Quantum Chemical Calculations of EPR Parameters for Transition Metal Complexes

Von der Fakultät Chemie der Universität Stuttgart zur Erlangung der Würde eines Doktors der Naturwissenschaften (Dr.rer.nat.) genehmigte Abhandlung

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Tag der mündlichen Prüfung: 16. 8. 2001

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2001
Abstract

This thesis reports a series of theoretical studies of electron paramagnetic resonance (EPR) parameters for 3d transition metal complexes. The work focusses on the validation of various approaches based on density functional theory (DFT), on the interpretation of the EPR parameters in terms of electronic structure, and on the understanding of the physical mechanisms underlying the EPR magnetic interactions.

The performance of several DFT approaches for the calculation of EPR hyperfine coupling constants has been evaluated critically by comparison with experimental data and coupled-cluster results for 21 first-row transition metal systems. Isotropic couplings and coupling anisotropies for both metal and ligand nuclei have been calculated and discussed. While both gradient-corrected and hybrid functionals allow the calculation of isotropic metal hyperfine coupling constants to within ca. 10-15% for the less critical cases, none of the functionals investigated performs well for all complexes. Gradient-corrected functionals tend to underestimate the important core-shell spin polarization. While this may be improved by exact-exchange mixing in some cases, the accompanying spin contamination may even lead to a deterioration of the results for other complexes. We also identify cases, where essentially none of the functionals performs satisfactorily. In the absence of a "universal functional", the functionals to be applied to the calculation of hyperfine couplings in certain areas of transition metal chemistry have to be carefully selected. Desirable, improved functionals should provide sufficiently large spin polarization for core and valence shells without exaggerating it for the latter.

To obtain an in-depth understanding of the challenging points in the DFT description of the hyperfine interactions, a detailed quantum chemical analysis of the underlying principles of hyperfine coupling in 3d transition metal complexes has been carried out. The explicit evaluation of one- and two-electron integrals for some atomic systems has been used to understand the spin polarization of the core shells. While spin polarization enhances the exchange interaction of the 2s and 2p shells with the singly occupied orbitals, the opposite spin polarization of the 3s and 3p shells arises from the
required orthogonality to the 2s and 2p shells, respectively. Core-shell spin-polarization in molecules is found to be proportional to the spin population in the valence 3d orbitals but to depend little on other details of bonding. In contrast, the spin polarization of the valence shell depends crucially on the overlap between the singly occupied and certain doubly occupied valence orbitals. Large overlap leads to pronounced spin polarization of these orbitals and, among other things, likely to spin contamination when using UHF wave functions or hybrid density functionals. The role of core- and valence-shell spin-polarization for dipolar hyperfine couplings in transition metal complexes is discussed. It is demonstrated that great care should be exercised in deriving spin populations or even orbital compositions from dipolar couplings alone.

A new DFT implementation of electronic g-tensors within the deMon code including all relevant perturbation operators has been validated in a further part of this thesis. In contrast to the good performance for main-group species, the overall g-shifts obtained for the 3d transition metal complexes are underestimated typically by ~40-50% upon inclusion of both one-electron and two-electron spin-orbit operators. We attribute this to a systematical underestimation of the paramagnetic contributions and expect that the inclusion of Hartree-Fock exchange in the density functional should improve the performance of the method.

In the last part of this work, DFT calculations of electronic g-tensors and metal hyperfine coupling tensors have been carried out for a series of four vanadyl complexes with structures ranging from nearly trigonal bipyramidal to nearly square pyramidal. The EPR spectroscopic parameters have been rationalized in terms of electronic and geometrical structures. Using all relevant perturbation operators together with local or gradient-corrected density functionals, Δg-tensor components are underestimated systematically by ca. 40%. Good agreement with experiment is obtained for hyperfine tensor components calculated with hybrid functionals. The rhombicity of the hyperfine tensor is reproduced well at all levels of theory applied. It is mainly determined by the SOMO composition. The latter explains the increasing rhombicity of the A-tensor with increasing square-pyramidal-to-trigonal-bipyramidal distortion along the series of complexes studied. The orientational dependence of the principal tensor components on the local vanadium coordination is much more pronounced for the g-tensor than for the A-tensor.
Acknowledgments

It is a pleasure to thank those who made it possible for me to write this thesis. I would particularly like to acknowledge my advisor, Professor Martin Kaupp (University of Würzburg), for the remarkable research cooperation and the continuous support of my interest in science. The years of our joint work would perhaps never have become a reality without the kind help of Professor Emil Roduner, University of Stuttgart, to whom I would like to express my sincere gratitude. Professor Wolfgang Kaim, University of Stuttgart, is acknowledged for reviewing and commenting the thesis.

The major part of my graduate studies took place at Max-Planck-Institute for Solid State Research in Stuttgart, Germany. I would like to thank Professors Hans Georg von Schnering and Martin Jansen, the heads of a solid state chemistry department, for placing the facilities at my disposal.

Many thanks are due to my coworkers and friends Drs. Juha Vaara (Helsinki), Bernd Schimmelpfennig (Stockholm), Vladimir G. Malkin, and Olga L. Malkina (Bratislava), and Daniel Sebastiani (Mainz). Besides the many useful discussions we have had, they created a very stimulating and encouraging working atmosphere that has been vital to me. Special thanks are due to Juha Vaara, Vladimir G. Malkin, and Daniel Sebastiani for reviewing and commenting chapters of this thesis.

Part of the work reported in this thesis has been done at Masaryk University in my home city of Brno. Docent Pavel Kubáček, my advisor there, is thanked not only for the support and research cooperation directly related to the work reported here, but also for encouraging my interest in quantum chemistry since the beginning of my undergraduate studies. I would like to thank my colleague Petr Holub for his help in many technical questions.

The last period of my graduate studies - an exchange stay at Cornell University - has not been directly related to the subject of this thesis, but it certainly left its mark on it and on me. I am grateful to Professor Roald Hoffmann and all members of his group for the many stimulating discussions, and for the privilege of sharing a truly exciting atmosphere of scientific cooperation and friendship.
I am grateful to my parents, sisters and brothers who have supported and believed in me over many years. The walls between scholarship and family life are often more permeable than they appear. I am grateful to Dominik, my partner in life, love and intellectual pursuits, for his help, support, and understanding over the years of my graduate studies. This thesis, that has been so much shaped by our joint discussions, is dedicated to him.

Brno, June 15 2001                                          Markéta Munzarová
## List of Abbreviations

<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AMFI</td>
<td>one-center mean-field approximation to SO integrals</td>
</tr>
<tr>
<td>ANO</td>
<td>atomic natural orbital (basis set)</td>
</tr>
<tr>
<td>BH</td>
<td>hybrid functional for exchange including 50% of exact exchange and 50% of Becke’s GGA for exchange</td>
</tr>
<tr>
<td>BHLYP</td>
<td>exchange-correlation functional with BH functional for exchange and LYP GGA for correlation</td>
</tr>
<tr>
<td>BHPW91</td>
<td>exchange-correlation functional with BH functional for exchange and PW91 GGA for correlation</td>
</tr>
<tr>
<td>BHP86</td>
<td>exchange-correlation functional with BH functional for exchange and P86 GGA for correlation</td>
</tr>
<tr>
<td>BLYP</td>
<td>exchange-correlation functional with Becke’s GGA functional for exchange and LYP GGA for correlation</td>
</tr>
<tr>
<td>BPW91</td>
<td>exchange-correlation functional with Becke’s GGA functional for exchange and PW91 GGA for correlation</td>
</tr>
<tr>
<td>BP86</td>
<td>exchange-correlation functional with Becke’s GGA functional for exchange and P86 GGA for correlation</td>
</tr>
<tr>
<td>B3</td>
<td>Becke’s three-parameter hybrid functional for exchange</td>
</tr>
<tr>
<td>B3LYP</td>
<td>exchange-correlation functional with B3 functional for exchange and LYP GGA for correlation</td>
</tr>
<tr>
<td>B3PW91</td>
<td>exchange-correlation functional with B3 functional for exchange and PW91 GGA for correlation</td>
</tr>
<tr>
<td>CC</td>
<td>coupled cluster (theory)</td>
</tr>
<tr>
<td>CCSD</td>
<td>CC with single and double substitutions</td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>CCSD with triple substitutions</td>
</tr>
<tr>
<td>CGTO</td>
<td>contracted Gaussian type orbital</td>
</tr>
<tr>
<td>CI(SD)</td>
<td>configuration interaction (with single and double excitations)</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DZ</td>
<td>double-(\zeta) (basis)</td>
</tr>
<tr>
<td>ECP</td>
<td>effective core potential</td>
</tr>
<tr>
<td>Term</td>
<td>Definition/Description</td>
</tr>
<tr>
<td>---------------</td>
<td>----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>GGA</td>
<td>generalized gradient approximation</td>
</tr>
<tr>
<td>GIAO</td>
<td>gauge-including atomic orbital</td>
</tr>
<tr>
<td>GTO</td>
<td>Gaussian type orbital</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock (theory)</td>
</tr>
<tr>
<td>HFC(C)</td>
<td>hyperfine coupling (constant)</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied MO</td>
</tr>
<tr>
<td>IGLO</td>
<td>individual gauge for localized orbitals (method)</td>
</tr>
<tr>
<td>KS</td>
<td>Kohn-Sham (theory)</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>L(S)DA</td>
<td>local (spin) density approximation</td>
</tr>
<tr>
<td>LYP</td>
<td>Lee-Yang-Parr (correlation functional)</td>
</tr>
<tr>
<td>MCSCF</td>
<td>multiconfigurational SCF (theory)</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>MP2</td>
<td>second-order Møller-Plesset many-body (perturbation) theory</td>
</tr>
<tr>
<td>MRCI</td>
<td>multireference configuration interaction</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>NR</td>
<td>nonrelativistic (approach)</td>
</tr>
<tr>
<td>PT</td>
<td>perturbation theory</td>
</tr>
<tr>
<td>PW91</td>
<td>Perdew-Wang (correlation functional)</td>
</tr>
<tr>
<td>P86</td>
<td>Perdew 1986 (correlation functional)</td>
</tr>
<tr>
<td>QR</td>
<td>quasi-relativistic (approach)</td>
</tr>
<tr>
<td>ROHF/KS</td>
<td>restricted open-shell HF/KS (method)</td>
</tr>
<tr>
<td>R/U CCSD</td>
<td>restricted/unrestricted CCSD</td>
</tr>
<tr>
<td>SCF</td>
<td>self consistent field</td>
</tr>
<tr>
<td>SO</td>
<td>spin-orbit (integral, contribution, Hamiltonian)</td>
</tr>
<tr>
<td>SOMO</td>
<td>singly-occupied MO</td>
</tr>
<tr>
<td>SOS-DFPT</td>
<td>sum-over-states density-functional perturbation theory</td>
</tr>
<tr>
<td>SQP-5</td>
<td>five-coordinate, square pyramidal (structure)</td>
</tr>
<tr>
<td>SOO</td>
<td>spin-other-orbit</td>
</tr>
<tr>
<td>SSO</td>
<td>spin-same-orbit</td>
</tr>
<tr>
<td>STO</td>
<td>Slater type orbital</td>
</tr>
<tr>
<td>SVWN</td>
<td>exchange-correlation functional with Dirac exchange and VWN correlation</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>TBP-5</td>
<td>five-coordinate, trigonal bipyramidal (structure)</td>
</tr>
<tr>
<td>TZ</td>
<td>triple-(\zeta) (basis)</td>
</tr>
<tr>
<td>UDFT</td>
<td>uncoupled DFT</td>
</tr>
<tr>
<td>UHF/KS</td>
<td>unrestricted HF/KS (method)</td>
</tr>
<tr>
<td>VS</td>
<td>valence shell</td>
</tr>
<tr>
<td>VWN</td>
<td>Vosko-Wilk-Nusair (correlation functional)</td>
</tr>
<tr>
<td>ZORA</td>
<td>Zero order regular approximation (for relativistic effects)</td>
</tr>
</tbody>
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1 Zusammenfassung

Zusammenfassung

Quantenchemische Untersuchungen der EPR-Parameter von Übergangsmetallverbindungen


Ein weiteres Vorhaben dieser Arbeit war die Anwendung von DFT-Berechnungen von EPR-Parametern auf Fragen aus der bioanorganischen Chemie. Ein interessantes Thema ist hier die biochemische Funktion von Vanadium, die mit der Fähigkeit des Vanadates, eine vierfachkoordinierte, tetraedrische Geometrie, sowie eine fünffachkoordinierte, trigonal-bipyramidale (TBP-5) Geometrie einzunehmen, oft verbunden ist. Die trigonal-bipyramidale Koordination scheint bei den Komplexen des Vanadiums (IV) und Vanadiums (V) auf sterisch eingeschränkte Systeme begrenzt zu

1.1 Kritische Untersuchung von Dichtefunktional- und coupled cluster Methoden zur Berechnung von EPR-Hyperfeinkopplungskonstanten für Übergangsmetallverbindungen


Keines der momentan zur Verfügung stehenden Austausch-Korrelations-Funktionalen liefert über den gesamten Bereich eine hinreichende Spinpolarisation von


1.2 Mechanismen der EPR-Hyperfeinkopplung in Übergangsmetallverbindungen


core’ $p$-Orbitalen (hauptsächlich die $3p$-Orbitalen für die erste Übergangsmetallreihe),
die eine sehr ähnliche radiale Ausdehnung wie die Valenz-$d$-Schale aufweisen. Die
Spinpolarisation beeinflußt nicht nur die doppelt besetzten Orbitale, sondern auch das
einzeln besetzte Orbital selbst. Für beispielsweise TiF$_3$ und MnO$_3$ hat die
Spinpolarisation eine interessante 3d/4s Rehybridisierung des einzeln besetzten Orbitals
zur Folge. Letzteres ist ein weiterer Grund, warum die Versuche, von der Anisotropie
des Kopplungstensors auf die Spinpopulation oder gar die Zusammensetzung der
Orbitale zu schließen, oft zu falschen Ergebnissen führen. Explizite quantenchemische
spin-polarisierte Berechnungen sollten hier bevorzugt werden.

Die Ergebnisse dieser Arbeit können außer zum Verständnis der Mechanismen
der EPR-Hyperfeinkopplung in Übergangsmetallverbindungen auch zur Identifizierung
von Fehlern in theoretischen Ansätzen dienen, und darüberhinaus hoffentlich zur
Entwicklung verbesserter Methoden führen.

1.3 DFT-Berechnung elektronischer $g$-Tensoren in
Übergangsmetallkomplexen mit Hilfe von Mean-Field Spin-Bahn-
Operatoren$^5$

Eine neue störungstheoretische DFT-Methode zur Berechnung elektronischer $g$-
Tensoren im Programm “deMon“ wurde für einen Satz von 14
Übergangsmetallverbindungen validiert. Die atomare Natur der verwendeten Mean-
Field Spin-Bahn-Operatoren erlaubte eine weitergehende Analyse und Interpretation
atomarer Beiträge zum beobachteten $g$-Tensor.

Im Gegensatz zu den guten Ergebnissen für Hauptgruppensysteme sind die
Abweichungen vom Experiment für die Übergangsmetallkomplexe relativ groß. Die
Verwendung von Zweielektronen-Spin-Bahn-Operatoren verschlechtert ganz erheblich
die Übereinstimmung mit dem Experiment. Die Zweielektronen-Operatoren reduzieren
die $g$-Verschiebungen um ~40-50%, so dass ein linearer Fit mit einer Richtwert von
0.59 erhalten wird wenn sowohl die die Einelektronenterme wie auch die
Zweielektronenterme eingerechnet werden. Diese Beobachtung entspricht
überraschenderweise den von Bühl at al.$^6,7$ berichteten Ergebnissen in einer
Validierungsuntersuchung von GGA-Dichtefunktionalmethoden für die Berechnung von NMR chemischen Verschiebungen für 3d-Übergangsmetallkernen. UDFT-GIAO-Berechnungen mit Hilfe gradientenkorrigierter Funktionale haben ein Richtwert von ~0.6 im Vergleich mit dem Experiment ergeben. Letzteres läßt sich auf die systematische Unterschätzung der paramagnetischen Anteile von ungefähr 40% zurückverfolgen.

In Übereinstimmung mit dem Vorschlag von Patchkowskii and Ziegler\(^8\) wird dies auf die Unfähigkeit der lokalen/gradientenkorrigierten Dichtefunktionalen zurückgeführt, die jeweiligen Störungsmatrixelemente sowie die Energienenner gut zu beschreiben. Bühl berichtete eine Verbesserung der Richtwert bis beinahe 1.0 bei der Anwendung von HF/DFT-Hybrid-Funktionalen (B3LYP bzw. B3PW91).\(^7\) Vom Gesichtspunkt der formalen Ähnlichkeit des Shieldingtensors und des \(g\)-Tensors ist eine Verbesserung der Ergebnisse bei der Anwendung von HF-DFT-Hybridfunktionalen auch für die \(g\)-Tensoren zu erwarten. Vorläufige Ergebnisse haben bestätigt, daß die Anwendung von HF/DFT-Hybrid-Funktionalen tatsächlich zur Verbesserung der Ergebnissen führen soll.\(^9\)

1.4 DFT-Berechnung der EPR-Parameter für Vanadyl-Schiff-Base-Komplexe\(^10\)

DFT-Untersuchungen der EPR-Hyperfeinkopplungstensoren und \(g\)-Tensoren für Vanadyl-Schiff-Base Komplexe wurden durchgeführt. Folgende Komplexe wurden untersucht: \([\text{N},\text{N}´\text{-ethylenbis(o-tert-butyl-p-methyalsalicylaldiminato)}]\) oxovanadium(IV), bis(\(N\)-methylsalicylaldiminato) oxovanadium(IV), bis(\(N\)-methyl-o-(tert-butyl-p-methyalsalicylaldiminato) oxovanadium(IV), und bis(2-methylquinolin-8-olat) oxovanadium(IV).

