyse the spectrum, the NMR spin Hamiltonian for a closed-shell system is usually written as¹

$$H^{\text{NMR}} = -\frac{1}{2\pi} \sum_K \gamma_K \mathbf{I}_K \cdot (\mathbf{1} - \underline{\underline{\sigma}}_K) \cdot \mathbf{B}_0 + \frac{1}{2} \sum_{K \neq L} \mathbf{I}_K \cdot (\mathbf{D}'_{KL} + \mathbf{J}_{KL}) \cdot \mathbf{I}_L + \sum_K \mathbf{I}_K \cdot \mathbf{B}'_K \cdot \mathbf{I}_K. \quad (4.1)$$

¹In frequency units.

Here, σ_K is the nuclear shielding tensor, \mathbf{D}'_{KL} and \mathbf{J}_{KL} are the direct and indirect spin-spin coupling tensors, and \mathbf{B}_K is the quadrupole coupling tensor. The nuclear shielding tensor represents the interaction of bare nuclei with the external magnetic field that has been modified by electrons. The direct dipolar coupling tensor arises from the magnetic interaction between the nuclear magnetic moments of bare nuclei K and L and the indirect spin-spin coupling tensor corresponds to the electron-mediated coupling. The quadrupole coupling tensor describes the interaction of the electric field gradient (EFG) at the site of an atomic nucleus possessing an electric quadrupole moment. This interaction vanishes for nuclei with cubic or higher site symmetry.

In general, the σ_K , \mathbf{D}'_{KL} , \mathbf{J}_{KL} , and \mathbf{B}'_K are non-symmetric second-rank tensors. For freely rotating systems, e.g. molecules in ordinary liquid or gas phase, the orientation distribution is isotropic and the NMR spin Hamiltonian obtains its static, isotropic form [146]

$$H_{\text{iso}}^{\text{NMR}} = -\frac{1}{2\pi} \sum_K \gamma_K (1 - \sigma_K) I_{K,Z} B_0 + \sum_{K < L} J_{KL} \mathbf{I}_K \cdot \mathbf{I}_L, \quad (4.2)$$

where $I_{K,Z}$ is the nuclear spin component in the direction of the external magnetic field, and the nuclear shielding and spin-spin coupling tensors are reduced to their isotropic parts, the shielding and spin-spin coupling constants

$$\sigma_K = \frac{1}{3} \text{Tr} \underline{\sigma}_K \quad (4.3)$$

$$J_{KL} = \frac{1}{3} \text{Tr} \mathbf{J}_{KL}. \quad (4.4)$$

σ_K defines the peak positions via the chemical shift

$$\delta_K = \sigma_K^{\text{ref}} - \sigma_K, \quad (4.5)$$

where σ_K^{ref} is the shielding constant of the same nucleus in a chosen reference compound. J_{KL} determines the fine structure of the spectrum, i.e. the peak splittings.

In a static, isotropic situation, the traceless \mathbf{D}'_{KL} and \mathbf{B}'_K vanish. Even in such a case, they provide valuable information in form of relaxation rates [1]. This thesis addresses only the time-independent spectral parameters.

4.1.2 ESR spin Hamiltonian

ESR or EPR (electron paramagnetic resonance) [1, 3] is the study of molecules and ions containing unpaired electrons by observing the magnetic fields of which they come into resonance with monochromatic, most often microwave-frequency, radiation. By using the concept of effective spin \mathbf{S} , where the electron spin momenta are combined, the effective ESR spin Hamiltonian is composed as

$$H^{\text{ESR}} = \mu_B \mathbf{B}_0 \cdot \mathbf{g} \cdot \mathbf{S} + \sum_K \mathbf{I}_K \cdot \mathbf{A}'_K \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}. \quad (4.6)$$

Here \mathbf{g} is the electronic g -tensor and \mathbf{A}'_K is the hyperfine coupling tensor, and μ_B is the Bohr magneton. \mathbf{g} modifies the free-electron interaction with the magnetic field, i.e. the

electronic $g_e = 2.002319\dots$ value, thus providing an analogue to the NMR shielding tensor. \mathbf{A}'_K describes the electron spin density at the site of nucleus K . \mathbf{D} represents the zero-field splitting i.e. the electronic spin-spin coupling, and is considered no further here.

4.1.3 Spectral parameters as derivatives of energy

When a molecular electronic system is exposed to external perturbations $\vec{\epsilon}_1, \vec{\epsilon}_2, \dots$, the energy of the system changes. The energy can be expressed as a power series with respect to the perturbations as

$$E(\vec{\epsilon}_1, \vec{\epsilon}_2, \dots) = E_0 + \sum_n \vec{\epsilon}_n \cdot \mathbf{E}_{\epsilon_n} + \frac{1}{2!} \sum_{m,n} \vec{\epsilon}_m \cdot \mathbf{E}_{\epsilon_n \epsilon_m} \cdot \vec{\epsilon}_n + \mathcal{O}(\vec{\epsilon}^3) \quad (4.7)$$

The coefficients $\{\mathbf{E}\}$ present the response of the system to the external perturbation, and are known as molecular properties. The molecular properties are characteristic of the molecular electronic system and its quantum state. When the perturbation can be considered to be static i.e. time-independent, the properties are obtained by differentiation at $\vec{\epsilon} = \mathbf{0}$,

$$\mathbf{E}_{\epsilon_n} = \left. \frac{\partial E}{\partial \epsilon_n} \right|_{\epsilon_n = \mathbf{0}} \quad (4.8)$$

$$\mathbf{E}_{\epsilon_n \epsilon_m} = \left. \frac{\partial^2 E}{\partial \epsilon_n \partial \epsilon_m} \right|_{\epsilon_n = \epsilon_m = \mathbf{0}}. \quad (4.9)$$

In the presence of external magnetic field and the nuclear magnetic moments, the energy is expanded as

$$\begin{aligned} E(\mathbf{B}_0, \{\mathbf{I}_K\}_{K=1\dots N}) &= E_0 + \mathbf{B}_0 \cdot \mathbf{E}_{B_0} + \sum_K \mathbf{I}_K \cdot \mathbf{E}_K + \frac{1}{2} \mathbf{B}_0 \cdot \mathbf{E}_{B_0^2} \cdot \mathbf{B}_0 \\ &+ \sum_K \mathbf{I}_K \cdot \mathbf{E}_{I_K B_0} \cdot \mathbf{B}_0 + \frac{1}{2} \sum_{K,L} \mathbf{I}_K \cdot \mathbf{E}_{I_K I_L} \cdot \mathbf{I}_L + \dots \end{aligned} \quad (4.10)$$