Die Hauptkomponenten der \(A\)- und \(g\)-Tensoren wurden berechnet und interpretiert. Zusätzlich liefert die Rechnung die Orientierung der \(A\)- und \(g\)-Tensoren relativ zum Molekulgerüst, die experimentell in diesen Fällen nicht zugänglich ist. Die Orientierung des \(A\)-Tensors relativ zum \(g\)-Tensor ist experimentell einfacher zu erhalten und konnte für bis(2-methylquinolin-8-olat) oxovanadium(IV) bestimmt werden.


Der experimentell gefundene Zusammenhang zwischen der Anisotropie des $A$-Tensors und der lokalen Oxovanadium-Koordination wurde auf der DFT-Niveau reproduziert, analysiert und mit Hilfe der V-$3d_{z^2}$-Beiträge zum einzeln besetzten Orbital (überwiegend V-$3d_{x^2}-y^2$) interpretiert. Letztere Beiträge sind dank der Verzerrung der SQ-5 Koordination zur TBP-5 Koordination möglich. Für den bis(N-methyl-o-(tert-butyl-p-methylsalicylaldiminato)oxovanadium(IV) Komplex, der überdies eine erhebliche Verzerrung von der $C_2$-Symmetrie aufweist, sind auch die voneinander verschiedenen Metall-$d_{xz}$, Metall-$d_{yz}$ Beimischungen in das einzeln besetzte Orbital von Bedeutung. Der Zusammenhang zwischen der Anisotropie des $A$-Tensors und der lokalen Metall-Koordination sollte für die EPR-unterstützte strukturelle Charakterisierung biochemisch relevanter Komplexe im Allgemeinen von Bedeutung sein.

Die vorliegende Arbeit dient nicht nur zur Interpretation experimenteller Trends in magnetischen Wechselwirkungen, sondern auch als eine weitere Validierungsuntersuchung von Dichtefunktionalmethoden zur Berechnung von EPR-Parametern für Übergangsmetallverbindungen. Die hier untersuchte Vanadyl-Komplexe weisen ein einzeln besetzte Orbital auf, welches relativ wenig mit den doppelt besetzten

Wie bereits in unserer Validierungsuntersuchung der DFT-Methode zur Berechnung elektronischer $g$-Tensoren gefunden,\textsuperscript{5} unterschätzen die lokale Dichtenäherung sowie die gradientenkorrigierten Austausch-Korrelations-Funktionale systematisch die paramagnetischen Anteile zu ungefähr 40\%. Eine Verbesserung der Ergebnisse ist jedoch bei Anwendung von HF-DFT-Hybridfunktionalen zu erwarten.\textsuperscript{9}
Literatur


2 Introduction

2.1 Background and Motivation

Electron paramagnetic resonance spectroscopy (EPR) is a branch of magnetic resonance spectroscopy dealing with molecules in which the total spin quantum number S is different from zero. In such molecules, the probability of finding at any point an electron with spin “up” minus the probability of finding there an electron with spin “down”, the spin density, is generally nonzero. Associated with this net electronic spin is a magnetic moment giving rise to two degenerate energy levels. In the presence of an external magnetic field, this degeneracy is lifted due to the electronic Zeeman interaction, and the levels are split by an amount proportional to the field strength. The basic EPR experiment consists of observing a transition between these two energy levels. Most of the EPR spectra, however, do not consist of a single line but do have a hyperfine structure that arises due to interactions between the electronic spin density and nuclear spins in the radical.

Most of the nondynamic information obtained from EPR is an information on the spin density distribution. This in turn provides information on the structure of the molecule observed. An important intermediate in the interpretation of the EPR spectra is the spin Hamiltonian, a model that summarizes the experimental data in terms of small number of parameters. Within the spin Hamiltonian concept, the electronic Zeeman interaction between the net electronic spin and the external magnetic field is parametrized by the electronic g-tensor; the hyperfine interaction between the electron and nuclear spins is described by the hyperfine $A$-tensor.
The hyperfine structure is often considered to be the most important part of information obtained from an EPR spectrum, due to a very direct connection between the spin density at (near the) nucleus and the isotropic (anisotropic) part of the hyperfine tensor. Since the early days of EPR, the interpretation of hyperfine coupling has been an example of a particularly fruitful interaction between theory and experiment. Substantial qualitative understanding has been obtained for organic free radicals as well as for transition metal complexes. Quantitative theoretical studies of the hyperfine coupling have, however, concentrated largely on organic molecules or on other light main group systems. This is understandable, as the accurate inclusion of electron-correlation effects is mandatory for quantitative calculations of electron-nuclear hyperfine interactions. To achieve this in traditional post-Hartree-Fock \textit{ab initio} calculations is far from trivial, and such treatments are not easily applicable to larger transition metal compounds. Yet, recent interest in applications of EPR to transition metal complexes in catalysis, bioinorganic chemistry, or materials research make the quantitative theoretical treatment of such systems highly desirable.

An alternative theoretical approach has been provided by recent developments in density functional theory (DFT) that includes electron correlation approximately, at moderate computational cost. A number of Kohn-Sham DFT studies on transition metal hyperfine coupling have appeared. However, only a limited number of density functionals and basis sets have been employed, and only a relatively small set of molecules and electronic-structure situations was covered. In order to be able to judge in detail the ability of the available DFT approaches to describe the hyperfine coupling for transition metal systems, further systematic studies were needed.

2.2 Objectives of the Study

The primary objective of the work reported in this thesis was to perform a validation study of density functional approaches for the calculations of EPR hyperfine coupling for a series of first-row transition metal complexes. The author's aim was to compare the results obtained for a series of density functionals with experiment, to identify functionals suitable for further application calculations, and to employ these
calculations for the interpretation of spectra of chemically interesting systems. Throughout the validation study, the author has learned much about the mechanisms of transfer of the spin density from the valence shell to the transition metal nuclei. These interpretational aspects became subjects of a separate study. The final objective was to validate a new DFT implementation of electronic $g$-tensor calculations within the deMon code for a series of $3d$ transition metal complexes, as well as to apply the new methods.

The present thesis consists of an introductory part (Chapters 1 through 3), four commented papers summarizing the author’s work in the field of theoretical studies of EPR parameters (Chapters 4 through 7), and a conclusion part (Chapter 8). The topics introduced in this chapter (Chapter 1) are dealt with in more detail in subsequent chapters. Chapter 2 describes the theory of the spectral parameters of electron paramagnetic resonance. The concept of the EPR spin Hamiltonian is introduced, followed by a discussion of the perturbation theory approach to the calculation of two of its parameters, $g$- and $A$-tensors. Chapter 3 is devoted to an overview of $ab\text{ initio}$ computational methods employed in this thesis for obtaining the field-free description of the molecular ground state. Chapter 4 reports the results of the extensive evaluation of DFT methods for the prediction of hyperfine coupling constants for both metals and ligands in $3d$ transition metal complexes. The results of the validation study of new DFT methods for the calculation of electronic $g$-tensors for a set of $3d$-transition metal complexes are reported in Chapter 5. Chapter 6 describes the results of a detailed study of the mechanisms of EPR hyperfine coupling in transition metal complexes. Finally, a DFT application study of $g$- and $A$-tensors for a series of vanadyl complexes is reported in Chapter 7. A number of general conclusions are given in Chapter 8.

SI conventions are assumed throughout this thesis and recommended symbols are employed, with three small exceptions. $4\pi\varepsilon_0$ ($\varepsilon_0$ being the permitivity of free space) is often denoted by the single symbol $\kappa_0$; $\beta_e$ has been retained for the Bohr magneton (recommended symbol $\mu_B$), and $\beta_N$ for the nuclear magneton (recommended symbol $\mu_N$). Instead of $\mu_0/4\pi$ ($\mu_0$ being the permeability of free space), we have used the equivalent combination $1/\kappa_0 c^2$, $c$ being the velocity of light.

Atomic units are employed throughout Chapter 3 of this thesis and the original papers. We note that in atomic units, $e$, $\hbar$, $m$ and $\kappa_0$ all take unit values and may thus be
dropped from all equations provided the symbols occurring are reinterpreted as the numerical (i.e. dimensionless) measures of the quantities they represent.
The electron is not as simple as it looks.

William Lawrence Bragg (1890-1971)

3 Electron Paramagnetic Resonance Parameters

This chapter discusses the theory of the spectral parameters of electron paramagnetic resonance. We introduce the concept of the EPR spin Hamiltonian and explain the perturbation-theory (PT) approach to the calculation of two of its parameters: the $g$- and $A$-tensors. Our approach is based on a PT treatment of the Breit-Pauli Hamiltonian. The conceptual sequence from the relativistic Dirac Hamiltonian through the Breit-Pauli Hamiltonian to the EPR spin Hamiltonian is sketched, following refs 1, 2, 3, and 4. A unified theoretical treatment of $g$- and $A$-tensors is provided up to second-order perturbation theory. Important links between the spin Hamiltonian parameters and qualitative aspects of electronic structure are established, following the discussion in refs 5 and 6.

3.1 Electron Spin: A Theoretical Rationale

The technique of electron paramagnetic resonance spectroscopy may be regarded as a fascinating extension of the famed Stern-Gerlach experiment. In one of the most fundamental experiments on the structure of matter, Stern and Gerlach in 1922 showed that an electron magnetic moment in an atom can take only discrete orientations in a magnetic field, despite the sphericity of the atom. As a theoretical rationalization of this striking observation that could not be explained along the lines of quantum mechanics, Uhlenbeck and Goudsmith postulated in 1925 that electrons possessed an intrinsic angular momentum – electron spin. This would give rise to an intrinsic magnetic momentum of the electron, independent of any translational motion.
3.1.1 Pauli Spin Matrices

The concept of electron spin has been incorporated into quantum mechanics in 1927 by Pauli\(^9\) who postulated that a full characterization of electronic behavior requires, in addition to a spatial function \(\phi(r)\), a parameter of electron spin \(\sigma\). The electron spin was suggested to be a combination of degenerate but orthogonal functions

\[
\alpha = \begin{bmatrix} 1 \\ 0 \end{bmatrix} ; \quad \beta = \begin{bmatrix} 0 \\ 1 \end{bmatrix} .
\]

(3.1)

It can be obtained as an expectation value of the operator \(\sigma = (\sigma_x, \sigma_y, \sigma_z)\), where

\[
\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}
\]

(3.2)

are the Pauli spin matrices.

3.1.2 The Dirac Equation

The Pauli treatment of spin inspired Dirac in his effort to develop a theory, in which the electron spin and magnetic moment would arise naturally: "The question remains as to why Nature should have chosen this particular model for the electron instead of being satisfied with the point-charge. One would like to find some incompleteness in the previous methods of applying quantum mechanics to the point-charge electron that, when removed, the whole of the duplexity phenomena [spin effects] follow without arbitrary assumptions."\(^10\) This goal has been achieved when Dirac rederived quantum mechanics within Einstein’s special relativity theory, providing thus a formalism in which it was possible to explain all magnetic effects known at the time and predict numerous additional phenomena.

Using Einstein’s relationship between total energy, momentum, and a rest mass \(m\) of a free particle, a relativistic version of the free-particle Schrödinger equation
\[ \frac{-\hbar}{i} \frac{\partial \Psi}{\partial t} = \pm c \sqrt{-\hbar^2 \nabla^2 + m^2 c^2} \Psi. \]  

(3.3)

can be obtained. It is, however, not clear how to interpret the square root in the relativistic Hamiltonian. Dirac circumvented this problem by setting

\[ \sqrt{-\hbar^2 \nabla^2 + m^2 c^2} = \frac{\hbar}{i} \nabla \alpha + \beta mc \]

(3.4)

where \( \beta \) is some scalar and \( \alpha=(\alpha_1, \alpha_2, \alpha_3) \). Equation (3.4) can only be satisfied if

\[ \begin{align*}
[\alpha_i, \alpha_j] &= 0 \quad , \quad i \neq j \quad ; \quad [\alpha_i, \beta] = 0 \quad ; \quad \alpha_i^2 = \beta^2 = 1 .
\end{align*} \]

(3.5)

In the simplest possible solution of the system (3.5), \( \alpha \) and \( \beta \) are (4x4) matrices, the explicit form of which can be found elsewhere.³ The important fact is that the (4x4) nature of the operators implies a four-component relativistic wave function

\[ \Psi(r,t) = \begin{bmatrix} \Psi_1(r,t) \\ \Psi_1'(r,t) \\ \Psi_2(r,t) \\ \Psi_2'(r,t) \end{bmatrix} . \]

(3.6)

The Dirac equation

\[ \frac{-\hbar}{i} \frac{\partial \Psi}{\partial t} = \left( \frac{hc}{i} \nabla \alpha + \beta mc^2 \right) \Psi \]

(3.7)

thus represents a set of four partial differential equations. Of its four solutions, only two correspond to normal electronic behavior. They account for the existence of the \( \alpha \) and \( \beta \) spin states postulated by Pauli (see next section), and for a number of other relativistic quantum effects. The two other solutions were found to describe a particle not known at the moment of Dirac’s publication - with electronic properties except for an opposite charge. Four years later, the discovery of the positron – a particle perfectly matching this description – upheld the triumph of Dirac theory.
3.1.3 Pauli Reduction of the Dirac Equation

The Dirac equation can be solved exactly only for the most simple systems. It is thus desirable to generate approximations that are more easily solved but still contain the essential features of the Dirac formalism. A common approach to such approximations is looking for the relationships between the fully relativistic Dirac theory of the electron and the nonrelativistic theory where spin is treated in the Pauli sense. There are two categories of reasons for wishing to establish a connection between these two theories. Firstly, understanding of a theory often depends to a large extent on a model in terms of which the predictions of the theory can be interpreted. There is a natural tendency to base new models on revisions of previous models, in this case to relate relativistic quantum mechanics to nonrelativistic quantum mechanics (and in turn, to classical mechanics). Secondly, in many cases relativistic effects are relatively small compared to the total quantities involved; it is thus advantageous from the computational point of view to treat them as perturbations with respect to the nonrelativistic case. The reduction of the fully relativistic theory with four-component wave functions to a non-relativistic theory with two-component wave functions is traditionally done using either the Foldy-Wouthuysen transformation or the partitioning approach. To demonstrate how Dirac theory accounts for the electronic Zeeman effect, we develop here the latter approach — the Pauli reduction of the Dirac equation, as applied to a free electron in a magnetic field.

For the description of the effect of a uniform magnetic field \( \mathbf{B} \) on an electron, we will use field-dependent momentum and energy operators

\[
\begin{align*}
\mathbf{p} &= -\frac{\hbar}{i} \nabla \\
\pi &= -\frac{\hbar}{i} \nabla + \frac{e}{c} \mathbf{A} \\
W &= -\frac{\hbar}{i} \frac{\partial}{\partial t} \\
\quad &\rightarrow \quad -\frac{\hbar}{i} \frac{\partial}{\partial t} + e\phi
\end{align*}
\]

(3.8)

Here \( \phi \) and \( \mathbf{A} \) are the scalar and vector potentials, from which the electric field strength \( E \) and magnetic flux density \( \mathbf{B} \), respectively, may be derived within classical
electromagnetic theory. Consequently, one obtains the field dependent version of the Dirac equation

$$\frac{-\hbar}{i} \frac{\partial \Psi}{\partial t} = (\epsilon \sigma \cdot \mathbf{a} + \beta mc^2 - e \phi) \Psi \ .$$

(3.9)

Because one is generally interested in the two electronic solutions only, it is desirable to reduce the (4x4) system of equations (2.9) to a (2x2) system by writing $\Psi$ in terms of two two-row spinors:

$$\Psi = \begin{bmatrix} \Psi_u \\ \Psi_l \end{bmatrix} ; \quad \Psi_u = \begin{bmatrix} \Psi_1 \\ \Psi_2 \end{bmatrix} ; \quad \Psi_l = \begin{bmatrix} \Psi_3 \\ \Psi_4 \end{bmatrix} \ .$$

(3.10)

Partitioning $\alpha$ and $\beta$ accordingly, one obtains

$$\alpha = \begin{bmatrix} 0 & \sigma \\ \sigma & 0 \end{bmatrix} , \quad \beta = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \ .$$

(3.11)

Here $1$ and $0$ are (2x2) unity and zero matrices, respectively; and the components $\sigma_x$, $\sigma_y$, $\sigma_z$ of the operator $\sigma$ are the Pauli spin matrices (3.2).

Within this formalism, the Dirac equation can be written as

$$mc^2 \Psi_u + c \sigma \cdot \mathbf{a} \Psi_l = W \Psi_u$$

$$c \sigma \cdot \mathbf{a} \Psi_u - mc^2 \Psi_l = W \Psi_l \ .$$

(3.12)

The total energy $W$ can be separated into a sum of the rest mass $mc^2$ and all additional energy $\varepsilon$; so that (3.12) becomes

$$c \sigma \cdot \mathbf{a} \Psi_l = \varepsilon \Psi_u$$

(3.13)

$$c \sigma \cdot \mathbf{a} \Psi_u = (\varepsilon + 2mc^2) \Psi_l \ .$$

(3.14)

If we express $\Psi_l$ in terms of $\Psi_u$ using (3.14) and substitute it into (3.13), we obtain
\[
\frac{e^2 (\sigma \cdot \pi)^2}{\varepsilon + 2mc^2} \Psi_u = \varepsilon \Psi_u. \\
(3.15)
\]

In most conventional systems, the dominating term in the total energy is the rest mass \( (W \approx mc^2 >> \varepsilon) \). Therefore, we can make the approximation \( \varepsilon + 2mc^2 \approx 2mc^2 \) \((first\ Pauli\ limit)\), in which (3.15) becomes

\[
\frac{1}{2m} (\sigma \cdot \pi)^2 \Psi_u = \varepsilon \Psi_u. \\
(3.16)
\]

The latter expression can be rewritten as

\[
\frac{1}{2m} (\sigma \cdot \pi)^2 \Psi_u = \frac{1}{2m} \left[ \pi^2 + \frac{e\hbar}{c} \sigma \cdot B \right] \Psi_u = \left[ \frac{\pi^2}{2m} + \beta_e \sigma \cdot B \right] \Psi_u = \varepsilon \Psi_u,
\]

which is identical to Pauli’s empirical incorporation of electron spin into quantum mechanics.

If we expand \( \sigma \) and expect the magnetic field \( B \) to be oriented in the \( z \)-direction, we obtain a system of equations

\[
\begin{bmatrix}
\frac{\pi^2}{2m} + \beta_e B & 0 \\
0 & \frac{\pi^2}{2m} - \beta_e B
\end{bmatrix}
\begin{bmatrix}
\Psi_1 \\
\Psi_2
\end{bmatrix}
= \begin{bmatrix}
\varepsilon_1 \\
\varepsilon_2
\end{bmatrix}
\]

\[\text{(3.18)}\]

with two nontrivial solutions

\[
\Psi_1 = 0 \quad ; \quad \Psi_2 \propto \left| n,l,m_i \right> \quad ; \quad \varepsilon = 2n\beta_e B + \frac{l^2 \hbar^2}{2m} - e\phi
\]  

\[\text{(3.19)}\]

\[
\Psi_1 \propto \left| n,l,m_i \right> \quad ; \quad \Psi_2 = 0 \quad ; \quad \varepsilon = (2n + 2)\beta_e B + \frac{l^2 \hbar^2}{2m} - e\phi.
\]  

\[\text{(3.20)}\]

Thus, when subjected to a magnetic field \( B \), two electronic states with identical spatial distribution vary in energy by an amount of \( 2\beta_e B \). Pauli’s approach, therefore, very closely approximates the Zeeman resonance condition for a free electron.
\[ h\nu = g_e \beta_e \mathbf{S} \cdot \mathbf{B}, \]

(3.21)

where \( \mathbf{S} \) is the electron spin angular momentum vector and \( g_e \) is the spectroscopic splitting factor. Dirac’s relativistic theory predicts \( g_e \) to be equal to 2 for a free electron. The discrepancy between this and the experimental value (2.002319304386) is attributed primarily to quantum electrodynamic effects.

In the first Pauli limit, eq (3.15) adopts a form where the terms proportional to \( 1/c^{2n} \) disappear, cf. (3.16). A transformation of eq (3.15) that keeps the terms proportional to \( 1/c^2 \) is called the second Pauli limit of the reduced Dirac equation. The resulting expression, called the Breit-Pauli Hamiltonian, provides tremendous insight into electromagnetic behavior of a free electron by accounting explicitly for the familiar spin-orbit coupling, the Darwin term, and the relativistic correction to the kinetic energy.

3.2 The Breit-Pauli Hamiltonian for Many-Particle Systems

The extension of the approach described above to many-particle systems is based on, first, a generalization of the Dirac Hamiltonian to two particles, and then its application to a many-particle system in which all pairwise interactions are taken as additive. Here we present the terms of the Breit-Pauli Hamiltonian for a many-electron molecule in the absence of any external electric charges. The fixed-nucleus approximation is employed. We follow ref 2 in writing the Hamiltonian in the form

\[ H = H_e + H_N + H_eN. \]

(3.22)

The pure electronic term is then

\[ H_e = \sum_{m=1}^{12} H^e_m, \]

(3.23)

where (using \( \kappa_0 \) to denote \( 4\pi\varepsilon_0 \))
\[ H_i^e = \sum_i \frac{\pi_i^2}{2m_i}, \]  
\[ H_2^e = -e \sum_i \phi_i, \]  
\[ H_3^e = g_\epsilon \beta_\epsilon \sum_i (1 - \frac{\pi_i^2}{2m_i \kappa_0 c^2}) \mathbf{s}_i \cdot \mathbf{B}, \]  
\[ H_4^e = -\sum_i \frac{\pi_i^4}{8m_i^3 c^2}, \]  
\[ H_5^e = -\frac{g_\epsilon \beta_\epsilon}{4m_i c^2} \sum_i \left[ \mathbf{s}_i \cdot \pi_i \times \mathbf{E}_i - \mathbf{s}_i \cdot \mathbf{E}_i \times \pi_i \right], \]  
\[ H_6^e = -\frac{h \beta_\epsilon}{4m_i c^2} \sum_i \text{div } \mathbf{E}_i, \]  
\[ H_7^e = -\frac{e^2}{2\kappa_0} \sum_{i,j} \frac{1}{r_{ij}}, \]  
\[ H_8^e = -\frac{2\pi \beta_\epsilon^2}{\kappa_0 c^2} \sum_{i,j} \delta(\mathbf{r}_i - \mathbf{r}_j), \]  
\[ H_9^e = -\frac{g_\epsilon \beta_\epsilon}{h \kappa_0 c^2} \sum_{ij} r_{ij}^{-3} \left[ 2\mathbf{s}_i \cdot \mathbf{r}_j \times \pi_j + \mathbf{s}_j \cdot \mathbf{r}_j \times \pi_i \right], \]  
\[ H_{10}^e = -\frac{\beta_\epsilon^2}{h^2 \kappa_0 c^2} \sum_{ij} r_{ij}^{-3} \left[ (r_j \cdot \pi_j \mathbf{r}_i + \mathbf{r}_j \cdot (\mathbf{r}_j \cdot \pi_j) \pi_i) \right]. \]
\[ H_{11}^e = -\frac{g_e^2 \beta_e^2}{2\kappa_0 e^2} \sum_{ij} r_i^{-5} \left[ 3(s_j \cdot r_j)(s_i \cdot r_j) - r_i^2 s_i \cdot s_j \right], \]

(3.34)

\[ H_{12}^e = -\frac{4\pi g_e^2 \beta_e^2}{3\kappa_0 e^2} \sum_{ij} s_i \cdot s_j \delta(r_i - r_j). \]

(3.35)

The pure nuclear term is

\[ H_N = \sum_{m=1}^{12} H_m^N, \]

(3.36)

where (within the fixed-nucleus approximation)

\[ H_1^N = -e \sum_N Z_N \phi_N, \]

(3.37)

\[ H_2^N = -\beta_N \sum_N g_N I_N \cdot B, \]

(3.38)

\[ H_3^N = \frac{e^2}{2\kappa_0} \sum_{N,N'} Z_N Z_{N'} R_{NN'}^{-1}, \]

(3.39)

\[ H_4^N = -\frac{\beta_N^2}{2\kappa_0 e^2} \sum_{N,N'} g_N g_{N'} R_{NN'}^{-5} \left[ 3(I_N \cdot R_{NN'}) (I_{N'} \cdot R_{NN'}) - R_{NN'}^2 I_N \cdot I_{N'} \right]. \]

(3.40)

Finally, the electron-nuclear term is

\[ H_{eN} = \sum_{m=1}^{6} H_m^{eN}, \]

(3.41)

where

\[ H_1^{eN} = -\frac{e^2}{\kappa_0} \sum_{iN} \frac{Z_i}{r_{iN}}, \]

(3.42)
\[ H_{2}^{\text{en}} = \frac{g_{e} \beta_{e} \beta_{N}}{\kappa \hbar c^{2}} \sum_{i,N} g_{N} r_{iN}^{3} \left[ 3(s_{i} \cdot \mathbf{r}_{N})(I_{N} \cdot \mathbf{r}_{N}) - r_{iN}^{2} s_{i} \cdot I_{N} \right], \]  

(3.43)

\[ H_{3}^{\text{en}} = \frac{8\pi}{3} \frac{g_{e} \beta_{e} \beta_{N}}{\kappa \hbar c^{2}} \sum_{i,N} g_{N} s_{i} \cdot I_{N} \delta(\mathbf{r}_{i} - \mathbf{r}_{N}), \]  

(3.44)

\[ H_{4}^{\text{en}} = \frac{2\beta_{e} \beta_{N}}{\hbar \kappa c^{2}} \sum_{i,N} g_{N} r_{iN}^{3} \left[ I_{N} \cdot \mathbf{r}_{i} \times \mathbf{\pi}_{i} \right], \]  

(3.45)

\[ H_{5}^{\text{en}} = \frac{g_{e} \beta_{e}^{2}}{\hbar \kappa c^{2}} \sum_{i,N} Z_{N} r_{iN}^{3} \left[ s_{i} \cdot \mathbf{r}_{N} \times \mathbf{\pi}_{i} \right], \]  

(3.46)

\[ H_{6}^{\text{en}} = \frac{2\pi \beta_{e}^{2}}{\kappa \hbar c^{2}} \sum_{i,N} Z_{N} \delta(\mathbf{r}_{i} - \mathbf{r}_{N}). \]  

(3.47)

In the above, \( s_{i} \) is the spin angular momentum vector of electron \( i \) and \( I_{N} \) is the spin angular momentum of nucleus \( N \). \( \phi \) is the external electric potential and \( E_{i} \) is the external electric field. The vectors

\[ \mathbf{r}_{iN} = \mathbf{r}_{i} - \mathbf{r}_{N} \]  

(3.48)

\[ \mathbf{r}_{iO} = \mathbf{r}_{i} - \mathbf{r}_{O} \]  

(3.49)

\[ \mathbf{r}_{ij} = \mathbf{r}_{i} - \mathbf{r}_{j} \]  

(3.50)

define the position of electron \( i \) with respect to the position of nucleus \( N \) (eq (3.48)), the position of some arbitrarily chosen gauge origin \( O \) (eq (3.49)), and the other integration variable \( \mathbf{r}_{j} \) (eq (3.50)), respectively. \( g_{N} \) is the nuclear g-value (that must be found experimentally) and \( Z_{N} \) is the proton number of nucleus \( N \). All signs are explicitly taken care of in the formulae (3.23)-(3.47), so \( e \) and \( Z_{N} \) should be regarded as positive numbers.

The terms in the Breit-Pauli Hamiltonian can be interpreted as follows\(^{1, 11}\).
The pure electronic terms:

(3.24) The electron’s kinetic energy,

(3.25) the energy of the interaction between the electron and the external electric field;

(3.26) the electron Zeeman interaction between $\mathbf{s}$, and $\mathbf{B}$;

(3.27) relativistic correction to the electron’s kinetic energy;

(3.28) the one-electron spin-orbit interaction;

(3.29) the Darwin correction to the electric field interaction;

(3.30) electron-electron Coulomb interaction (electron repulsion);

(3.31) two-electron Darwin operator;

(3.32) two-electron spin-orbit interaction

(3.33) the orbit-orbit interaction between electrons

(3.34) electron spin-spin dipolar interaction;

(3.35) electron spin-spin contact interaction.

The pure nuclear terms

(3.37) Energy of interaction between the nuclei and the external electric field;

(3.38) nuclear Zeeman term;

(3.39) nuclear-nuclear Coulomb interaction;

(3.40) nuclear dipole-dipole interaction.

The electron-nuclear terms:
(3.42) Electron-nuclear Coulomb interaction (Coulomb attraction);
(3.43) dipolar hyperfine interaction;
(3.44) Fermi contact hyperfine interaction;
(3.45) orbital hyperfine interaction;
(3.46) electron-electron spin-orbit hyperfine correction;
(3.47) electron-nuclear Darwin term.

3.3 The Spin Hamiltonian

3.3.1 The Concept of the Spin Hamiltonian

The form of the Breit-Pauli Hamiltonian suggests the possibility of constructing a "phenomenological" Hamiltonian that contains only spin operators and applied fields, together with numerical parameters that serve as "coupling constants". Indeed, the results of magnetic resonance experiments are most commonly interpreted in terms of a spin Hamiltonian referring to a model spin system whose behavior may be determined by solving

$$H_z \Theta = E \Theta$$

(3.51)

in a basis of electron-nuclear spin functions, referring to spins of various nuclei $I_N$ and to the total electron spin $S$. With a proper choice of coupling constants, the eigenvalues of (3.51) fit the observed energy levels. The spin Hamiltonian is conventionally written in the form\(^1\)

$$H_z = S \cdot g \cdot B + \sum_N S \cdot A_N \cdot I_N + S \cdot D \cdot S$$

$$+ \sum_N I_N \cdot (1 - \sigma_N) \cdot B + \sum_{M,N} I_M \cdot (\overrightarrow{D}_{MN} + K_{MN}) \cdot I_N \cdot .$$

(3.52)
The last two terms in expansion (3.52) correspond to the nuclear Zeeman and nuclear spin-spin coupling terms, respectively. The following parameters are involved: the nuclear magnetic shielding tensors \( \sigma_{\text{NN}} \), which describe the magnetic shielding effects of the electrons on the nuclei; the classical dipolar interaction tensors \( \mathbf{D}_{\text{MN}} \), which describe the direct couplings of the nuclear magnetic dipole moments; and the reduced indirect nuclear spin-spin coupling tensors \( \mathbf{K}_{\text{MN}} \), which describe the indirect coupling of the nuclear dipoles, mediated by the surrounding electrons. These terms are of importance in NMR but are not normally so in EPR.\(^1\)

The crucial parameters of electron paramagnetic resonance are introduced in the first three terms of (3.52). The \( \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \) term involves the zero field splitting tensor \( \mathbf{D} \) that describes the electron-spin-electron-spin dipolar interaction in systems with more than one unpaired electron. Our interest in this thesis concentrates on the electron Zeeman term, \( \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} \), and the hyperfine interaction term, \( \mathbf{S} \cdot \mathbf{A}_N \cdot \mathbf{I}_N \), of (3.52). The former term involves the electronic \( g \)-tensor \( \mathbf{g} \) that parameterizes the interaction between the total electron spin and the magnetic field; the latter term introduces the hyperfine tensor \( \mathbf{A}_N \) that parameterizes the interaction between the total electron spin and the magnetic nucleus \( N \).

The tensor components can be obtained as formal second derivatives of the total energy:

The Cartesian \( uv \)-components of the \( g \)-tensor are given by

\[
g_{uv} = \frac{1}{\beta_e} \left. \frac{\partial^2 E}{\partial B_u \partial S_v} \right|_{\mathbf{B} = \mathbf{S} = 0} ;
\]

the Cartesian \( uv \)-components of the \( A \)-tensor are given by

\[
A_{N,uv} = \left. \frac{\partial^2 E}{\partial I_{N,\alpha} \partial S_v} \right|_{I_{N,\alpha} = S_v = 0} .
\]

Before giving the explicit expressions for the \( g \) and \( A \) tensors (Section 2.4), we will discuss the forms adopted by \( H_S \) in different media to obtain a feeling for the actual parameters. The spectral observables obtained from the resonance experiment correspond to the time average of the components of the second rank EPR tensors \( \mathbf{T} = \mathbf{g} \).
**A**, along the direction of the external magnetic field. The latter is chosen to be the \( z' \) axis of the laboratory coordinate system \((x', y', z')\).

The transformation equation for a general second rank tensor between any two Cartesian coordinate systems \((\alpha, \beta, \gamma)\) and \((a, b, c)\) is given by

\[
T_{ab} = \sum_{\alpha\beta} \cos \theta_{\alpha a} \cos \theta_{\beta b} T_{\alpha\beta} ,
\]

(3.55)

where \( \theta_{\alpha a} \) is the angle between the \( \alpha \) and \( a \) axes. From this follows that

\[
T_{zz'} = \sum_{\alpha\beta} \cos \theta_{\alpha a} \cos \theta_{\beta z} T_{\alpha\beta} ,
\]

(3.56)

and, for the time average,

\[
\langle T_{zz'} \rangle = T_{iso} + T_{aniso} = \frac{1}{3} \sum_{\alpha} \langle T_{\alpha\alpha} \rangle + \frac{2}{3} \sum_{\alpha\beta} S_{\alpha\beta} \langle T_{\alpha\beta} \rangle ,
\]

(3.57)

where \( \alpha \) and \( \beta \) denote any of the molecule-fixed coordinates \((x, y, z)\). The symmetric, traceless matrix \( U \) represents the orientation tensor with respect to the magnetic field

\[
U_{\alpha\beta} = \frac{1}{2} \{ 3 \cos \theta_{\alpha z'} \cos \theta_{\beta z'} - \delta_{\alpha\beta} \} ,
\]

(3.58)

that carries the information on the probability distribution of molecular orientation with respect to \( B \). Equation (3.57) defines the decomposition of the EPR tensors in their isotropic and anisotropic parts,

\[
T_{iso} = \frac{1}{3} \text{Tr} \mathbf{T} = \frac{1}{3} \left( \langle T_{xx} \rangle + \langle T_{yy} \rangle + \langle T_{zz} \rangle \right)
\]

(3.59)

and

\[
T_{aniso} = \frac{2}{3} \mathbf{U} \cdot \langle \mathbf{T} \rangle ,
\]

(3.60)
respectively. The angle brackets in the formulas given above indicating the time averaging will be dropped throughout the following discussion.