When the NMR spin Hamiltonian is compared to Eq. (4.10), it is seen that by using Eq. (4.9), NMR parameters can be written as

$$\underline{\underline{\sigma}}_K = \frac{1}{\gamma_K} \left. \frac{\partial^2 E(\mathbf{I}_K, \mathbf{B}_0)}{\partial \mathbf{I}_K \partial \mathbf{B}_0} \right|_{\mathbf{I}_K = \mathbf{B}_0 = \mathbf{0}} + \mathbf{1} \quad (4.11)$$

$$\mathbf{J}_{KL} = \frac{1}{2\pi} \left. \frac{\partial^2 E(\mathbf{I}_K, \mathbf{I}_L)}{\partial \mathbf{I}_K \partial \mathbf{I}_L} \right|_{\mathbf{I}_K = \mathbf{I}_L = \mathbf{0}} - \mathbf{D}'_{KL}. \quad (4.12)$$

The quadrupole coupling tensor \mathbf{B}'_K is obtained by

$$\mathbf{B}'_K = \left. \frac{1}{2\pi} \frac{\partial E(\mathbf{I}_K)}{\partial \mathbf{I}_K \mathbf{I}_K} \right|_{\mathbf{I}_K = \mathbf{0}}. \quad (4.13)$$

The term that is quadratic in the magnetic field in expansion (4.10) describes the direct interaction of the system with the external field and is represented by the magnetisability tensor ξ . This tensor does not enter the effective NMR spin Hamiltonian. The first-order terms vanish for closed-shell systems. Open-shell treatments for NMR properties (shieldings) have only recently appeared [147, 148]. Higher than second-order terms that correspond e.g. to the magnetic-field dependence of the previously introduced spectral parameters are usually neglected due to their assumed smallness. However, one of the topics of this thesis is that these terms can cause observable effects in NMR spectroscopy, and the concept of field-dependent parameters in NMR will be introduced later.

Expressions for the ESR g and hyperfine coupling tensors are

$$\mathbf{g} = \frac{1}{\mu_B} \left. \frac{\partial^2 E(\mathbf{B}_0, \mathbf{S})}{\partial \mathbf{B}_0 \partial \mathbf{S}} \right|_{\mathbf{B}_0 = \mathbf{S} = \mathbf{0}} \quad (4.14)$$

$$\mathbf{A}'_K = \left. \frac{\partial^2 E(\mathbf{I}_K, \mathbf{S})}{\partial \mathbf{I}_K \partial \mathbf{S}} \right|_{\mathbf{I}_K = \mathbf{S} = \mathbf{0}}. \quad (4.15)$$

These obtain their rise from the second and third term of expansion (4.10) and the internal perturbation by the effective spin.

4.2 NMR and ESR spectral parameters in the Breit-Pauli framework

The expressions for the magnetic resonance parameters in terms of the Breit-Pauli Hamiltonian are obtained by combining the energy expressions presented in Tables 2.1, 2.2 and 2.3 in different orders of perturbation theory. According to Eq. (4.11), energy expressions linear in \mathbf{I}_K and \mathbf{B}_0 contribute to the nuclear shielding tensor. Similarly, according to Eqs. (4.12) and (4.13), energy terms that are linear in \mathbf{I}_K and \mathbf{I}_L contribute to \mathbf{J}_{KL} , and terms bilinear in \mathbf{I}_K to \mathbf{B}'_K . Continuing along the same line, energy terms linear in \mathbf{B}_0 and \mathbf{s}_i contribute to the g -tensor and terms linear in \mathbf{I}_K and \mathbf{s}_i to \mathbf{A}'_K . Here, the discussion is limited to one-electron contributions, as they are expected to be significantly larger than two-electron contributions in magnetic properties, which are predominantly one-electron-like in origin [149]. Also the numerical studies in Paper II deal with one-electron effects only. In the following, linear, quadratic and cubic response function notations ($\langle\langle A; B \rangle\rangle_0$, $\langle\langle A; B, C \rangle\rangle_{0,0}$, and $\langle\langle A; B, C, D \rangle\rangle_{0,0,0}$, respectively) are used, which correspond to standard second, third and fourth-order PT expressions involving the time-independent operators A to D [95, 96]. $\langle A \rangle$ denotes the expectation value of an operator. As H^{BP} is not variationally stable [150], its singular operators should only be used up to first order i.e. leading relativistic effects, with only one such operator at a time in expressions featuring multiple perturbations [151, 152].

4.2.1 Non-relativistic contributions

When operators of the Breit-Pauli Hamiltonian are considered as described in Section 4.2 up to $\mathcal{O}(\alpha^2)$ and $\mathcal{O}(\alpha^4)$ for shielding and spin-spin coupling, respectively, expressions are obtained that correspond to Ramsey’s non-relativistic perturbation theory [6, 8]. “NR”² contributions to the ESR g -tensor are similarly obtained to $\mathcal{O}(\alpha^2)$. The NR theory of quadrupole coupling is not as straightforward, since the h_K^{NQCC} operator describing the interaction of the nuclear quadrupole moment with EFG does not rise from the presented treatment of H^{BP} but follows from the inclusion of the finite nuclear model. The leading-order expressions of NMR and ESR observables provided by this approach are presented in Table 4.1.

4.2.2 Relativistic effects

All the observables of magnetic resonance spectroscopies probe the atomic core region and are hence sensitive to the effects of special relativity [153]. The computational expense of rigorous four-component methods, especially in studying non-Coulombic properties such as magnetic resonance parameters, motivates the development of approximate relativistic methods. A review of both four-component approaches and those based on quasi-relativistic Hamiltonians as well as PT is presented e.g. in [154]. A brief literature survey is also given in Papers I and II of the present thesis, which provide the basis for the following discussion on the perturbational relativistic theory of NMR shielding and spin-spin coupling. An analogous theory for the ESR g -tensor is presented in Paper III.

The leading-order relativistic correction terms appear two powers of α higher than the NR expressions in the present unit system. The contributions are classified as “passive” or “active” effects, of which the passive effects feature magnetic field free relativistic operators that provide first-order relativistic modification of the wave function. The relativistic operators of the active terms contain a functional dependence on the degrees of freedom in the effective spin Hamiltonian relevant for the property under consideration. A further categorisation into heavy atom effects on heavy atom (HAHA) and heavy atom effects on light atoms (HALA) [155] is presented as well.

4.2.2.1 NMR parameters

As implied previously, the relativistic corrections appear to $\mathcal{O}(\alpha^4)$ for $\underline{\underline{\sigma}}$ and $\mathcal{O}(\alpha^6)$ for \mathbf{J} . These corrections are collected in Tables 4.2 and 4.3, respectively. For \mathbf{B}'_K , only the passive scalar relativistic corrections, i.e. contributions $B_K^{\text{NQCC}/\text{mv}} \propto \langle\langle h_K^{\text{NQCC}}; h^{\text{mv}} \rangle\rangle_0$ and $B_K^{\text{NQCC}/\text{Dar}} \propto \langle\langle h_K^{\text{NQCC}}; h^{\text{Dar}} \rangle\rangle_0$ appear to the leading order. They are not further considered in this thesis.

²In fact, already the leading-order treatment contains operators that are absent in the NR limit of H^{BP} .

Table 4.1. Non-relativistic contributions to the spectral parameters of NMR and ESR.

Property	First-order terms, $\langle A \rangle$		Second-order terms, $\langle\langle A; B \rangle\rangle_0$		Tensor ^d
	Symbol	A	Symbol	A and B	
$\underline{\underline{Q}}_K$	d	$h_{KB_0}^{DS}$	p	h_K^{PSO} and $h_{B_0}^{OZ}$	singlet 0,2,1
J_{KL}	DSO	h_{KL}^{DSO}	PSO	h_K^{PSO} and h_L^{PSO}	singlet
			FC	h_K^{FC} and h_L^{FC}	triplet
			SD	h_K^{SD} and h_L^{SD}	triplet
			SD/FC	h_K^{SD} and $h_L^{FC}(K \leftrightarrow L)^c$	triplet
B'_K	NQCC	h_K^{NQCC}	2		
Δg	CG	$h_{B_0}^{SO}$	OZ/ISO	$h_{B_0}^{OZ}$ and $h^{SO}(1)$	0,2,1 0,2,1
	SZ-KE	$h_{B_0}^{SZ-KE}$			
A'_K	iso	h_K^{FC}			0
	aniso	h_K^{SD}			0,2,1 2

^a Contributions to tensorial ranks: 0 corresponds to the isotropic part, $T = \frac{1}{3}(T_{xx} + T_{yy} + T_{zz})$, 2 to the anisotropic but symmetric contributions $T_{\tau\tau}^S = \frac{1}{2}(T_{\tau\tau} + T_{\tau\tau}) - T\delta_{\tau\tau}$ and 1 to the anisotropic and antisymmetric contributions $T_{\tau\tau}^A = \frac{1}{2}(T_{\tau\tau} - T_{\tau\tau})$.

^b Spin symmetry of the intermediate states when the ground state is a singlet.

^c Contributions from both perturbations of nuclear indices K and L .

Table 4.2. Leading-order, $\mathcal{O}(\alpha^4)$, one-electron relativistic contributions to the nuclear magnetic shielding tensor.^a

First-order terms, $\langle A \rangle$					
Symbol	A	Tensor	Type ^b		
con	$h_{KB_0}^{\text{con}}$	0	Act.		
dip	$h_{KB_0}^{\text{dip}}$	2	Act.		
d -ke	$h_{KB_0}^{\text{DS-KE}}$	0,2,1	Act., HAHA? ^c		
p -OZ	$h_{KB_0}^{\text{PSO-OZ}}$	0,2,1	Act., HAHA? ^c		
Second-order terms, $\langle\langle A; B \rangle\rangle_0$					
Symbol	A and B	Interm. states	Tensor	Type	
p -ke/OZ	$h_K^{\text{PSO-KE}}$ and $h_{B_0}^{\text{OZ}}$	singlet	0,2,1	Act.	
p /OZ-KE	h_K^{PSO} and $h_{B_0}^{\text{OZ-KE}}$	singlet	0,2,1	Act.	
d /mv	$h_{KB_0}^{\text{DS}}$ and h^{mv}	singlet	0,2,1	Pass.	
d /Dar	$h_{KB_0}^{\text{DS}}$ and $h^{\text{Dar}(1)}$	singlet	0,2,1	Pass.	
FC/SZ-KE	h_K^{FC} and $h_{B_0}^{\text{SZ-KE}}$	triplet	0	Act., HAHA	
SD/SZ-KE	h_K^{SD} and $h_{B_0}^{\text{SZ-KE}}$	triplet	2	Act.	
FC-II	h_K^{FC} and $h_{B_0}^{\text{SO}(1)}$	triplet	0,2,1	Act., HAHA	
SD-II	h_K^{SD} and $h_{B_0}^{\text{SO}(1)}$	triplet	0,2,1	Act.	
Third-order terms, $\langle\langle A; B; C \rangle\rangle_{0,0}$					
Symbol	A, B and C	Interm. states	Tensor	Type	
p /mv	$h_K^{\text{PSO}}, h_{B_0}^{\text{OZ}}$ and H^{mv}	singlet	0,2,1	Pass.	
p /Dar	$h_K^{\text{PSO}}, h_{B_0}^{\text{OZ}}$ and $h^{\text{Dar}(1)}$	singlet	0,2,1	Pass.	
FC-I	$h_K^{\text{FC}}, h_{B_0}^{\text{OZ}}$ and $h^{\text{SO}(1)}$	triplet and singlet ^d	0,2,1	Pass., HALA	
SD-I	$h_K^{\text{SD}}, h_{B_0}^{\text{OZ}}$ and $h^{\text{SO}(1)}$	triplet and singlet ^d	0,2,1	Pass., HALA	

^a See footnotes in Table 4.1.