### 3.3.2 Spin Hamiltonian Parameters from Condensed-Phase EPR

In liquids with low viscosity, the orientation of the molecules is not ordered and the tumbling of the molecules is isotropic. The spectral observables are reduced to their isotropic parts: the $g$ tensor to the $g$-factor ($g$-value)

$$g = \frac{1}{3} \text{Tr} \, g$$

(3.61)

the $A$ tensor to the isotropic hyperfine coupling constant (HFCC)

$$A_{iso} = \frac{1}{3} \text{Tr} \, A$$

(3.62)

Much more information on the spin Hamiltonian parameters can be obtained from solid-state EPR spectroscopy. In the ideal case, the measurement is being performed for a single crystal sample where the orientation of the molecules with respect to the applied magnetic field is well defined. It is often difficult to make single crystals large enough; a powder sample must be used then, for which the orientation of the molecules with respect to the magnetic field is not known.

For single crystal samples, the elements of the matrix $(g \cdot g^T)$, $(A \cdot A^T)$ can be obtained by the successive rotations of the sample with respect to the magnetic field. Any of the $(g \cdot g^T)$, $(A \cdot A^T)$ matrices can be transformed to diagonal form by moving from the laboratory coordinate system to a principal-axes system. Once the diagonal elements of the $(g \cdot g^T)$, $(A \cdot A^T)$ tensors in the principal-axes system, the principal values, are found, one wishes to obtain the matrices $g$, $A$ themselves. Two kinds of problems are encountered here: of matrix antisymmetry and of signs. If $g$ is an antisymmetric matrix, then its principal axes system is not an orthogonal one. Such a “true” $g$ tensor is obtainable from theory only and is not directly comparable to the symmetric tensor derived from the experimental $(g \cdot g^T)$ matrix. EPR experiments on powder samples or
polycrystalline substances provide information on the isotropic and anisotropic components of the $A$ and $g$ tensors in the principal axes system as well. However, the orientation of the principal axes system with respect to the molecular framework can be obtained from single-crystal EPR experiments only.

Symmetry concepts are extensively applied in the interpretation of solid-state EPR spectra. From the point of view of local symmetry, three categories are used for the specification:

(1) **Cubic:** Anisotropy of EPR properties is absent.

(2) **Uniaxial** (often shortened as “axial”): linear rotational symmetry about a unique axis is contained; anisotropy is observable except with the field $B$ in the plane perpendicular to the unique axis. Two principal values of the $g$ and $A$-tensors are equal but differ from the third one, they are conventionally labeled as $(g_\perp, g_\perp, g_\parallel)$; $(A_\perp, A_\perp, A_\parallel)$.

(3) **Rhombic.** Three unequal principal values are contained in each parameter matrix.

The solid-state measurements provide the most complete information about the spin Hamiltonian parameters. However, the environmental effects can influence the values of the parameters due to both structural and electronical effects. This complicates the comparison of our calculated data with experiment. In general, we cannot aim at a better agreement between our calculation on isolated species with condensed-phase experiment that 10-15%. This comparison is further complicated by the fact that neither solid nor liquid-state EPR measurements provide the signs of the spin Hamiltonian parameters.

### 3.3.3 Spin Hamiltonian Parameters from Gas-Phase Spectroscopy

By definition, atoms and molecules in the gas-phase differ from those in the condensed phase in that they are almost perfectly free to perform translational and rotational motion. Literally free molecular rotation does allow observation of the quantized rotational energy levels. The ensuing rotation-magnetic interactions significantly influence the spectra so that more information on spin Hamiltonian parameters can be obtained than in liquids. On the other hand, due to the complexity of
the rotational-magnetic patterns, gas-phase microwave spectra have been resolved for monoatomic, diatomic, and very simple polyatomic species only.

Most of the experimental data for the diatomics we refer to in this thesis have been obtained using the gas-phase spectroscopy. The hyperfine parameters have been determined from the analysis of the rotational level splittings. The relative positions of the energy levels were obtained either directly by monitoring the absorption/emission (“pure” microwave rotational spectroscopy) or indirectly (through fluorescence or laser beam deflection). The accuracy of such measurements is usually very high, e.g. in the kHz range (~1 ppm) for the hyperfine parameters when using microwave optical double resonance. Unlike the situation in liquids, the spin Hamiltonian parameters are not averaged by the molecular tumbling, so that, e.g., for diatomics all of the \( g_\parallel \), \( g_\perp \), \( A_\parallel \), \( A_\perp \) parameters can be determined. The set of total angular-momentum vectors \( \mathbf{F} \) of molecules can be thought of as randomly oriented, but each is fixed in its direction until disturbed by a collision, which is a relatively rare event on the EPR time scale in most studies. In molecular beam studies such interactions between molecules are completely absent. The quantum number \( M_F \) thus remains constant and can be measured after an external magnetic field is applied, i.e., once the quantization direction is specified. Missing or weak intermolecular perturbations, together with the great accuracy of the measurement, make gas-phase data the most reliable for comparison with our computed data on isolated molecules. Moreover, unlike in the condensed phase, the sign of the hyperfine coupling constants is obtainable from the gas-phase experiments.

### 3.4 Perturbation Expressions for the Electron Zeeman and Hyperfine Interaction Terms

In the preceding two sections, we have shown that it is possible, from a relativistic theory, to derive operators necessary for a complete description of the electronic Zeeman and hyperfine effects, and that these effects enter the concept of the spin Hamiltonian as the \( g \) and \( A \) tensors. The next step to be taken is to discuss which of the many terms of the Breit-Pauli Hamiltonian are needed for a treatment of the \( g \) and \( A \) tensors, and to give the explicit expressions for these parameters. Conceptually, the
simplest approach would be to determine the eigenvalues of the Schrödinger equation involving all the necessary terms of the Breit-Pauli Hamiltonian (3.22), and to calculate the \( g \) and \( A \) tensors using relations (3.53), (3.54). Unfortunately, even the regular time-independent Schrödinger equation without any magnetic operators can be solved exactly only for some one-electron systems. Variational approaches that are conventionally applied to find solutions for problems not involving the effects of the magnetic field prove prohibitively difficult when many magnetic operators are required.

Since the magnetic effects are generally very small compared to the total molecular energy, it is very convenient to adopt a different, perturbational treatment. The philosophy of perturbation theory (PT) approaches is the partitioning of the total molecular Hamiltonian into a zeroth-order part \( (H_0) \), which has known eigenfunctions and eigenvalues, and a remaining part – the perturbation \( (V) \). The exact energy is then expressed as a sum of contributions of increasing complexity, and converges quickly if the partitioning of the Hamiltonian leaves the perturbation \( V \) small. In our case, the natural choice for \( H_0 \) is the magnetic-field-free part of the total Hamiltonian, leaving the field-dependent parts to represent the perturbation \( V \). The perturbation approach breaks the problem down into two separate tasks. The first step (that we will deal with in Chapter 3) involves a description of the field-free problem. Here we concentrate on the second step - quantifying the changes (perturbations) in the description that are induced by a magnetic field, and that enter the \( A \) and \( g \) tensors. We start with recapitulating the basic features of the PT approach.

### 3.4.1 Rayleigh-Schrödinger Perturbation Theory

The general problem is to solve the eigenvalue equation

\[
H \left| \Phi_i \right\rangle = \left( H^{(0)} + V \right) \left| \Phi_i \right\rangle = E_i \left| \Phi_i \right\rangle ,
\]

supposing that we have solved the electronic Schrödinger equation
\[
H_i^{(0)} \left| \Phi_i^{(0)} \right\rangle = E_i^{(0)} \left| \Psi_i^{(0)} \right\rangle \tag{3.64}
\]

for a set of eigenfunctions \( \left| \Phi_i^{(0)} \right\rangle \) (below denoted as \( \left| i \right\rangle \)) and eigenvalues \( E_i^{(0)} \). The exact eigenfunctions and eigenvalues of the perturbed system with Hamiltonian \( H \) can be written in terms of a Taylor series in the ordering parameter \( \lambda \):

\[
E_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ... ,
\tag{3.65}
\]

\[
\left| \Phi_i \right\rangle = \left| \Phi_i^{(0)} \right\rangle + \lambda \left| \Phi_i^{(1)} \right\rangle + \lambda^2 \left| \Phi_i^{(2)} \right\rangle + ... .
\tag{3.66}
\]

If we choose the eigenfunctions of \( H_i^{(0)} \) to be normalized and the wave function \( \Phi_i \) to be intermediately normalized (\( \langle i \Phi_i \rangle = 0 \)), we obtain by multiplication of eq (3.66) by \( \left| i \right\rangle \)

\[
\langle i \Phi_i \rangle = \langle i \left| i \right\rangle + \lambda \langle i \left| \Psi_i^{(1)} \right\rangle + \lambda^2 \langle i \left| \Psi_i^{(2)} \right\rangle + \rangle = 1 .
\tag{3.67}
\]

As (3.67) holds for all values of \( \lambda \), one sees that

\[
\langle i \left| \Phi_i^{(n)} \right\rangle = 0 \quad n = 1, 2, 3, ... .
\tag{3.68}
\]

Thus, substituting eqs (3.65), (3.66) into eq 0 and equating the coefficients of \( \lambda^n \) gives

\[
E_i^{(0)} = \langle i \left| H_i^{(0)} \right| i \rangle ,
\tag{3.69}
\]

\[
E_i^{(1)} = \langle i \left| V \right| i \rangle ,
\tag{3.70}
\]

\[
E_i^{(2)} = \langle i \left| V \right| \Psi_i^{(1)} \rangle .
\tag{3.71}
\]
The zeroth- and first-order energies are thus defined in terms of the zeroth-order wave function. Expanding \( \Psi_i^{(1)} \) in terms of eigenfunctions of \( H^{(0)} \), we obtain a similar expression for the second-order energy:

\[
E_i^{(2)} = \sum_{n \neq i} \frac{\langle i | V | n \rangle \langle n | V | i \rangle}{E_i^{(0)} - E_n^{(0)}}.
\]

(3.72)

The details of the derivation of these and higher-order contributions can be found elsewhere.\(^1^6\)

In section 2.3, the spin Hamiltonian parameters have been defined as energy derivatives. In non-degenerate perturbation theory, the first- and second-order energy derivatives with respect to a perturbation \( x \), known as the \textit{first- and second-order molecular properties}, are given by

\[
\frac{\partial E(x)}{\partial x_i} = \langle 0 | \frac{\partial H}{\partial x_i} | 0 \rangle
\]

(3.73)

\[
\frac{\partial^2 E(x)}{\partial x_i \partial x_j} = \langle 0 | \frac{\partial^2 H}{\partial x_i \partial x_j} | 0 \rangle + 2 \sum_{n \neq 0} \frac{\langle 0 | \frac{\partial H}{\partial x_i} | n \rangle \langle n | \frac{\partial H}{\partial x_j} | 0 \rangle}{E_0 - E_n}
\]

(3.74)

where the derivatives are taken at \( x=0 \) (e.g., zero field and zero magnetic moments). The first derivative of a first-order property eq (3.73) is thus simply the expectation value of the first-order Hamiltonian (this is a consequence of the \textit{Hellmann-Feynman theorem}) and requires only a knowledge of the unperturbed state \( | 0 \rangle \). The second derivative of the second order property eq (3.74) contains an expectation-value term analogous to the first-order properties but also a sum-over-states contribution from each excited state \( | n \rangle \) of energy \( E_n \). For magnetic properties, the expectation-value contribution to the second-order property is known as the \textit{diamagnetic} part, the sum-over-states contribution is referred to as the \textit{paramagnetic} part.\(^1^7\) To arrive at the explicit expressions for \( A \) and \( g \)-tensors, we must consider the relevant terms of the Breit-Pauli Hamiltonian, as we do in the next section.
3.4.2 Operators Relevant for the Electron Zeeman Effect and for the Hyperfine Interaction

In order to establish a connection between the terms of the Breit-Pauli Hamiltonian (3.22) and the parameters of the spin Hamiltonian (3.52), the form of the latter operator should be discussed briefly. We first note that (3.52) contains only terms bilinear in the magnetic operators \( \mathbf{B}, \mathbf{I}, \) and \( \mathbf{S} \). No terms linear in (only one of the) \( \mathbf{B}, \mathbf{I}, \) or \( \mathbf{S} \) are involved, as any of the corresponding operators is pure imaginary and is characteristic of the spatial components of time-odd interactions. The requirement of time-reversal invariance of the nonvanishing energy terms thus enforces the absence of terms linear in \( \mathbf{B}, \mathbf{I}, \) or \( \mathbf{S} \) from the spin Hamiltonian. The exclusion of terms involving powers higher than second of \( \mathbf{B}, \mathbf{I}, \) and \( \mathbf{S} \) or their combination from the spin Hamiltonian is not rigorous, but is a convenient and usually good approximation. Such terms would clearly arise if we went higher than to second order in perturbation theory. In order to retain gauge invariance of the results for both the \( \mathbf{g} \) and the \( \mathbf{A} \) tensor, it is necessary to include all relevant contributions to these tensors up to a certain order of the fine-structure constant \( \alpha \). Below, we give the operators of the Breit-Pauli Hamiltonian relevant for the 2\(^{nd}\)-order perturbation theory expressions up to \( O(\alpha^2) \) for both the \( \mathbf{g} \)- and the \( \mathbf{A} \)-tensor, including also the spin-orbit terms (\( \sim O(\alpha^4) \)) for the latter.

The main contribution to the \( g \)-tensor up to \( O(\alpha^2) \) involves the electron Zeeman interaction \( H'^z \), given by (3.25). The part of \( H'^z \) that depends on \( s_i \) and \( \mathbf{B}(i) \) only (corresponding to the term “1” in the brackets following the summation)

\[
H_{sz} = g_e \beta \sum_i s_i \cdot \mathbf{B}
\]

(3.75)

is usually referred to as the spin-Zeeman operator. The part corresponding to the field-independent part of \( \pi_i \)

\[
H_{RMC-sz} = -\frac{g_e \beta}{2m^2 \kappa_0 \epsilon^2} \sum_i p_i^z s_i \cdot \mathbf{B}
\]

(3.76)
is called the spin-Zeeman relativistic mass correction operator, where \( p_i^2 = p_i \cdot p_i \) is the square of linear momentum operator for electron \( i \). Both \( H_{SZ} \) and \( H_{RMC-SZ} \) give first-order contributions to the electronic \( g \)-tensor. \( H_{SZ} \) results in the free-electron \( g \)-tensor (\( g_e \)), whereas \( H_{RMC-SZ} \) contributes in first order to the \( \Delta g \) tensor that is defined as

\[
\Delta g = g - g_e 1.
\] (3.77)

The main second-order contributions to both the \( g \)- and \( A \)-tensors (and the dominant contributions to the components \( \Delta g \), the \( g \)-shifts) arise from the one-electron spin-orbit interaction term (\( H_{SO}^{en} \)) of the Breit-Pauli Hamiltonian. \( H_{SO}^{en} \) involves the field-dependent momentum \( \pi_i \), and, for the purposes of practical calculations, it is necessary to expand it into field-dependent and field-independent parts. By retaining only the field-independent part of \( \pi_i \), \( H_{SO}^{en} \) reduces to

\[
H_{SO(1e)} = \frac{2g_e \beta_e^2}{\hbar \kappa \epsilon c^2} \sum_N Z_N \sum_i \frac{s_i \cdot l_{N}}{r_{N}^3}.
\] (3.78)

\( H_{SO(1e)} \) thus describes the interaction between the spin \( g_e \beta_e s_i \) and orbital \( \beta_e l_{N} \) magnetic moments of the electron. The angular momentum operators \( l_{N} \), \( l_{O} \), and \( l_{ij} \) employed here and below for the sake of shortening the expressions are defined in the following fashion:

\[
l_{N} = r_{N} \times p_j
\] (3.79)

and correspond to the different vectors defined in eqs (3.48)-(3.50). It is the term (3.78), rather than eq (3.28), which is normally equated with the concept of the one-electron spin-orbit coupling, and we will retain such a naming throughout this thesis.

The other part of \( H_{SO}^{en} \), involving the field-dependent part of \( \pi_i \), is given by

\[
H_{GC-SO(1e)} = \frac{g_e \beta_e^2 e}{2h \kappa \epsilon c^2} \sum_N Z_N \sum_i \frac{[s_i \cdot B(r_{N} \cdot r_{O}) - s_i \cdot r_{N} (r_{O} \cdot B)]}{r_{N}^3}.
\] (3.80)
Due to its origin in $H_{SO}^{\text{eN}}$, the $H_{GC-SO}^{\text{eN}}$ term may be regarded as the portion of the spin-orbit coupling which is dependent on the external field $B$, and is called the one-electron spin-orbit gauge correction.\textsuperscript{18} Gauge correction refers to the dependence of this term on the origin $O$ of the computational coordinate system. $H_{GC-SO}^{\text{eN}}$ contributes in the first order PT to the electronic $g$-tensor.