^b Classification into passive/active as well as into HAHA/HALA (if known) categories.

^c The results of Ref. [156] point to the HAHA character.

^d Both triplet and singlet intermediate states contribute.

Ab initio calculations using the outlined theory for relativistic corrections to $\underline{\sigma}$ are presented in Papers I and II. In Paper II, calculations using SCF and MCSCF reference states and analytical response theory are carried out for both the isotropic shielding constants and second-rank anisotropic properties of the shielding tensors in hydrogen chalcogenides H_2X ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}$), hydrogen halides HX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{At}$), and noble gas atoms ($\text{Ne}, \text{Ar}, \text{Kr}, \text{Xe}, \text{Rn}$). The results are compared with data obtained from the 4-component calculations of Refs. [157] for H_2X , Ref. [151] for HX , and Ref. [140] for noble gases, as well as from experiments. No comparison with experimental results for heavy-atom shielding constants is presented, since the relationship between the shielding tensor and spin-rotation constant measurements, on which the available experimental data is based on, is not valid in the relativistic framework. The results of Paper II are illustrated in Fig. 4.1. Non-negligible relativistic effects are found both for the ^1H nuclei in heavy-

Table 4.3. Leading order, $\mathcal{O}(\alpha^6)$, relativistic contributions to the indirect spin-spin coupling tensor.^a

First-order terms, $\langle A \rangle$				
Symbol	A	Tensor	Type	
con-dip	$h_{KL}^{\text{con-dip}}$	2	Act.	
dip-dip	$h_{KL}^{\text{dip-dip}}$	0,2,1	Act.	
DSO-KE	$h_{KL}^{\text{DSO-KE}}$	0,2,1	Act.	
PSO-PSO	$h_{KL}^{\text{PSO-PSO}}$	0,2,1	Act.	
Second-order terms, $\langle\langle A; B \rangle\rangle_0$				
Symbol	A and B	Interm. states	Tensor	Type
DSO/mv	h_{KL}^{DSO} and h^{mv}	singlet	0,2,1	Pass.
DSO/Dar	h_{KL}^{DSO} and $h^{\text{Dar}(1)}$	singlet	0,2,1	Pass.
PSO/PSO-KE	H_K^{PSO} and $H_L^{\text{PSO-KE}}$ ($K \leftrightarrow L$)	singlet	0,2,1	Act.
FC/FC-KE	h_K^{FC} and $h_L^{\text{FC-KE}}$ ($K \leftrightarrow L$)	triplet	0	Act.
FC/SD-KE	h_K^{FC} and $h_L^{\text{SD-KE}}$ ($K \leftrightarrow L$)	triplet	2	Act.
SD/FC-KE	h_K^{SD} and $h_L^{\text{FC-KE}}$ ($K \leftrightarrow L$)	triplet	2	Act.
SD/SD-KE	h_K^{SD} and $h_L^{\text{SD-KE}}$ ($K \leftrightarrow L$)	triplet	0,2,1	Act.
FC/SO	h_K^{FC} and $h_L^{\text{SO}(1)}$ ($K \leftrightarrow L$)	triplet	0,2,1	Act.
SD/SO	h_K^{SD} and $h_L^{\text{SO}(1)}$ ($K \leftrightarrow L$)	triplet	0,2,1	Act.
Third-order terms, $\langle\langle A; B; C \rangle\rangle_{0,0}$				
Symbol	A, B and C	Interm. states	Tensor	Type
PSO/mv	$h_K^{\text{PSO}}, h_L^{\text{PSO}}$ and h^{mv}	singlet	0,2,1	Pass.
PSO/Dar	$h_K^{\text{PSO}}, h_L^{\text{PSO}}$ and $h^{\text{Dar}(1)}$	singlet	0,2,1	Pass.
FC/mv	$h_K^{\text{FC}}, h_L^{\text{FC}}$ and h^{mv}	triplet and singlet	0	Pass.
SD/mv	$h_K^{\text{SD}}, h_L^{\text{SD}}$ and h^{mv}	triplet and singlet	0,2,1	Pass.
FC/Dar	$h_K^{\text{FC}}, h_L^{\text{FC}}$ and $h^{\text{Dar}(1)}$	triplet and singlet	0	Pass.
SD/Dar	$h_K^{\text{SD}}, h_L^{\text{SD}}$ and $h^{\text{Dar}(1)}$	triplet and singlet	0,2,1	Pass.
SD/FC/mv	$h_K^{\text{SD}}, h_L^{\text{FC}}$ and h^{mv} ($K \leftrightarrow L$)	triplet and singlet	2	Pass.
FC/PSO	$h_K^{\text{FC}}, h_L^{\text{PSO}}$ and $h^{\text{SO}(1)}$ ($K \leftrightarrow L$)	triplet and singlet	0,2,1	Pass.
SD/PSO	$h_K^{\text{SD}}, h_L^{\text{PSO}}$ and $h^{\text{SO}(1)}$ ($K \leftrightarrow L$)	triplet and singlet	0,2,1	Pass.

^a See footnotes in Tables 4.1 and 4.2.

atom molecules, as well as for the heavy nuclei themselves, starting already in the second-row systems. According to this study, the active cross-term of the Fermi contact hyperfine operator and the relativistic modification of the spin-external field-Zeeman interaction (FC/SZ-KE) is mainly responsible for the large relativistic contribution of the shielding constant of the heavy nuclei. This mechanism is isotropic and of the HAHA [155] type. For the ^1H shielding tensor, in agreement with previous studies of e.g. Refs. [132, 133], the passive spin-orbit interaction contributions, FC-I and SD-I, were observed to be the dominant ones. The other terms were found to give smaller but non-negligible contributions. Among these contributions, a mutual cancellation occurs between terms that can be interpreted as dia- and paramagnetic relativistic corrections, in analogy with the NR theory.

According to the studies in Paper II, the present perturbational method is able to qual-

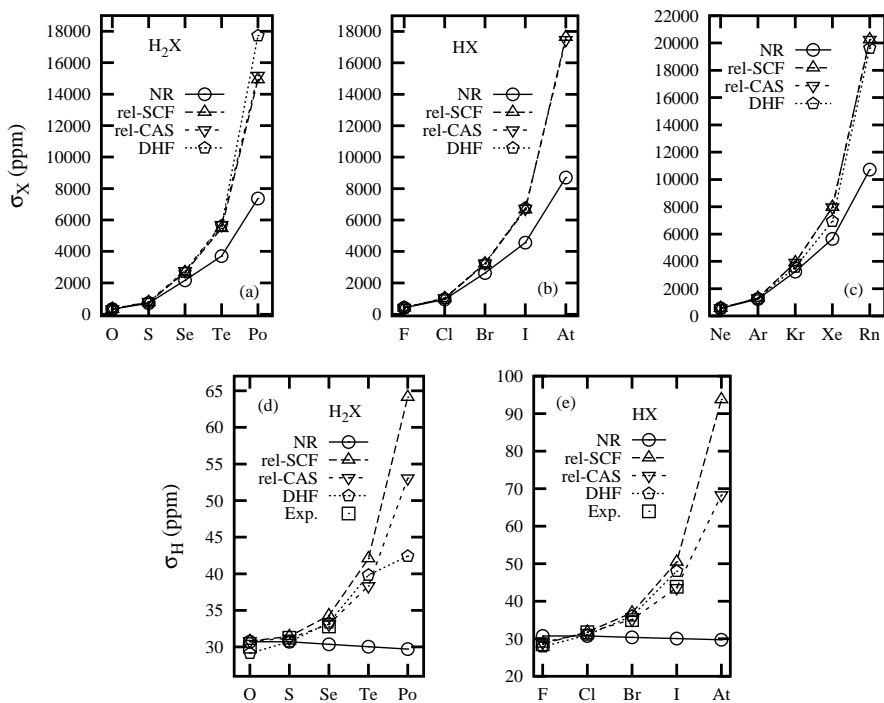


Figure 4.1. Nonrelativistic SCF (NR) as well as uncorrelated (rel-SCF) and correlated (rel-CAS), relativistically corrected nuclear shielding constants of X in (a) H_2X ($X = O, S, Se, Te, Po$), (b) HX ($X = F, Cl, Br, I, Ar$), and (c) X ($X = Ne, Ar, Kr, Xe, Rn$), and 1H in (d) H_2X and (e) HX . The reference data from four-component calculations and experiments is also presented.

itatively reproduce the shielding constants obtained using the computationally intensive four-component, fully relativistic method for both the heavy nuclei and the protons. In addition, the present accuracy is comparable to that obtained in the published quasi-relativistic calculations using the ZORA (e.g. Refs. [158–161]) or DKH (Refs. [162–166]) methods. Whereas the dominating HAHA contribution is very correlation-independent, the correlated calculations are in good agreement with the available experimental data for 1H shieldings in the studied systems. Nevertheless, all the first-order terms as well as the p -ke/OZ term were disregarded in this study.

Part of the presented relativistic contributions to \mathbf{J} are evaluated for the H_2Te molecule in Paper I. However, no systematic studies have been made thus far. In contrast to the rather promising performance in shieldings, the leading relativistic coupling contributions, in which two singular operators appear simultaneously, are found to diverge upon addition of high-exponent primitives to the basis set. Therefore, the present approach is less applicable to couplings than to shieldings. Among the studied contributions, the FC/SO term, introduced [152] and evaluated earlier [134], is dominating. Also, the PSO/mv and PSO/Dar contributions provide corrections of a few percent to the NR value.

The obtained coupling constants in Paper I ($J_{\text{HTe}} = -230.65$ Hz and $J_{\text{HH}} = -20.15$ Hz at SCF level and $J_{\text{HTe}} = -243.89$ Hz and $J_{\text{HH}} = -17.53$ Hz at CASSCF level) are significantly different to those obtained by four-component calculation ($J_{\text{HTe}} = 92.21$ Hz and $J_{\text{HH}} = -23.45$ Hz) as well as to the experimental value $J_{\text{HTe}} = -59 \pm 2$ Hz. Nevertheless, very definitive conclusions of the scheme cannot be made due to the lack of systematic numerical treatment.

4.2.2.2 ESR parameters

One-electron expressions that are linear in the electron spin and the external magnetic field up to $\mathcal{O}(\alpha^4)$ constitute the leading-order relativistic corrections to \mathbf{g} . These are presented in Table 4.4.

Paper III evaluates the contributions presented in Table 4.4 in dihalogen anions X_2^- ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) at the CASSCF level of theory, using large active spaces and basis sets. The results of Paper III are presented and compared to experimental data in Fig. 4.2. It was found that the largest relativistic contributions are provided by the mass-velocity and Darwin corrections of the leading-order $\mathcal{O}(\alpha^2)$ terms, and that the significance of the relativistic corrections grow rapidly, proportional to Z^4 with respect to the atomic number Z , whereas Paper II noted Z^3 dependence in the case of nuclear shielding constants. These two observations imply that a large part of the relativistic effects emerge from the core orbitals, which makes the ECP inclusion of relativistic effects [167] dubious. One of the other main conclusions of the study is that electron correlation has little significance in the relativistic corrections, at least in σ -type radicals. This may justify uncorrelated Dirac-Fock calculations of ESR g -tensors [168, 169].

When compared to the available experimental data, it is observed that the pronounced

Table 4.4. $\mathcal{O}(\alpha^4)$ contributions to the ESR g -tensor.^a

Second-order terms, $\langle\langle A; B \rangle\rangle_0$			
Symbol	A and B	Tensor	Type
CG/mv	$h_{B_0}^{\text{SO}}$ and h^{mv}	0,2,1	Pass.
CG/Dar	$h_{B_0}^{\text{SO}}$ and h^{Dar}	0,2,1	Pass.
SZ-KE/mv	$h_{B_0}^{\text{SZ-KE}}$ and h^{mv}	0	Pass.
SZ-KE/Dar	$h_{B_0}^{\text{SZ-KE}}$ and h^{Dar}	0	Pass.
OZ-KE/SO	$h_{B_0}^{\text{OZ-KE}}$ and $h^{\text{SO}(1)}$	0,2,1	Act.
Third-order terms, $\langle\langle A; B; C \rangle\rangle_{0,0}$			
Symbol	A, B and C	Tensor	Type
OZ/SO/mv	$h^{\text{SO}(1)}$, $h_{B_0}^{\text{OZ}}$, and h^{mv}	0,2,1	Pass.
OZ/SO/Dar	$h^{\text{SO}(1)}$, $h_{B_0}^{\text{OZ}}$, and h^{Dar}	0,2,1	Pass.