From equation (3.32), it is possible to derive the two-electron analogues of $H_{SO}^{\text{eN}}$ and $H_{GC-SO}^{\text{eN}}$ - the two-electron spin-orbit coupling term

$$H_{SO}^{\text{2e}} = -\frac{g_{\text{e}}}{\hbar c} \sum_{ij} \frac{(s_i + 2s_j) \cdot \mathbf{l}_{ij}}{r_{ij}} ,$$

(3.81)

and the two-electron spin-orbit gauge correction term

$$H_{GC-SO}^{\text{2e}} = \frac{g_{\text{e}}}{2\hbar c^2} \sum_{ij} \sum_{\alpha} \left[ (s_i + 2s_j) \cdot \mathbf{B} \right] (r_{ij} \cdot r_{i\alpha}) - \left[ (s_i + 2s_j) \cdot r_{ij} \right] (r_{i\alpha} \cdot \mathbf{B}) .$$

(3.82)

These terms may be regarded as conceptually identical to their one-electron analogues (3.78), (3.80). In this case, however, the magnetic interactions take place under an electric field arising from electron-electron Coulomb repulsion, rather than electron-nuclear attraction. The corresponding one- and two-electron terms thus have opposite signs. $H_{SO}^{\text{2e}}$ - analogously to $H_{SO}^{\text{eN}}$ - gives second-order contributions to both the $g$- and $A$-tensors; $H_{GC-SO}^{\text{2e}}$ - like $H_{GC-SO}^{\text{eN}}$ - contributes to the $g$-tensor in the first order.

The second-order contributions to the $g$-tensor involving $H_{SO}^{\text{eN}}$ and $H_{SO}^{\text{2e}}$ arise as cross terms between any of the spin-orbit operators and the orbital Zeeman operator

$$H_{OZ} = -\frac{e}{m_e} \sum_i \mathbf{A}(\mathbf{r}_i) \cdot \mathbf{p}_i = -\frac{g_{\text{e}}}{\hbar} \sum_i \mathbf{l}_{i\alpha} \cdot \mathbf{B} .$$

(3.83)

$H_{OZ}$ is obtained from the operator $H_{i}^{\text{e}}$ upon the expansion of the field-dependent momentum $\pi$ (cf. (3.8)).\textsuperscript{3} It reflects the interaction between the external field $\mathbf{B}$ and the orbital magnetic moment $\mathbf{\mu}_i = \beta_{\text{e}} \mathbf{l}_i$. 

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The dominant, first-order contributions to the $A$-tensor are the Fermi-contact operator corresponding to nucleus $N$ (from $H^{CN}_3$, (3.44))

$$H^{N}_{FC} = \frac{8\pi}{3} g_e g_N \beta_e \beta_N \frac{\kappa_0 c^2}{\kappa_0 c^2} \sum_i \delta(r_i) \mathbf{s}_i \cdot \mathbf{I}_N,$$

(3.84)

and the spin-dipolar operator (from $H^{CN}_5$, (3.43))

$$H^{N}_{SD} = g_e g_N \beta_e \beta_N \frac{\kappa_0 c^2}{\kappa_0 c^2} \sum_i 3r_{iN} \mathbf{r}_{iN} - 1 \mathbf{r}_{iN}^2 \cdot \frac{\mathbf{I}_N}{r_{iN}^3}.$$

(3.85)

If second-order contributions to the $A$-tensor are to be considered, then for consistency certain additional but small first-order contributions should be included. These are analogous to the “gauge correction” terms contributing to $\Delta g$ but with the vector potential due to the nuclear moment replacing that due to the uniform external field. The vector potential due to the magnetic nucleus $N$ is given by

$$A_N(r_i) = \frac{g_N \beta_N}{\kappa_0 c^2} \frac{\mathbf{I}_N \times \mathbf{r}_{iN}}{r_{iN}^3}.$$

(3.86)

From the 1-electron part of the spin-orbit (SO) Hamiltonian $H^{eN}_5$, cf. eq (3.46), we obtain the one-electron spin-orbit hyperfine correction term

$$H^{N}_{HC-SO(1e)} = \frac{e}{2m_e} g_e g_N \beta_e \beta_N \sum_{i,j} \sum_{N,N'} r_{iN} r_{jN'} \frac{Z_{N'}}{r_{iN}^3} \times [(r_{iN} \cdot \mathbf{r}_{jN'}) (\mathbf{s}_i \cdot \mathbf{I}_N) - (\mathbf{s}_j \cdot \mathbf{r}_{iN}) (\mathbf{I}_N \cdot \mathbf{r}_{jN})].$$

(3.87)

From the spin-spin and the spin-other-orbit parts of the 2-electron SO Hamiltonian $H^e_5$, cf. eq (3.32), arise the spin-spin-orbit hyperfine correction term

$$H^{N}_{HC-SO} = \frac{e}{2m_e} g_e g_N \beta_e \beta_N \sum_{i,j} \sum_{N} \frac{1}{r_{iN}^2} \times [(r_{ji} \cdot \mathbf{r}_{iN}) (\mathbf{s}_j \cdot \mathbf{I}_N) - (\mathbf{s}_i \cdot \mathbf{r}_{jN}) (\mathbf{I}_N \cdot \mathbf{r}_{ji})].$$

(3.88)

and the spin-other-orbit hyperfine correction term
\[ H_{\text{HC-SOO}}^N = \frac{e}{2m_e} g_N g_N \beta_N \beta_N \sum \sum \frac{1}{r_{ij}^3} \times \left[ (r_{ij} \cdot \mathbf{r}_{ij}) (s_i \cdot \mathbf{I}_N) - (r_{ij} \cdot \mathbf{I}_N) (r_{ij} \cdot s_i) \right] \cdot \]

(3.89)

The latter two terms are usually treated together as the two-electron hyperfine correction term

\[ H_{\text{HC-SOO}}^N = H_{\text{HC-SOO}}^N + H_{\text{HC-SOO}}^N \cdot \]

(3.90)

Second-order contributions to the hyperfine tensor arise as cross-terms between any of the spin-orbit operators (3.78), (3.81), and the paramagnetic nuclear spin - electron orbit operator

\[ H_{\text{PSO}}^N = \frac{e}{m_e} g_N \beta_N \sum \frac{I_N^2}{r_{iN}^3} \cdot \]

(3.91)

\( H_{\text{PSO}}^N \) is obtained by expanding the kinetic-energy term \( H_1 \), cf. eq (3.24), considering the contribution given by the magnetic dipole of the nucleus \( N \) to the field-dependent momentum \( \pi \).

To summarize, the second-order expressions for the g-tensor up to \( O(\alpha^2) \) involve the following 7 operators: the spin-Zeeman operator \( H_{SZ} \), the spin-Zeeman relativistic mass correction operator \( H_{RMC-SZ} \), the one-electron and the two-electron gauge correction terms \( H_{GC-SO(1e)}^N, H_{GC-SO(2e)}^N \), the one-electron and the two-electron spin-orbit coupling operators \( H_{SO(1e)}^N, H_{SO(2e)}^N \), and the orbital Zeeman operator \( H_{OZ} \). First-order contributions are given by \( H_{SZ}, H_{RMC-SZ}, H_{GC-SO(1e)}^N \), and \( H_{GC-SO(2e)}^N \), second-order contributions arise from cross-terms between \( H_{OZ} \) and any of the \( H_{SO(1e)}^N, H_{SO(2e)}^N \) terms.

The second-order expressions for the A-tensor up to \( O(\alpha^2) \) including the spin-orbit terms up to \( O(\alpha^4) \) involve the Fermi-contact operator \( H_{FC}^N \), the spin-dipolar operator \( H_{SD}^N \), the one-electron and the two-electron spin-orbit hyperfine correction terms \( H_{HC-SO(1e)}^N \) and \( H_{HC-SO(2e)}^N \), the one-electron and the two-electron spin-orbit coupling...
operators $H_{SO(1e)}$, $H_{SO(2e)}$, and the paramagnetic nuclear spin - electron orbit operator $H^N_{PSO}$.

### 3.4.3 Perturbation-Theory Expressions for the Electronic $g$-Tensor

As discussed above, the perturbation $V$ is in the case of $g$-tensor calculations given by

$$V = H_{SZ} + H_{RMC-SZ} + H_{GC-SO(1e)} + H_{GC-SO(2e)} + H_{SO(1e)} + H_{SO(2e)} + H_{OZ}.$$ \(3.92\)

The perturbation treatment can be simplified as follows:

1. The 0th order contribution $E^{(0)}_i$ does not contribute to the Zeeman splitting and can thus be ignored.

2. It can be shown that the operators $H_{SO(1e)}$, $H_{SO(2e)}$, and $H_{OZ}$ do not contribute to $E^{(1)}_i$. The first-order perturbation can thus be written as

$$V^{(1)} = H_{SZ} + H_{RMC-SZ} + H_{GC-SO(1e)} + H_{GC-SO(2e)}.$$ \(3.93\)

3. Recall that we look for contributions to the Zeeman splitting bilinear in the magnetic field $B$ and effective electronic spin $S$. We can therefore exclude from the 2nd-order contributions operators $H_{SZ}$, $H_{RMC-SZ}$, $H_{GC-SO(1e)}$ and $H_{GC-SO(2e)}$, which have quadratic dependence on $S$ or $B$. Thus,

$$V^{(2)} = H_{SO(1e)} + H_{SO(2e)} + H_{OZ}.$$ \(3.94\)

The requirement of the bilinearity in $B$ and $S$ further restricts the 2nd-order contributions to two cross terms: between $H_{SO(1e)}$ and $H_{OZ}$, and between $H_{SO(2e)}$ and $H_{OZ}$.

The second-order expressions up to $O(\alpha^2)$ for the $g$-tensor components can be obtained using the expression (3.74) for second-order molecular properties. We recall that the spin-Zeeman operator $H_{SZ}$ results in the free-electron $g$-tensor ($g_e$) and does
not contribute to the $g$-shifts. The Cartesian $uv$-components of the $\Delta g$ tensor involve contributions from the spin-Zeeman relativistic mass correction operator $H_{\text{RMC-SZ}}$

$$\Delta g^{(1)}_{\text{RMC-SZ},uv} = -\frac{g_e \beta_e}{2m_e^* \kappa_0 c^2} \delta_{uv} \sum_i \left(-\frac{1}{2} \nabla_i^2\right)s_{ix} |0\rangle,$$

(3.95)

the one-electron gauge correction term $H_{\text{GC-SO}(1e)}$

$$\Delta g^{(1)}_{\text{GC-SO}(1e),uv} = -\frac{g_e \beta_e^2 e}{2h \kappa_0 c^2 \langle S_Z \rangle} \sum_N Z_N \sum_n \sum_i r_i^N \left(\frac{1}{r_i^N} - (r_i^N)_{uv} \cdot (r_i^N)_{uv} \right) \delta_{uv} \cdot |0\rangle,$$

(3.96)

the two-electron gauge correction term $H_{\text{GC-SO}(2e)}$

$$\Delta g^{(1)}_{\text{GC-SO}(2e),uv} = \frac{g_e \beta_e^2 e}{2h \kappa_0 c^2 \langle S_Z \rangle} \sum_N Z_N \sum_n \sum_i \left(\frac{1}{r_i^N} - (r_i^N)_{uv} \cdot (r_i^N)_{uv} \right) \delta_{uv} \cdot |0\rangle,$$

(3.97)

the cross terms between the one-electron spin-orbit coupling operator $H_{\text{SO}(1e)}$ and the orbital Zeeman operator $H_{\text{OZ}}$

$$\Delta g^{(2)}_{\text{SO/OZ}(1e),uv} = \frac{2g_e \beta_e^3}{h^2 \kappa_0 c^2 \langle S_Z \rangle} \sum_N Z_N \sum_n \left\{ \left(\frac{1}{r_i^N} \times (1_{iv} + s_{ix}) |n\rangle \langle n\rangle \sum_j (1_{jv})_+ |0\rangle \right) \right\} \left( E^{(0)}_n - E^{(0)}_0 \right) + \text{c.c.},$$

(3.98)

and the cross terms between the two-electron spin-orbit coupling operator $H_{\text{SO}(2e)}$ and the orbital Zeeman operator $H_{\text{OZ}}$

$$\Delta g^{(2)}_{\text{SO/OZ}(2e),uv} = \frac{2g_e \beta_e^3}{h^2 \kappa_0 c^2 \langle S_Z \rangle} \sum_N Z_N \sum_n \left\{ \left(\frac{1}{r_i^N} \times (\nabla_i - 2\nabla_0) \right)_+ s_{ix} |n\rangle \langle n\rangle \sum_k (r_k \times \nabla_k)_+ |0\rangle \right\} \left( E^{(0)}_n - E^{(0)}_0 \right) + \text{c.c.},$$

(3.99)

where “+ c.c.” indicates addition of the complex conjugate of the preceding term.
The total result for $\Delta g_{uv}$ up to $O(\alpha^2)$ is the sum of contributions

$$\Delta g_{uv} = \Delta g_{RMc-SZ,uv}^{(1)} + \Delta g_{GC-SO(1e),uv}^{(1)} + \Delta g_{GC-SO(2e),uv}^{(1)} + \Delta g_{SO/SOZ(1e),uv}^{(2)} + \Delta g_{SO/SOZ(2e),uv}^{(2)}$$

(3.100)

In the application calculations reported in this thesis, all contributions given in (3.100) except for $\Delta g_{GC-SO(2e),uv}^{(1)}$ have been included. The latter term has been neglected due to its general smallness (see refs 3 and 19) and the lack of computationally efficient approximations thereto.

### 3.4.4 Perturbation-Theory Expressions for the $A$-Tensor

The perturbation $V$ is in the case of $A$-tensor calculations given by

$$V = H_{FC}^N + H_{SD}^N + H_{HC-SO(1e)}^N + H_{HC-SO(2e)}^N + H_{SO(1e)}^N + H_{SO(2e)}^N + H_{PSO}^N.$$

(3.101)

Along similar lines as for the $g$-tensor, the first- and second-order contributions to the $A$-tensor up to $O(\alpha^2)$ including the spin-orbit terms up to $O(\alpha^4)$ can be obtained.

The contribution from the Fermi-contact hyperfine operator $H_{FC}^N$ is given by

$$A_{FC,uv}^{N(1)} = \frac{8\pi}{3} \frac{g_e g_N \beta_e \beta_N}{\kappa_0 c^2} \frac{1}{\langle S_Z \rangle} \langle 0 \sum_i \delta(r_{iN}) s_{iz} | 0 \rangle.$$

(3.102)

The contribution of the spin-dipolar hyperfine operator $H_{SD}^N$ is equal to

$$A_{SD,uv}^{N(1)} = \frac{g_e g_N \beta_e \beta_N}{\kappa_0 c^2} \frac{1}{\langle S_Z \rangle} \langle 0 \sum_i \frac{\delta_{\alpha \beta}(r_{iN}^2) - 3(r_{iN})_\alpha (r_{iN})_\beta}{r_{iN}^2} s_{iz} | 0 \rangle.$$

(3.103)

The one-electron spin-orbit hyperfine correction term $H_{HC-SO(1e)}^N$ contributes as

$$A_{HC-SO(1e),uv}^{N(1)} = \frac{e}{2m_e} \frac{g_e g_N \beta_e \beta_N}{\kappa_0 c^4} \frac{1}{\langle S_Z \rangle} \langle 0 \sum_i \sum_{N'N(\neq N)} \frac{Z_{iN}}{3} \sum_{NN'} [\delta_{\alpha \beta}(r_{iN}) \delta_{\alpha \beta}(r_{iN'}) - (r_{iN})_\alpha (r_{iN'})_\beta] s_{iz} | 0 \rangle.$$

(3.104)
The two-electron spin-orbit hyperfine correction term $H_{N}^{SO}$ (cf. eq (3.90)) contributes as
\[
A^{N(1)}_{HC-SO(2e),av} = \frac{e g_{e} g_{N} \beta_{e} \beta_{N}}{2 m_{e} \kappa_{0}^{2} c^{4} \langle S_{z} \rangle} \cdot \left\{ \langle 0 | \sum_{i,j} \frac{1}{r_{ij}^{3}} \mathbf{r}_{ij} \cdot (2\mathbf{r}_{ij} - \mathbf{r}_{ij}) \delta_{ij} - (2\mathbf{r}_{ij} - \mathbf{r}_{ij}) \mathbf{z}_{ij} \rangle \mathbf{S}_{z} | 0 \rangle \right\}.
\]
(3.105)