^a See footnotes in Table 4.1.

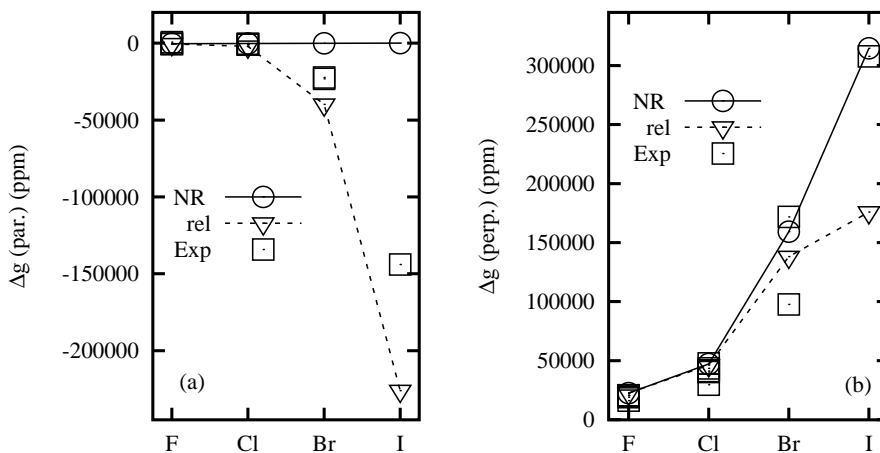


Figure 4.2. Non-relativistic (NR), relativistically corrected (rel), as well as experimental (Exp, Table IV of Paper V) (a) parallel and (b) perpendicular components of the g -shift tensor in X_2^- (X = F, Cl, Br, I) series.

decrease of the parallel (to the bond) g -tensor component as a result of relativistic effects is supported by the experiments. On the other hand, the calculated perpendicular components are in not as good an agreement with the experiments that also were in disagreement with one another. The lack of quantitative agreement is concluded to be partly due to the neglected environmental and matrix effects, and partly to the approximations used in the calculations, such as the neglect of two-electron contributions and the use of the singlet excitation manifold.

Relativistic corrections to the hyperfine coupling tensor are not among the topics of the present thesis. A perturbational relativistic approach to the SO effects on the hyperfine coupling tensor, similar to the ones discussed in this thesis, have recently been presented in Refs. [170, 171].

Papers I–III presented a framework for the perturbational inclusion of relativistic effects, based on expressions of the Breit-Pauli Hamiltonian, in magnetic resonance parameters. The effects of special relativity on magnetic resonance observables are known to be extremely important, and the studied method provides a keen method for their inclusion, as compared to both four-component and other quasi-relativistic approaches.

4.3 Magnetic-field dependence of NMR parameters

The magnetic field strengths used in modern NMR experiments are increasing. Therefore, it is important to understand the limits of the validity of the conventional assumption of field-independent NMR parameters. The possibility of field-dependent shielding was

proposed in Ref. [17], and an experimental observation was made in two Co(III) compounds [18]. Field-induced and -dependent quadrupole coupling in ^{131}Xe was reported in Ref. [172], and Ref. [173] provided a quantitative explanation for this observation. The theory formulated in that work was applied to molecules in Paper IV of the present thesis.

By expanding the electronic energy in a power series of perturbations \mathbf{I}_K and \mathbf{B}_0 , keeping only terms linear in \mathbf{I}_K and using Eq. (4.11), the nuclear shielding tensor can be written as (cf. Papers IV and V)

$$\begin{aligned}
\sigma_{K,\varepsilon\tau} &= \frac{1}{\gamma_K} \left(\frac{\partial^2 E}{\partial I_{K,\varepsilon} \partial B_{0,\tau}} \right)_0 + \frac{1}{3! \gamma_K} \sum_{\alpha\beta} \left(\frac{\partial^4 E}{\partial I_{K,\varepsilon} \partial B_{0,\tau} \partial B_{0,\alpha} \partial B_{0,\beta}} \right)_0 B_{0,\alpha} B_{0,\beta} \\
&+ \frac{1}{5! \gamma_K} \sum_{\alpha\beta\gamma\delta} \left(\frac{\partial^6 E}{\partial I_{K,\varepsilon} \partial B_{0,\tau} \partial B_{0,\alpha} \partial B_{0,\beta} \partial B_{0,\gamma} \partial B_{0,\delta}} \right)_0 B_{0,\alpha} B_{0,\beta} B_{0,\gamma} B_{0,\delta} \\
&+ \frac{1}{7! \gamma_K} \sum_{\alpha\beta\gamma\delta\zeta\eta} \left(\frac{\partial^8 E}{\partial I_{K,\varepsilon} \partial B_{0,\tau} \partial B_{0,\alpha} \partial B_{0,\beta} \partial B_{0,\gamma} \partial B_{0,\delta} \partial B_{0,\zeta} \partial B_{0,\eta}} \right)_0 \\
&\quad \times B_{0,\alpha} B_{0,\beta} B_{0,\gamma} B_{0,\delta} B_{0,\zeta} B_{0,\eta} \\
&+ \dots
\end{aligned} \tag{4.16}$$

Here the Greek subindices denote Cartesian coordinates and subscript 0 that the derivatives are taken at vanishing values of the perturbations. The terms with an even number of the components of \mathbf{B}_0 are not time-reversal invariant³ and are omitted from the expansion. The first term is the field-independent shielding tensor, denoted as $\underline{\underline{\sigma}}^{(0)}$. In the second term, the leading-order field-dependence tensor is the first derivative of the energy with respect to \mathbf{I}_K and the third derivative with respect to the components of \mathbf{B}_0 . It is denoted with four-index tensor $\underline{\underline{\tau}}_K$.

A similar treatment leads to expansions of the spin-spin and quadrupole couplings,

$$\begin{aligned}
J_{KL,\varepsilon\tau} &= \frac{1}{2\pi} \left(\frac{\partial^2 E}{\partial I_{K,\varepsilon} \partial I_{L,\tau}} \right)_0 + \frac{1}{2\pi} \frac{1}{3!} \sum_{\alpha\beta} \left(\frac{\partial^4 E}{\partial I_{K,\varepsilon} \partial I_{L,\tau} \partial B_{0,\alpha} \partial B_{0,\beta}} \right)_0 B_{0,\alpha} B_{0,\beta} \\
&+ \dots
\end{aligned} \tag{4.17}$$

$$\begin{aligned}
B'_{K,\varepsilon\tau} &= \frac{1}{2\pi} \left(\frac{\partial E}{\partial I_{K,\varepsilon} I_{K,\tau}} \right)_0 + \frac{1}{2\pi} \frac{1}{2!} \sum_{\alpha\beta} \left(\frac{\partial^3 E}{\partial I_{K,\varepsilon} I_{K,\tau} \partial B_{0,\alpha} \partial B_{0,\beta}} \right)_0 B_{0,\alpha} B_{0,\beta} \\
&+ \dots
\end{aligned} \tag{4.18}$$

The derivatives in the second term in both equations are the leading-order, quadratic, field-dependent contributions, which are $\underline{\underline{\kappa}}_{KL}$ for the spin-spin coupling and $\mathbf{B}'_K^{(2)}$ for quadrupole coupling.

The expressions of the field-dependence tensors show that energy terms that are linear in \mathbf{I}_K and contain a power three in the field contribute to $\underline{\underline{\tau}}_K$, terms that are linear in \mathbf{I}_K and \mathbf{I}_L and quadratic in the field to $\underline{\underline{\kappa}}_{KL}$, and terms that are bilinear in \mathbf{I}_K and quadratic in the field to $\mathbf{B}'_K^{(2)}$. Consideration of the relevant energy expressions formed from the one-electron terms of H^{BP} up to the power in α , in which the corresponding NR expressions

³Upon time reversal, $t \rightarrow -t$, the electron spin $s \rightarrow -s$, the nuclear spin $I \rightarrow -I$, and the magnetic field $B \rightarrow -B$, but for energies, $E \rightarrow E$ must hold. Therefore the energy term must be proportional to $I_K B_0^{2n+1}$ (shielding), $I_K I_L B_0^{2n}$ (spin-spin coupling) or $I_K^2 B_0^{2n}$ (quadrupole coupling), where $n = 1, 2, \dots$

Table 4.5. Leading-order contributions to the field-dependence of NMR observables.

Tensor	Second-order terms, $\langle\langle A; B \rangle\rangle_0$		Third-order terms, $\langle\langle A; B; C \rangle\rangle_{0,0}$	
	Symbol	A and B	Symbol	A, B and C
$\underline{\underline{I}}_K$	dia	$h_{KB_0}^{DS}$ and $h_{B_0^2}^{SUSC}$	dia-para	$h_{KB_0}^{DS}$, $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$
$\underline{\underline{K}}_{KL}$	DSO/dia	h_{KL}^{DSO} and $h_{B_0^2}^{SUSC}$	para-dia	h_K^{PSO} , $h_{B_0}^{OZ}$ and $h_{B_0^2}^{SUSC}$
	DS/dia	$h_{KB_0}^{DS}$ and $h_{LB_0}^{DS}$	para-dia	h_K^{PSO} , h_L^{PSO} and $h_{B_0^2}^{SUSC}$
$\mathbf{B}_K^{(2)}$	dia	h_K^{NQCC} and $h_{B_0^2}^{SUSC}$	FC/dia	h_K^{DSO} , $h_{B_0}^{OZ}$ and $h_{B_0^2}^{SUSC}$
			SD/dia	h_K^{SD} , h_L^{SD} and $h_{B_0^2}^{SUSC}$
			SD/FC/dia	h_K^{SD} , h_L^{FC} , $h_{B_0}^{SUSC}$ ($K \leftrightarrow L$)
			DS/PSO/OZ	$h_{KB_0}^{DS}$, h_L^{PSO} and $h_{B_0}^{OZ}$ ($K \leftrightarrow L$)
			para	h_K^{NQCC} , $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$
Fourth-order terms, $\langle\langle A; B; C; D \rangle\rangle_{0,0,0}$				
Symbol		A, B, C and D	Symbol	
$\underline{\underline{I}}_K$	para	h_K^{PSO} , $h_{B_0}^{OZ}$, $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$	A, B, C and D	
$\underline{\underline{K}}_{KL}$	para	h_K^{PSO} , h_L^{PSO} , $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$	FC/para	h_K^{FC} , h_L^{FC} , $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$
	SD/para	h_K^{SD} , h_L^{SD} , $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$	SD/FC/para	h_K^{SD} , h_L^{FC} , $h_{B_0}^{OZ}$ and $h_{B_0}^{OZ}$ ($K \leftrightarrow L$)

appear, yields the leading-order contributions to field-dependent NMR observables that are presented in Table 4.5. The field-dependence is seen to arise from the modification of the corresponding NR expressions by the operators responsible for dia- and paramagnetic magnetisability [174]. Purely diamagnetic (“dia”) and paramagnetic (“para”) terms can be described as elongations of the electronic cloud in the direction of or perpendicular to the field, respectively. In field-dependent spin-spin coupling, also cross-terms DS/DS and DS/PSO/OZ appear, the interpretation of which is not as straightforward. The analysis of field-dependent shielding is presented in Papers IV and V, and of quadrupole coupling in Paper VI, whereas the analysis of the field-dependent spin-spin coupling is previously unpublished.

In Paper IV, analytical response theory calculations for closed-shell alkali metal and halogen ions, as well as noble gas atoms, using high-quality multiconfigurational wave functions and large basis sets revealed that the effect is not of observable magnitude in closed-shell atomic systems. Due to the spherical symmetry of the reference state, contributions containing the $h_{B_0}^{OZ}$ operator do not participate, and only the zz component of the shielding tensor is modified by the field. In addition to the leading-order dependence coefficients, also the higher-order field-dependence coefficients of Eq. (4.17) were evaluated. The leading-order, quadratic corrections are positive in all the systems studied, as they are $\mathcal{O}(10^{-9})$ ppm/T² in magnitude, which corresponds maximally to 10^{-6} ppm in NMR spectrometers with ¹H resonance frequency of 1 GHz. This is far beyond being observable in current NMR spectrometers, and it is likely to remain so in the near future. The fourth- and sixth-power field-dependencies were of an order of 10^{-18} ppm/T² and 10^{-26} ppm/T², respectively.