Finally, two second-order contributions to the $A$-tensor are obtained as cross terms between any of the spin-orbit operators $H_{SO_{1e}}$, $H_{SO_{2e}}$, and the paramagnetic nuclear spin - electron orbit operator $H_{PSO}$:
\[
A^{N(2)}_{SO_{1e} / SO_{2e},av} = \frac{e}{m_{e}} \frac{2 g_{e} g_{N} \beta_{e}^{2} \beta_{N}}{\hbar \kappa_{0}^{2} c^{4} \langle S_{z} \rangle} \cdot \left\{ \sum_{n} \left[ \langle 0 | \sum_{i} Z_{i} \frac{1}{r_{i}} (\mathbf{1}_{i})_{v} \times \mathbf{s}_{i} | n \rangle \langle n | \sum_{j} \frac{1}{r_{j}} (\mathbf{1}_{j})_{v} | 0 \rangle \right] E_{0}^{(0)} - E_{n}^{(0)} \right\} + \text{c.c.},
\]
(3.106)
\[
A^{N(2)}_{SO_{2e} / PSO_{av}} = \frac{e}{m_{e}} \frac{2 g_{e} g_{N} \beta_{e}^{2} \beta_{N}}{\hbar \kappa_{0}^{2} c^{4} \langle S_{z} \rangle} \cdot \left\{ \sum_{n} \left[ \langle 0 | \sum_{i,j} \frac{1}{r_{ij}} \mathbf{r}_{ij} \times (2\nabla_{i} - \nabla_{j}) | n \rangle \langle n | \sum_{k} \frac{1}{r_{k}} (\mathbf{1}_{k})_{v} | 0 \rangle \right] E_{0}^{(0)} - E_{n}^{(0)} \right\} + \text{c.c.}.
\]
(3.107)

The total result for $A^{N}_{av}$ up to $O(\alpha^{2})$ including the spin-orbit terms up to $O(\alpha^{4})$ is the sum of contributions
\[
A^{N}_{av} = A^{N(1)}_{FC,av} + A^{N(1)}_{SD,av} + A^{N(1)}_{HC-SO_{1e},av} + A^{N(1)}_{HC-SO_{2e},av} + A^{N(2)}_{SO_{1e} / SO_{2e},av} + A^{N(2)}_{SO_{2e} / PSO_{av}}.
\]
(3.108)

The density-functional calculations of the $A$-tensor reported in this thesis are nonrelativistic. Only the Fermi-contact contribution $A^{N(1)}_{FC,av}$ and the spin-dipolar
contribution $A^{(1)}_{SO,m}$ have thus been included. Rough semiempirical estimates of spin-orbit contributions to the HFCCs has been obtained along the perturbation theoretical approach of Abragam and Pryce.\(^\text{20}\)

### 3.5 Qualitative and Semi-Quantitative Relationships between the Spin Hamiltonian Parameters and Electronic Structure

The phenomenon of hyperfine coupling is often considered to be the most important interaction in EPR spectroscopy. This is mainly due to a very simple qualitative connection between the hyperfine tensor components and the electronic and geometrical structure of the paramagnetic species. First-order contributions to the hyperfine tensor directly reflect the spin density at the point of the magnetic nucleus (isotropic part) and the anisotropy of the spin density distribution in the proximity of the magnetic nucleus (anisotropic part). The spin density distribution throughout the molecule is dominated by the direct contribution of the singly-occupied molecular orbital(s) (SOMO). For many transition-metal complexes, the SOMOs are mainly – if not for symmetry reasons purely – metal $d$ orbitals. As a result, the direct contribution to the $A_{iso}$ given by the SOMOs is negligible, and negative spin density arises at the nucleus due to the spin polarization of the doubly occupied molecular orbitals. When significant admixture of the outer $s$ orbital into the SOMO occurs, the spin density at the nucleus may become positive. Simple semi-quantitative estimates of the $s$ character of the SOMO from the $A_{iso}$ are often employed that are based on known values of spin-polarization and direct contributions to the hyperfine coupling for unit occupations of metal $d$ and $s$ orbitals, respectively.\(^\text{21}\) Estimates of the $d$ character of the SOMO are being obtained from the anisotropic hyperfine tensor components, completely neglecting the spin polarization contributions to the hyperfine coupling anisotropy.\(^\text{21,22,23}\) Such estimates are very useful for establishing simple qualitative bonding schemes from the spin Hamiltonian parameters, or vice versa. As we discuss in Chapter 7, any quantitative usage of such orbital composition estimates should be used with great care.

The interpretation of electronic $g$-tensor components is more complex. The dominant contributions to $g$-shifts are given by the SO coupling.\(^\text{3,24}\) Thus, not only the
composition of the singly-occupied orbital, but also compositions and relative energies of the virtual and doubly-occupied orbitals determine the $g$-tensor. The definitive work in understanding spin Hamiltonian parameters of transition metal complexes on the basis of the crystal-field theory has been done by Abragam and Pryce\textsuperscript{20} and by Abragam and Bleaney.\textsuperscript{5} This approach is very informative and useful when very ionic complexes, especially in sites of very high symmetry, are involved. The interest of the author in Chapter 8 was rather in understanding $g$- and $A$-tensor components for less symmetrical complexes, where both $\sigma$ and $\pi$ bonding plays an important role. The most suitable way to obtain such understanding, and to relate it to the results of quantum chemical calculations, is the molecular orbital approach discussed in great detail by Mabbs and Collison\textsuperscript{6} that is introduced briefly in Chapter 8. This approach also enables us to make a rough semiempirical estimate of SO to the hyperfine coupling that are not accounted for yet in our present DFT calculations of HFCCs.
References


7 Gerlach, W.; Stern, O. *Z. Phys. 1922*, 9, 349.


18 This gauge-correction term is also related to the spin-Zeeman interaction, cf. ref 3.


It seems that if one is working from the point of view of getting beauty in one’s equations, and if one has really a sound insight, one is on a sure line of progress.

Paul Adrien Maurice Dirac (1902-84)

4 Computational Methods

In the previous Chapter, the electronic $g$-tensor and the hyperfine $A$-tensor have been related to the field-free description of the system’s electronic structure. In this respect, a crucial role is played by the molecular ground state $|0\rangle$ that is needed for determining both the first-order, diamagnetic contributions and, as a reference state, also the second-order, paramagnetic contributions to the spin-Hamiltonian parameters. This chapter provides an overview of ab initio computational methods used in this thesis for obtaining the field-free description of the molecular ground state. First, the Hartree-Fock approach is introduced as a basic one-electron approximation and discussed in both its spin-restricted and spin-unrestricted forms for open-shell systems. Then, the philosophy of the post-Hartree-Fock approaches is discussed for the cases of the Configuration Interaction (CI) and the Coupled Cluster (CC) methods. The crucial concept of spin polarization is introduced at two levels: at the spin-unrestricted one-electron (unrestricted Hartree-Fock) level, and at the spin-restricted correlated level (CI based on a spin-restricted reference wave function). Next, the theorems of the density-functional theory and the Kohn-Sham approach are presented, followed by a discussion of the various exchange-correlation functionals. Finally, basis sets and the pseudopotential approximation used in the present applications are described. The discussion of the wave function approaches in this Chapter is based on refs 1, 2 and 3, that of the density functional approaches on refs 4 and 5.
4.1 Approximations to the Solution of the Schrödinger Equation

The starting point for a nonrelativistic quantum mechanical description of stationary molecular properties is the time-independent Schrödinger equation

\[ H \Psi (r, R_N) = E \Psi (r, R_N), \]  

(4.1)

where the Hamiltonian operator for a system of electrons and nuclei described by position vectors \( r_i \) and \( R_N \), respectively, is

\[ H^{(0)} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_i \sum_N \frac{Z_N}{2M} - \sum_i \sum_N \frac{Z_N}{r_{iN}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} + \sum_N \sum_{M>N} \frac{Z_M Z_N}{R_{MN}}. \]  

(4.2)

The exact solution of the Schrödinger equation requires a complete description of the interparticle interactions and is impossible for systems with more than two particles. The central issue of quantum chemistry is thus an approximation of the many particle problem by a set of single-particle problems, often followed by a subsequent inclusion of many-particle interactions using variational or perturbational techniques. The first common step in such reduction is the Born-Oppenheimer approximation, which separates the fast electronic movements from the slow nuclear movements by supposing that one can consider the electrons to be moving in the field of fixed nuclei. The true molecular wave function is then approximated as

\[ \psi(q_i; q_N) = \psi_e(q_i; q_N) \psi_N(q_N), \]  

(4.3)

where \( q_i \) and \( q_N \) stand for the electronic and nuclear coordinates, respectively, and \( \psi_e \) is the eigenstate of the electronic Hamiltonian

\[ H_{\text{elec}}^{(0)} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_i \sum_N \frac{Z_N}{r_{iN}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}. \]  

(4.4)

This leaves us with an electronic Schrödinger equation.
\[ H^{(0)}_{\text{elec}} \Psi_{\text{elec}}(r_i, R_N) = E_{\text{elec}} \Psi_{\text{elec}}(r_i, R_N), \]  \tag{4.5} 

where the Hamiltonian \( H^{(0)}_{\text{elec}} \) has only a parametric dependence on the nuclear positions.

## 4.2 The Hartree-Fock Approximation

### 4.2.1 The Hartree Approximation

The electronic Schrödinger equation (4.5) for many-electron atoms and molecules cannot be solved analytically. The mathematical difficulties are brought about by the last term in the Hamiltonian (4.4) that describes the instantaneous Coulomb repulsion of every pair of electrons. A fundamental approximation of quantum chemistry is to replace any of these interactions with a repulsion which the particular electron would feel when moving in a time-averaged field of the other electron. This approach has been introduced by Hartree, who assumed that each electron in a multielectron system is described by its own wave function and is thus subject to the Coulomb potential due to the remaining electrons:

\[ V_{\text{coul}}(r_i) = \sum_{j \neq i} \int \frac{1}{r_{12}} |\psi_j(r_2)|^2. \]  \tag{4.6} 

It is convenient to define a *Coulomb operator* 

\[ J_i(r_i) = \int |\psi_i(r_2)|^2 \frac{1}{r_{12}^i}. \]  \tag{4.7} 

that represents the average potential at \( r_i \) arising from the charge distribution due to the \( i \)-th electron.

The one-electron wave functions for a many-electron system are then obtained by solving a system of equations of the form
where

\[ h(1) = -\frac{1}{2} \nabla^2 - \sum_{i=1}^{N} \frac{Z_i}{r_{1i}} \]  

(4.9)

is the operator of kinetic energy and potential energy for the attraction to the nuclei, corresponding to a single electron chosen to be the first electron. This must be done iteratively, since the orbitals \( \psi_i \) that solve the problem appear in the operator \( J \). Consequently, the Hartree method is a nonlinear “self-consistent-field” method. One begins with a guessed set of orbitals \( \psi_i \), constructs the set of operators \( J_i \) as given by (4.7), then finds new set of orbitals from (4.8), constructs a new set of operator \( J_i \), etc. The total Hartree wave function is given by a simple product of the one-electron wave functions. The correlations between the movements of different electrons are thus completely neglected. In addition, such wave function does not fulfill the Pauli’s requirement of antisymmetry with respect to an exchange of two particles.

### 4.2.2 The Hartree-Fock Approximation

The symmetry requirements have been included in the Hartree method in a generalization due to Fock and Slater. Within this so-called Hartree-Fock theory, the Hartree product is substituted by a determinantal wave function (Slater determinant) of the form

\[ \Psi_{HF}(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_a(\mathbf{x}_1) & \chi_b(\mathbf{x}_1) & ... & \chi_d(\mathbf{x}_1) \\ \chi_a(\mathbf{x}_2) & \chi_b(\mathbf{x}_2) & ... & \chi_d(\mathbf{x}_2) \\ ... & ... & ... & ... \\ \chi_a(\mathbf{x}_N) & \chi_b(\mathbf{x}_N) & ... & \chi_d(\mathbf{x}_N) \end{vmatrix}, \]

(4.10)

where
\[ x_j = (r_j, \sigma_j) \]  

(4.11)

and the one-electron wave functions

\[ \chi_j(x_j) = \psi_j(r_j) \omega_j(\sigma_j) \]  

(4.12)

depend on both spatial \( r_i \) and spin \( \sigma_i \) coordinates.

It is useful to introduce a shorthand notation, which includes the normalization constant and only shows the diagonal elements of the determinant,

\[ \Psi_{HF}(x_1, x_2, \ldots, x_N) = \left| \chi_1(x_1) \chi_2(x_2) \ldots \chi_N(x_N) \right| \]  

(4.13)

Provided that we always choose the electron labels to be in the order \( x_1, x_2, \ldots, x_N \), eq (4.13) can be further shortened to

\[ \Psi_{HF}(x_1, x_2, \ldots, x_N) = \chi_1 \chi_2 \ldots \chi_N \]  

(4.14)

The energy of the Slater determinant can be minimized using the variational condition

\[ \delta \langle \Psi_{HF} | H_{elec} | \Psi_{HF} \rangle = 0 \]  

(4.15)

\( H_{elec} \) refers to eq (4.4)), and we require that all orbitals are normalized. Using the rules for matrix elements between determinantal wave functions, condition (4.15) results in the Hartree-Fock (HF) equations:

\[
\begin{align*}
\left[ h(1) + \sum_j \int \frac{1}{r_{i2}} |\psi_j(r_2)|^2 \right] \psi_j(r_i) &
- \sum_j \delta(m_{ij}, m_{ij}) \left[ \int \frac{1}{r_{i2}} \psi_j^*(r_2) \psi_i^*(r_2) \right] \psi_j(r_i) = \epsilon_i \psi_i(r_i)
\end{align*}
\]

(4.16)

The term \( \delta(m_{ij}, m_{ij}) \) results from an integration over the spin coordinates and indicates that the corresponding summation runs only over electrons with the same spin as that of
the electron $i$. The eigenvalue $\varepsilon_i$ appears here as the Lagrange multiplier ensuring the normalization of the orbitals.

The Hartree-Fock equation (4.16) can be written as an eigenvalue equation

$$
\left[ h(1) + \sum_j J_j(r_i) - \sum_j \delta(m_{ij}, m_{ij}) K_j(r_i) \right] \psi_i(r_i) = \varepsilon_i \psi_i(r_i),
$$

(4.17)

if we define an exchange operator $K_j(r_1)$ by its effect when operating on an orbital $\psi_i(r_1)$,

$$
K_j(r_1) \psi_i(r_1) = \int \text{d}r_2 \psi_j^*(r_2) r_{12}^{\dagger} \psi_i(r_2) \psi_j(r_1).
$$

(4.18)

The solution of the Hartree-Fock equations proceeds is found using the self-consistent-field approach.

The Hartree-Fock equation (4.17) differs from the Hartree equation (4.8) by the fact that the summation of the Coulomb operators runs over all values of $j$ (including $j=i$), and by the presence of the exchange operators. These are nonlocal operators and arise from the determinantal form of the wave function. Had we used a product trial wave function this term would be missing and we would have obtained Hartree’s equation. The presence of the nonlocal term ensures that the Hartree-Fock equation represents an eigenvalue problem for a Hermitian operator, and the eigenfunctions corresponding to different eigenvalues are thus orthogonal. On the contrary, the Hartree equation does not correspond to a single eigenvalue problem, as the potential (4.6) is different for different one-electron wave functions, and the orthogonality of the orbitals is thus not enforced.

The nonclassical exchange term incorporates in the HF theory not only the antisymmetry properties, but also a correlation of electrons with the same spin. The probability of finding two electrons with the same spin simultaneously at the same place is zero. A Fermi hole is said to exist around each electron, which keeps electrons of the same spin separated.
Up to now, we have discussed the HF method independently of the particular spin state of the atom or molecule. A closed-shell system with \( N \) electrons can be described by two sets of spin-orbitals:

\[
\psi_1(\mathbf{r})\alpha, \psi_2(\mathbf{r})\alpha, ..., \psi_N(\mathbf{r})\alpha; \\
\psi_1(\mathbf{r})\beta, \psi_2(\mathbf{r})\beta, ..., \psi_N(\mathbf{r})\beta.
\]

(4.19)

If we denote a spin-orbital by its spatial part only, using a bar or lack of a bar to indicate whether it has the \( \beta \) or \( \alpha \) spin function, we can write a singlet closed-shell Slater determinant as

\[
\Psi_{\text{HF}}(x_1, x_2, ..., x_N) = \psi_1 \bar{\psi}_2 \bar{\psi}_2 ... \bar{\psi}_N \bar{\psi}_N.
\]

(4.20)

In this work, however, we will be handling exclusively open-shell systems with \( N^\alpha \) electrons of \( \alpha \) spin and \( N^\beta \) electrons of \( \beta \) spin, \( N^\alpha > N^\beta \). For this purpose, two modifications of the HF method are used: the unrestricted HF method and the restricted-open-shell HF method.