Paper V introduces DFT and SCF calculations for the field-dependence of ⁵⁹Co nuclear shielding in the same Co(III) complexes in which the dependence was experimentally claimed in Ref. [18], [Co(NH₃)₆]³⁺ and Co(acetylacetonate)₃. The calculated isotropic averages of τ_K give rise to a decrease in the ⁵⁹Co shielding constant as compared to the normal field-independent shielding of -2.5×10^{-3} ppm/T² and -6.0×10^{-3} ppm/T² for [Co(NH₃)₆]³⁺ and Co(acetylacetonate)₃, respectively. The para-term is clearly the dominant one, at least in these systems, others giving three or more orders of magnitude smaller contributions. The calculated τ is of the same negative sign as observed experimentally, but one order of magnitude smaller than the experimental observation. In contrast to the case of closed-shell atoms discussed in Paper I, these changes may be observable in forthcoming experiments.

No numerical studies corresponding to the theoretical outline for $\underline{\underline{K}}_{KL}$ have yet been carried out because there are no implementations of fourth-order PT that involve triplet operators. The field-dependence of spin-spin coupling is clearly of scientific interest and will hopefully be addressed in the future.

Paper VI presented SCF, MCSCF, and DFT calculations of contributions to $\mathbf{B}'_K^{(2)}$ as well as their mass-velocity and Darwin corrections, for ²¹Ne, ³⁶Ar and ⁸³Kr nuclei in noble gas atoms, and ³³S in the SF₆ molecule. In addition, ^{47/49}Ti in TiF₄ and TiCl₄, ⁹¹Zr in ZrF₄, and ^{177/179}Hf in HfF₄ were estimated with SCF and DFT calculations. The field-independent quadrupole splitting vanishes in these systems due to the high site symmetry, which is spherical in noble gas atoms, O_h in SF₆ and T_d in group(IV) tetrahalides. A thus far experimentally unobserved quadrupole splitting of completely field-induced origin in molecules was predicted to amount to multiplet widths of 38.4 mHz/T² and 353.5 mHz/T²

in the experimentally most promising candidates, the ^{47}Ti resonance in TiCl_4 and ^{177}Hf resonance in HfF_4 . Furthermore, the field-induced splitting could be observable also in the ^{83}Kr spectrum, where the width of the nonet is predicted to be 5.2 mHz/T^2 .

In Papers IV–VI, the physical mechanisms of the field-dependence of shielding and quadrupole coupling (on the basis of Ref. [173]) were identified and evaluated. The field-dependence of both shielding and quadrupole coupling was concluded, albeit being experimentally observable in certain species, to have little significance in most NMR applications.

5 Conclusions

Theoretical and computational studies of the spectral parameters of magnetic resonance spectroscopies provide an independent supplement to experimental research. Within the last few years, theoretical studies of molecular properties have become routine, among them the spectral parameters of magnetic resonance. Molecular systems are studied using more accurate and more advanced techniques as well as more efficient computational strategies than ever before.

This thesis has two major themes, the perturbational treatment of the effects of special relativity as well as the external magnetic field-dependence of the parameters of magnetic resonance spectroscopies using second and higher-order analytical response theory and the standard Breit-Pauli molecular Hamiltonian. The studies are presented in the form of five research articles published in international journals and of one book chapter. The book chapter, Paper I, is a systematic survey of the inclusion of relativistic effects in nuclear magnetic shielding and indirect spin-spin coupling tensors in the Breit-Pauli framework. Paper II consists of numerical studies using this theory on a central nuclear magnetic resonance parameter, the nuclear magnetic shielding tensor. Paper III applies this approach to the g -tensor of electron spin resonance spectroscopy. The last three articles consider the external magnetic-field dependence of the NMR spectral parameters. Paper IV studies the case of field-dependent nuclear magnetic shielding in closed-shell atomic systems, and Paper V extends this discussion into molecules, studying the cobalt complexes in which an experimental observation of this phenomena has been claimed. Paper VI studies field-dependent and field-induced nuclear quadrupole coupling in noble gas atoms and molecular systems.

The non-relativistic treatment of magnetic resonance parameters is inevitably insufficient, and the effects of special relativity must be taken into account already in systems containing second-row elements. Not only those of heavy nuclei, but also the parameters of light nuclei are subjected to relativistic effects in such systems. The first main conclusion of this thesis is that the presented framework of perturbational inclusion of relativistic effects, using the Breit-Pauli level of theory, provides a straightforward tool to calculate these corrections, simultaneously allowing rigorous treatments of electron correlation and high-quality description of one-electron space. This scheme requires less programming effort than the alternative formulations based on other quasi-relativistic Hamiltonians, and its integrals are widely supported by the existing quantum chemical codes. The contribu-

tions are also straightforwardly interpretable with established chemical concepts. Despite the variational instability of the Breit-Pauli Hamiltonian, no divergencies or perturbation theory break-down occur in the calculation of nuclear shielding tensors in Paper II and g -tensors in Paper III. However, Paper I shows that these features limit the applicability of the scheme to spin-spin coupling tensors.

The second main conclusion is that the assumption of the field-independent nuclear magnetic shielding is, in the light of the results of this thesis, mostly justified. The calculations verify that these effects are vanishingly small in closed-shell atoms. In the case of molecules, the results qualitatively support the previous experimental observation. This effect, although certainly of experimentally observable magnitude in certain compounds, is small enough to be safely neglected in most nuclear magnetic resonance applications. The same conclusions apply to quadrupole coupling.

The Breit-Pauli framework provides a workable, practical method for the inclusion of the effects of special relativity in many molecular magnetic resonance properties, and it allows the identification of different physical mechanisms contributing to these complicated properties. This makes the presented approach a very valuable tool – after all, the main goal of computational chemistry is not to produce numbers, but to provide insight.

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