### 4.2.3 The Unrestricted Hartree-Fock Method

The Hartree-Fock equation (4.17) has the form of a Schrödinger equation for a particle moving in a nonlocal potential. For an open-shell system, the presence of the exchange term in (4.17) makes the potential depend on the spin of the particular electron \( i \). Consequently, one has to solve two sets of equations

\[
f^\alpha(\mathbf{r}_i) \psi_i^\alpha = \epsilon_i^\alpha \psi_i^\alpha,
\]

(4.21)

\[
f^\beta(\mathbf{r}_i) \psi_i^\beta = \epsilon_i^\beta \psi_i^\beta,
\]

(4.22)

where the Fock operators \( f^\alpha(\mathbf{r}_i), f^\beta(\mathbf{r}_i) \) are given by
\[ f^\alpha (\mathbf{r}_i) = h(1) + \sum_j^N [J^\alpha_j (\mathbf{r}_i) - K^\alpha_j (\mathbf{r}_i)] + \sum_j^N J^\beta_j (\mathbf{r}_i) , \]  
\[ \text{(4.23)} \]

\[ f^\beta (\mathbf{r}_i) = h(1) + \sum_j^N [J^\beta_j (\mathbf{r}_i) - K^\beta_j (\mathbf{r}_i)] + \sum_j^N J^\alpha_j (\mathbf{r}_i) . \]  
\[ \text{(4.24)} \]

The unrestricted Coulomb and exchange operators are defined in analogy to our previous definitions (4.7) and (4.18) of the restricted Coulomb and exchange operators:

\[ J^\alpha_j (\mathbf{r}_i) = \int d\mathbf{r}_2 \psi^\alpha_j (\mathbf{r}_2) \psi^\dagger_j (\mathbf{r}_2) , \]  
\[ \text{(4.25)} \]

\[ K^\alpha_j (\mathbf{r}_i) \psi^\alpha_j (\mathbf{r}_i) = \left[ \int d\mathbf{r}_2 \psi^\alpha_j (\mathbf{r}_2) \psi^\dagger_j (\mathbf{r}_2) \right] \psi^\alpha_j (\mathbf{r}_i) . \]  
\[ \text{(4.26)} \]

The definitions of \( J^\beta_j \) and \( K^\beta_j \) are strictly analogous to the above. Equations (4.23) and (4.24) are coupled through the Coulomb operators and must thus be solved by a simultaneously. The exchange interactions of the \( \alpha \)-spin electrons are different from those of their \( \beta \)-counterparts. As a result, even within an electron “pair”, both the spatial parts \( \psi^\alpha_i (\mathbf{r}) \), \( \psi^\beta_i (\mathbf{r}) \) and the energies of the optimized spin-orbitals \( \psi^\alpha_i (\mathbf{r})\alpha \), \( \psi^\beta_i (\mathbf{r})\beta \) are slightly different. Thus, an unrestricted Hartree-Fock (UHF) wave function for an open-shell system can be written as

\[ \psi^{\text{UHF}} (\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \left\{ \psi^\alpha_1, \psi^\beta_1, \psi^\alpha_2, \psi^\beta_2, \ldots, \psi^\alpha_N, \psi^\beta_N \right\} . \]

\[ \text{(4.27)} \]

The total energy corresponding to an UHF wave function may be written as

\[ E^{\text{UHF}} = \sum_i h^\alpha_i + \sum_i h^\beta_i + \frac{1}{2} \sum_i \sum_j (J^{\alpha\alpha}_{ij} - K^{\alpha\alpha}_{ij}) + \frac{1}{2} \sum_i \sum_j (J^{\beta\beta}_{ij} - K^{\beta\beta}_{ij}) + \sum_i \sum_j J^{\alpha\beta}_{ij} , \]

\[ \text{(4.28)} \]

with \( \alpha \) and \( \beta \) denoting spin, where \( h^\alpha_i, h^\beta_i, J^{\alpha\alpha}_{ij}, J^{\beta\beta}_{ij}, J^{\alpha\beta}_{ij}, K^{\alpha\alpha}_{ij}, K^{\beta\beta}_{ij} \) are matrix elements of the corresponding operators involving the spatial orbitals \( \psi^\alpha_i (\mathbf{r}), \psi^\beta_i (\mathbf{r}), \psi^\alpha_j (\mathbf{r}), \text{and } \psi^\beta_j (\mathbf{r}) \). The expectation values of the one-electron operator \( h \)
\[ h_{\alpha\alpha} = \langle \psi_{\alpha}^\alpha | h | \psi_{\alpha}^\alpha \rangle \quad \text{and} \quad h_{\beta\beta} = \langle \psi_{\beta}^\beta | h | \psi_{\beta}^\beta \rangle \]  

(4.29)

represent the average kinetic and nuclear-attraction energy of the unrestricted orbitals \( \psi_{\alpha}^\alpha \) and \( \psi_{\beta}^\beta \), respectively.

Matrix elements

\[ J_{\alpha\alpha}^{\alpha\beta} = \langle \psi_{\alpha}^\alpha | J_{\beta\beta} | \psi_{\beta}^\beta \rangle = \langle \psi_{\beta}^\beta | J_{\alpha\alpha} | \psi_{\alpha}^\alpha \rangle = :\langle \psi_{\alpha}^\alpha \psi_{\beta}^\beta | \psi_{\alpha}^\alpha \psi_{\beta}^\beta \rangle : \]  

(4.30)

\[ J_{\alpha\alpha}^{\beta \beta} = \langle \psi_{\alpha}^\alpha | J_{\beta\beta} | \psi_{\beta}^\beta \rangle = \langle \psi_{\beta}^\beta | J_{\alpha\alpha} | \psi_{\alpha}^\alpha \rangle = :\langle \psi_{\alpha}^\alpha \psi_{\beta}^\beta | \psi_{\alpha}^\alpha \psi_{\beta}^\beta \rangle : \]  

(4.31)

and

\[ J_{\alpha\alpha}^{\alpha\alpha} = \langle \psi_{\alpha}^\alpha | J_{\alpha\alpha} | \psi_{\alpha}^\alpha \rangle = \langle \psi_{\alpha}^\alpha | J_{\alpha\alpha} | \psi_{\alpha}^\alpha \rangle = :\langle \psi_{\alpha}^\alpha \psi_{\alpha}^\alpha | \psi_{\alpha}^\alpha \psi_{\alpha}^\alpha \rangle : \]  

(4.32)

express the classical Coulomb repulsion between the charge clouds \( |\psi_{\alpha}(r_i)|^2 \) and \( |\psi_{\beta}(r_j)|^2 \) for electrons of different or the same spin and are referred to as the Coulomb integrals.

Finally, matrix elements

\[ K_{\alpha\alpha}^{\alpha\alpha} = \langle \psi_{\alpha}^\alpha | K_{\alpha}^\alpha | \psi_{\alpha}^\alpha \rangle = \langle \psi_{\alpha}^\alpha | K_{\alpha}^\alpha | \psi_{\alpha}^\alpha \rangle = :\langle \psi_{\alpha}^\alpha \psi_{\alpha}^\alpha | \psi_{\alpha}^\alpha \psi_{\alpha}^\alpha \rangle : \]  

(4.33)

and

\[ K_{\beta\beta}^{\beta \beta} = \langle \psi_{\beta}^\beta | K_{\beta}^\beta | \psi_{\beta}^\beta \rangle = \langle \psi_{\beta}^\beta | K_{\beta}^\beta | \psi_{\beta}^\beta \rangle = :\langle \psi_{\beta}^\beta \psi_{\beta}^\beta | \psi_{\beta}^\beta \psi_{\beta}^\beta \rangle : \]  

(4.34)

the so-called exchange integrals, represent the exchange interaction energy of the two electrons with parallel spins. There is no exchange interaction between electrons of opposite spin.

The summations in eq (4.28) are not restricted to pairs of different spin orbitals. Therefore, the (unphysical) electrostatic interaction of an electron with itself is
accounted for in the Coulomb part and again subtracted in the exchange part. This allows a unique orbital decomposition of the total electron repulsion energy into exchange and Coulomb parts. The Coulomb part may be interpreted as the classical electrostatical energy of a charge cloud of density $\rho(r)$, whereas the exchange part includes all nonclassical effects, (see ref 4, pp 34,39).

The total spin density corresponding to an UHF wave function is given by:

$$Q^{\text{UHF}}(r) = \sum_{j=N+1}^{n} |\psi_j^\alpha(r)|^2 + \sum_{j=1}^{n} \left( |\psi_j^\alpha(r)|^2 - |\psi_j^\beta(r)|^2 \right).$$

(4.35)

The first sum represents the direct contribution from the unpaired electrons, the second sum is the spin polarization contribution from the remaining “paired” electrons. The inclusion of the spin polarization is a crucial property of the UHF method. As will be shown below, it provides a one-electron-level understanding of the spin-density transfer from the valence space to the nucleus. At the same time, the spin polarization leads to a serious drawback of the UHF method, namely that the UHF wave functions do not correspond to pure spin states. A nominal doublet state, e.g., contains small amounts of quartet, sextet and higher spin states. Before evaluating spin properties from an UHF wave function, the spin contaminants are often eliminated using spin-projection techniques. However, the justification for doing so is doubtful. A strong argument against using the spin projection is that the UHF method yields the correct diagrams in a perturbation theory development of the exact wave function, whereas the spin-projected UHF does not do so.6

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a When self interaction is not accounted for, the decomposition of the electron repulsion energy into Coulomb and exchange parts may be arbitrary. E.g., for a $p$-shell fully occupied with six electrons, both the total Coulomb and the total exchange energy depends on the orbital basis (angular momentum eigenfunctions or real functions). The reason is that

$$\langle p_x p_y | p_x p_y \rangle = \langle p_x p_z | p_x p_z \rangle = \langle p_y p_z | p_y p_z \rangle = \langle p_1 p_0 | p_1 p_0 \rangle = \langle p_{-1} p_0 | p_{-1} p_0 \rangle \neq \langle p_{-1} p_1 | p_{-1} p_1 \rangle.$$
4.2.4 The Restricted Open-Shell Hartree-Fock Method

The spin-contamination problem in the HF description of open-shell systems can be avoided using a more complicated restricted open-shell Hartree-Fock (ROHF) method. Whereas at the UHF level of theory, MOs $\psi_i^\alpha(\mathbf{r})$ and $\psi_i^\beta(\mathbf{r})$ are allowed to differ, within the ROHF method they are required to be identical for every $i \leq N^\beta$. We are thus looking for a Slater determinant of the form

$$
\Psi_{\text{ROHF}}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \left| \psi_1 \varphi_1 \psi_2 \varphi_2 \ldots \psi_{N^\beta} \varphi_{N^\beta} \psi_{N^\beta+1} \ldots \psi_{N^\alpha} \right>
$$

which minimizes the total electronic energy.

To achieve this, the $N^\beta$ electron pairs (i.e. the closed shell) are treated separately from the $N^\alpha - N^\beta$ unpaired (open-shell) electrons and the virtual orbitals. This approach results in two sets of equations:

$$
f^\prescript{\alpha}{}(\mathbf{r}_i) \psi_i^\prescript{\alpha}{} = \varepsilon_i^\prescript{\alpha}{} \psi_i^\prescript{\alpha}{} \quad ,
$$

$$
f^\prescript{\beta}{}(\mathbf{r}_i) \psi_i^\prescript{\beta}{} = \varepsilon_i^\prescript{\beta}{} \psi_i^\prescript{\beta}{} \quad .
$$

The Fock operators $f(\mathbf{r}_i)$, $f^\beta(\mathbf{r}_i)$ are defined as

$$
f^\prescript{\alpha}{}(\mathbf{r}_i) = \hbar(1) + 2 \sum_{j}^{N^\beta} \left[ J_j(\mathbf{r}_i) - K_j(\mathbf{r}_i) + \kappa^j L_j^\prescript{\alpha}{}(\mathbf{r}_i) - \lambda^j M_j^\prescript{\alpha}{}(\mathbf{r}_i) \right]
$$

(4.39)

$$
f^\prescript{\beta}{}(\mathbf{r}_i) = \hbar(1) + \sum_{j}^{N} \left[ J_j(\mathbf{r}_i) - K_j(\mathbf{r}_i) \right]
$$

$$
+ \sum_{j \neq i}^{N^\alpha} \left[ \kappa^j J_j(\mathbf{r}_i) - \lambda^j K_j(\mathbf{r}_i) \right] + \sum_{j \neq i}^{N^\beta} \left[ \kappa^j L_j^\prescript{\beta}{}(\mathbf{r}_i) - \lambda^j M_j^\prescript{\beta}{}(\mathbf{r}_i) \right] \quad .
$$

(4.40)

where
\[ L_j^*(\mathbf{r}_i) = \nu \sum_{m=1}^{N} |\psi^*_m \rangle \langle \psi_m | J_j (\mathbf{r}_i) \ , \]  

(4.41)

\[ M_j^*(\mathbf{r}_i) = \nu \sum_{m=1}^{N} |\psi^*_m \rangle \langle \psi_m | K_j (\mathbf{r}_i) \ , \]  

(4.42)

\[ L_j^c (\mathbf{r}_i) = \sum_{m=1}^{N} |\psi^*_m \rangle \langle \psi_m | J_j (\mathbf{r}_i) \ , \]  

(4.43)

\[ M_j^c (\mathbf{r}_i) = \sum_{m=1}^{N} |\psi^*_m \rangle \langle \psi_m | K_j (\mathbf{r}_i) \]  

(4.44)

are necessary in order to preserve the orthogonality of the ROHF solutions. The quantities \( \kappa, \kappa', \lambda, \lambda' \) and \( \nu \) are dependent on the particular spin state and are described elsewhere. In ROHF theory, the treatment yields a single-determinant expression that satisfies all spin and symmetry requirements.\(^7\)

The total energy corresponding to an ROHF wave function is given by:

\[ E^{\text{ROHF}} = 2 \sum_{i=1}^{N^d} h_i + \sum_{i=N^d+1}^{N^a} h_i + \sum_{i=1}^{N^d} \sum_{j=1}^{N^d} (2J_{ij} - K_{ij}) + \frac{1}{2} \sum_{i=N^d+1}^{N^a} \sum_{j=N^d+1}^{N^a} (J_{ij} - K_{ij}) \ . \]  

(4.45)

The spin density in this model is the sum of probability distributions of the open-shell orbitals

\[ Q^{\text{ROHF}} (\mathbf{r}) = \sum_{j=N^d+1}^{N^a} |\psi_{i} (\mathbf{r})|^2 \ . \]  

(4.46)

The closed-shell (doubly-occupied) orbitals do not contribute to \( Q(\mathbf{r}) \), as the contributions of the \( \alpha \) spin-orbitals are always exactly cancelled by the contributions of the \( \beta \) spin-orbitals. Spin-polarization contributions can be included in the ROHF wave function using the configuration interaction approach.
4.3 The Configuration Interaction Method

The Hartree-Fock method is a one-electron approximation. As such it describes the electron-repulsion interactions in an averaged way and does not include important electron-correlation effects. The exact wave function for the ground as well as the excited states of the system can be written as a linear combination of all possible $N$-electron Slater determinants formed from a complete set of spin-orbitals. Since any determinant can be described in reference to the HF determinant $|\text{HF}\rangle$, we can write (within the second quantization formalism):

$$
\Phi = \left( 1 + \sum_i c_i^a a_i^a + \sum_{i,j} c_{ij}^u a_i^u a_j^+ \right) |\text{HF}\rangle,
$$

(4.47)

where the creation and annihilation operators $a_i^+$ and $a_i$ create a particle in the virtual orbital $u$ and annihilate a particle in the occupied orbital $i$, respectively. The summations over $i,j,...$ and $u,v,...$ run over all occupied spin-orbitals and virtual spin-orbitals, respectively. The lowest eigenvalue of the Hamiltonian matrix with elements $\langle \Psi_k | H | \Psi_j \rangle$ formed from the complete set $\{|\Psi_k\rangle\} = \{|\text{HF}\rangle, a_i^+ a_i |\text{HF}\rangle, a_i^+ a_j^+ a_i a_j |\text{HF}\rangle, ... \}$ is the exact nonrelativistic ground state energy of the system within the Born-Oppenheimer approximation.

In practical calculations, various approximations to the full wave function of eq (4.47) are obtained by working with a finite (rather than complete) set of spin-orbitals and truncating the expansion at some excitation level. The values of the coefficients $c_{ij...}^{uv...}$ are optimized using the variational principle, as the resulting total energy is always an upper bound to the exact energy. This is the so-called configuration interaction (CI) method. A serious drawback of truncated CI methods is that they are not size consistent: the total energy of a system composed of non-interacting molecules does not scale linearly with the number of the molecules.

The CI formalism improves the HF description of the spin density distribution by including the electron-correlation effects. Particularly, it augments the ROHF spin density with the spin-polarization contributions. As the spin density is a one-electron property, for a CI wave function it can be written as a sum over matrix elements
between configurations belonging to the same excitation class or differing in one excitation. The first term in eq (4.48) represents the contribution arising from matrix elements between the ROHF determinant and singly excited determinants. The second term gives the contributions of diagonal matrix elements, the third and fourth terms provide contributions of nondiagonal matrix elements between singly-excited determinants. The sum over \( a \) in the second term runs over all occupied orbitals in the wave function \( a_i^a |\text{ROHF}\rangle \). The last term gives the single-double contributions. Further contributions arise from double-double, double-triple excitations, etc. The most important contributions come from the singly and doubly excited determinants. To obtain accurate isotropic HFCCs, however, one has to take into account also higher than double excitations. As the higher excitations contribute mainly indirectly, by influencing the coefficients of the lower excitations, it is sufficient to include their effect perturbatively.

4.4 The Coupled-Cluster Method

In the coupled-cluster method, the trial many-electron wave function is written as

\[
\Phi_{CCA} = \exp \left( T_1 + T_2 + \ldots \right) |\text{HF}\rangle ,
\]

where
\[ T_1 = \left( \frac{1}{1!} \right)^2 \sum_{i} c_i \sigma_a \sigma_i, \]
\[ T_2 = \left( \frac{1}{2!} \right)^2 \sum_{i,j} c_{ij} \sigma_a \sigma_i \sigma_a \sigma_j, \]
\[ T_3 = \ldots \]  

(4.50)

The total energy \( E^{CC} \) is found by projecting the Schrödinger equation \( (e^{-T} H e^{T} - E)\langle HF \rangle = 0 \) to the HF reference state \( \langle HF \rangle \) as
\[ E = \langle HF | H e^{T} | HF \rangle, \]

(4.51)

and the cluster amplitudes \( c \) are found similarly by projecting to states of the corresponding excitation level, e.g., for the single particle-hole pair amplitudes \( c_i^a \)
\[ \langle HF | a_i^a a_u e^{-T} H e^{T} | HF \rangle = 0. \]

(4.52)

This process leads to a non-linear system of equations to be solved iteratively.

In practical calculations, the CC wave functions are truncated at certain excitation level, and the cluster expansion (4.49) ensures that – unlike for the CI methods – the size consistence is retained. The present work uses the CCSD truncation that includes the singles and doubles operators \( T_1, T_2 \) in \( e^{T} \), and the CCSD(T) truncation which is an approximate form of the CC method including the singles, doubles, and triples operators \( T_1, T_2, \) and \( T_3 \) in \( e^{T} \). The price paid for the size consistency is that truncated CC methods are not variational.

The expressions for the total energy and the spin density within the CC method are given elsewhere.\(^1,^{10}\)
4.5 Density Functional Theory

4.5.1 The Hohenberg-Kohn Theorems

The quantum chemistry methods discussed above use the many-electron wave function, and consequently the external potential \( v(r) \) and the number of electrons \( N \), which specify the electronic Hamiltonian, as the source for the determination of all electronic properties. The basic theorem of the density functional theory states that the electron density \( \rho(r) \) can be used as the basic variable instead. The external potential \( v(r) \) is determined, within a trivial additive constant, by the electron density \( \rho(r) \) (the first Hohenberg-Kohn theorem). Obviously, \( \rho(r) \) determines also \( N \).

The total electronic energy can thus be written as

\[
E[\rho] = T[\rho] + V_{ne}[\rho] + V_{ee}[\rho] = \int \rho(r) v(r) \, dr + F_{hk}[\rho] ,
\]

where \( T[\rho] \) represents the kinetic energy, \( V_{ne}[\rho] \) and \( V_{ee}[\rho] \) the potential energy due to the nuclei and the electrons, respectively, and

\[
F_{hk}[\rho] = T[\rho] + V_{ee}[\rho]
\]

is a universal functional of the electronic density, which does not depend on the particular system.

The electron-electron repulsion term \( V_{ee}[\rho] \) can be partitioned as

\[
V_{ee}[\rho] = J[\rho] + \text{nonclassical term} ,
\]

where

\[
J[\rho] = \frac{1}{2} \iiint_{\mathbb{R}^3} \frac{\rho(r_1) \rho(r_2)}{r_{12}} \, dr_1 \, dr_2
\]

\[(4.56)\]
is the classical self-repulsion energy of a distribution $\rho(\mathbf{r})$, i.e. the Coulomb energy defined above, cf. eqs (4.25), (4.28).

The second Hohenberg-Kohn theorem represents the energy variational principle. For a trial density $\tilde{\rho}(\mathbf{r})$ such that $\tilde{\rho}(\mathbf{r}) \geq 0$ and

$$\int \tilde{\rho}(\mathbf{r}) \, d\mathbf{r} = N \quad ,$$  

(4.57)

the energy $E[\tilde{\rho}(\mathbf{r})]$ is always an upper bound to the exact energy $E_0$:

$$E_0 \leq E[\tilde{\rho}(\mathbf{r})] \quad .$$  

(4.58)

The latter requires that the ground-state density satisfies the stationary principle

$$\delta [E[\rho]] - \mu \left[ \int \rho(\mathbf{r}) \, d\mathbf{r} - N \right] = 0$$  

(4.59)

which gives the Euler-Lagrange equation

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} = v(\mathbf{r}) + \frac{\delta F_{HK}[\rho]}{\delta \rho(\mathbf{r})} \quad .$$  

(4.60)

The Lagrange multiplier $\mu$ is the chemical potential and has been introduced in order to constrain the minimization (4.58) by the normalization condition (4.57). If we knew the exact $F_{HK}[\rho]$, (4.58) would be an exact equation for the ground-state electron density.

4.5.2 The Kohn-Sham Method

Due to the unfortunate (but challenging) fact that the functional $F_{HK}[\rho]$ is hard to come by in explicit form, accurate calculational implementations of the density-functional theory are far from easy to achieve. Approximate forms of $F_{HK}[\rho]$ are required and can be constituted using a direct approach, whereby one constructs explicit approximate forms for $T[\rho]$ and $V_{ee}[\rho]$. Unfortunately, there are seemingly insurmountable difficulties in going beyond the crude level of approximation of $T[\rho]$. 
An ingenious indirect approach to the kinetic energy functional has been
developed within the Kohn-Sham (KS) method. It introduces a (hypothetical) non-
interacting reference system with exactly the same electron density as that of the real
system. The exact wave function of the noninteracting system is a Slater determinant
formed from \( N \) spin-orbitals (Kohn-Sham orbitals) \( \psi_i(x) \). The exact kinetic energy for
the reference system

\[
T_s = \sum_i^{N} \left| \psi_i \right| \left\{ -\frac{1}{2} \nabla^2 \right\} \left| \psi_i \right|
\]

(4.61)
can be – by virtue of the first Hohenberg-Kohn theorem – considered a functional of the
charge density

\[
\rho(r) = \sum \left| \psi_i(x) \right|^2 .
\]

(4.62)

The quantity \( T_s[\rho] \) is of course not equal to the true kinetic energy of the interacting
system \( T[\rho] \). The very clever idea of Kohn and Sham is to set up a problem of interest
in such a way that \( T_s[\rho] \) is its kinetic-energy component, exactly.

To produce the desired separation out of \( T_s[\rho] \) as the kinetic energy component, we
rewrite (4.54) as

\[
E_{\text{HK}}[\rho] = T_s[\rho] + J[\rho] + E_{\text{xc}}[\rho]
\]

(4.63)

where

\[
E_{\text{xc}}[\rho] \equiv T[\rho] - T_s[\rho] + V_{\text{xc}}[\rho] - J[\rho] .
\]

(4.64)
The defined quantity \( E_{\text{xc}}[\rho] \) is called the exchange-correlation energy; it contains the
difference between \( T \) and \( T_s \) (presumably fairly small), and the nonclassical part of
\( V_{\text{xc}}[\rho] \).

The Euler equation (4.60) now becomes
where the Kohn-Sham (KS) effective potential is defined by

\[
v_{\text{eff}}(\mathbf{r}_i) = v(\mathbf{r}_i) + \frac{\delta J[\rho]}{\delta \rho(\mathbf{r}_i)} + \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r}_i)} = v(\mathbf{r}_i) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_2 + v_{xc}(\mathbf{r}_i)
\]  

(4.66)

with the exchange-correlation potential

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

(4.67)

The Kohn-Sham treatment runs as follows. Equation (4.65) represents a conventional DFT approach when applied to a system of noninteracting electrons moving in the external potential \( v_{\text{eff}}(\mathbf{r}) \). Therefore, for a given \( v_{\text{eff}}(\mathbf{r}) \), one obtains the \( \rho(\mathbf{r}) \) that satisfies (4.65) simply by solving the \( N \) one-electron equations

\[
\left[ -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i = \epsilon_i \psi_i
\]  

(4.68)

and setting

\[
\rho(\mathbf{r}) = \sum_i \psi_i(\mathbf{x})
\]  

(4.69)

Here, \( v_{\text{eff}}(\mathbf{r}) \) depends on \( \rho(\mathbf{r}) \) through (4.67); hence, (4.66), (4.68), and (4.69) must be solved self-consistently.

The total Kohn-Sham energy is given by

\[
E = \sum_i h_{ii} - \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1) \rho(\mathbf{r}_2)}{r_{12}} \, d\mathbf{r}_1 \, d\mathbf{r}_2 + E_{xc}[\rho] - \int v_{xc}(\mathbf{r}_i) \rho(\mathbf{r}_i) \, d\mathbf{r}_i
\]  

(4.70)

where
\[
\sum_{i} h_{ii} = \sum_{i} \langle \nu_{i} | -\frac{1}{2} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \rangle \nu_{i} \rangle = T_{\text{s}}[\rho] + \int v_{\text{eff}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}.
\]

(4.71)

The KS equations are formally very similar to the HF equations. Nevertheless, in HF theory, electron correlation effects are by definition neglected and can be accounted for only using multi-determinantal trial wave functions. On the contrary, the more general local potential \( v_{\text{xc}} \) in the KS equations ensures that the Kohn-Sham theory is in principle exact, as it fully incorporates the exchange-correlation effects. Kohn-Sham equations can be improved by improving approximations to \( E_{\text{xc}}[\rho] \). In this sense, Kohn Sham theory represents the best one-electron approach. A crucial advantage is that KS theory is typically computationally much less expensive than the correlated methods based on HF, and enables thus the treatment of larger systems.

The methods for the treatment of the open-shell systems within the KS theory - the unrestricted Kohn-Sham (UKS) and the restricted open-shell Kohn-Sham (ROKS) methods - are analogous the the HF-based approaches introduced in sections 4.2.3 and 4.2.4. The expressions for the UKS and ROKS spin densities are identical to those given by (4.35) and (4.46), respectively, where the optimized Kohn-Sham orbitals are considered instead of the optimized Hartree-Hock orbitals.

### 4.5.3 Exchange-Correlation Functionals

The explicit form of the exchange-correlation functional \( E_{\text{xc}}[\rho] \) that specifies the Kohn-Sham potential (4.66) is not known and represents the greatest challenge in DFT. Various approximations have been suggested for \( E_{\text{xc}}[\rho] \), the simplest one being the local density approximation (LDA)

\[
E_{\text{xc}}^{\text{LDA}}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{\text{xc}}(\rho) d\mathbf{r},
\]

(4.72)

where \( \varepsilon_{\text{xc}}(\rho) \) is the exchange and correlation energy per particle in a uniform electron gas of density \( \rho(\mathbf{r}) \). Thus, we associate with the density \( \rho(\mathbf{r}) \) the exchange and correlation energies and potentials that a homogenous electron gas of equal, but
constant density would have, and assume that the exchange-correlation functionals depend only on the \textit{local} value of $\rho(r)$.

The exchange part of the LDA functional is

$$E_{x}^{LDA}[\rho] = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \int \rho^{4/3}(r) d\mathbf{r} .$$

$E_{x}^{LDA}$ can not be written in a such an explicit form, but highly accurate numerical values are available for this property on the basis of Monte Carlo calculations of the homogeneous electron gas.\textsuperscript{12} On the basis of these results, various authors have presented analytical expressions of $E_{x}^{LDA}$ based on sophisticated interpolation schemes. The most widely used representation of $E_{x}^{LDA}$ is due to Vosko, Wilk, and Nusair (VWN).\textsuperscript{13} The exchange (4.73) together with the VWN correlation functional forms the so-called SVWN functional, used in our deMon calculations.

The local density approximation provides, however, only moderate accuracy and is thus insufficient for most applications in chemistry. The logical first step in the going beyond LDA is to consider functionals that are functions of both the local density, $\rho(r)$, and the gradient of the density, $\nabla \rho(r)$. Functionals that include the gradients of the charge density are collectively known as \textit{generalized gradient approximations} (GGA). These functionals are the workhorses of current density functional theory (they have been extensively applied throughout this thesis) and can generally be written as

$$E_{xc}^{GGG} \left[ \rho_{\alpha}, \rho_{\beta} \right] = \int f(\rho_{\alpha}, \rho_{\beta}, \nabla \rho_{\alpha}, \nabla \rho_{\beta}) d\mathbf{r} .$$

Finally, there is a great interest recently in applications of exchange-correlation functionals that include some exact, nonlocal exchange. Such \textit{hybrid functionals} have also been used for the calculations employed in this thesis. These, as well as the generalized gradient approximations, are discussed in detail elsewhere.\textsuperscript{5}
4.6 Basis Sets and Pseudopotentials

Practical electronic structure calculations of polyatomic molecules typically use the linear-combination-of-atomic-orbitals (LCAO) approximation

$$\left| \psi_k \right> = \sum c^k_\mu \left| \chi_\mu \right> ,$$

(4.75)

where \( \{\chi_\mu\} \) is the basis set of atomic orbitals.

The most common LCAO basis functions employed presently in quantum chemistry are Gaussian type orbitals (GTOs) centered on atomic nuclei. In spherical coordinates, their form is

$$\chi_\mu (r, \theta, \varphi) = Y_{lm} (\theta, \varphi) \ r^{l-1} \ e^{-\zeta r^2} ,$$

(4.76)

where \( Y_{lm} \) are the spherical harmonics; \( \zeta \) is the so-called exponent of the GTO. Due to their convenient mathematical properties, GTOs are more popular than the physically more correct Slater type orbitals (STO). The better physical behavior of STOs at \( r=0 \) and at large \( r \) is simulated by working with fixed linear combinations of primitive gaussian functions \( \chi_\mu \). These linear combinations lead to contracted Gaussian functions (CGTOs); each of them being specified by a set of exponents and another set of contraction coefficients which are not allowed to change during the calculation. Depending on the number of CGTOs used per atomic shell, basis sets are referred to as single-\( \zeta \) (1 CGTO), double-\( \zeta \) (DZ, 2 CGTOs), triple-\( \zeta \) (TZ, 3 CGTOs), etc. The flexibility of a basis set is improved by adding functions of higher angular momentum than corresponds to occupied orbitals in the ground state of the particular atom. These are called the polarization functions and are \( p \)-type functions for H and He, \( d \)-type functions for the first-row atoms Li-F, etc. Diffuse functions are those with very small exponents and allow the charge distribution to be spread widely in the space.
For the purposes of this work, we have constructed a \((15s11p6d)/[9s7p4d]\) basis as a standard medium-size basis set for the 3d transition metal atoms. Our starting point was the DZ basis of Schäfer et al.,\(^{14}\) to which we added the most diffuse functions (a 1s2p1d set) from the ECP valence basis of Dolg et al.\(^{15}\) IGLO-III basis sets\(^{16}\) were used for the main group atoms.

Hyperfine properties reflect the spatial coincidence of the spin density and the magnetic nuclei; proper treatment of the core electrons is thus necessary. In structure optimizations, however, the role of the core electrons is negligible in comparison to the valence electrons. Instead of the explicit treatment of the core electrons, their influence on the valence electrons can be simulated by using an effective core potential (ECP).\(^{17}\) The properties of the valence pseudo-orbitals obtained in an ECP calculation are at the same time required to be the same as those obtained in an all-electron treatment. Our structure optimizations employed small-core ECPs and \((8s7p6d)/[6s5p3d]\) GTO valence basis sets of the Stuttgart group for the transition metals.\(^{18}\) For the first-row ligand atoms, ECPs with \((4s4p1d)/[2s2p1d]\) basis sets have been used.\(^{19}\) For hydrogen, a \((4s1p)/[2s1p]\) basis\(^ {20}\) has been employed.

\(^{b}\) The notation \((15s11p6d)/[9s7p4d]\) indicates a contraction of the basis set and has the following meaning: The numbers in parentheses are the total numbers of primitive gaussian functions, the numbers in square brackets are those of CGTOs.
References


11 Such reference systems exists always when the density is noninteracting v-representable, cf. ref 4.


I think that there is a moral to this story, namely that it is more important to have beauty in one’s equations than to have them fit experiment .... If there is not complete agreement between the results of one’s work and experiment, one should not allow oneself to be too discouraged, because the discrepancy may well be due to minor features that are not properly taken into account and that will get cleared up with further developments of the theory.

Paul Adrien Maurice Dirac (1902-84)

5 A Critical Validation of Density Functional and Coupled-Cluster Approaches for the Calculation of EPR Hyperfine Coupling Constants in Transition Metal Complexes

Introduction

Hyperfine coupling constants (tensors) are considered to be the most important part of the information obtained from an EPR spectrum, due to a very direct connection between the magnitude of the hyperfine coupling and the electronic structure of the paramagnetic species. In spite of the richness of experimental data on the hyperfine coupling in transition metal complexes, previous theoretical studies of HFCCs concentrated largely on light main group systems for which the post-Hartree-Fock \textit{ab initio} treatment of electron correlation is still applicable. Recent developments in density functional theory provided an alternative by including electron correlation approximately, at moderate computational cost, and enabled thus calculations on systems of larger size and/or including heavier elements like transition metals. The following paper represents the first extensive evaluation of DFT methods for the prediction of hyperfine coupling constants for both metals and ligands in 3d transition metal complexes. Results obtained for a series of 21 complexes using eight different density functionals have been compared with reliable experimental data and results from elaborate coupled cluster calculations. The author of this thesis performed all of the calculations included in the study and contributed significantly to the preparation of the manuscript.
Results

In the present study, no generally valid hierarchy of the tested functionals for the calculation of hyperfine coupling constants of transition-metal complexes could be established, since the performance of a given functional varies significantly for different classes of complexes. The subtleties of the electronic structures, the degree of spin contamination as well as other factors seem to be responsible for these variations. On the other hand, for a significant number of complexes a ca. 10-15% agreement with experiment has been achieved with essentially all of the functionals. In other subsets of molecules, the analysis of the electronic structure suggests the range of functionals that might be most appropriate.

Conclusions and outlook

The present study has shown that the functionals to be applied to the calculation of hyperfine couplings in certain areas of transition metal chemistry have to be carefully selected. Desirable, improved functionals should provide sufficiently large spin polarization for core and valence shells without exaggerating it for the latter, and thus introducing spin contamination. Generally, hyperfine coupling constants, in particular for transition metal systems, may turn out to be a particularly fruitful testing ground for new DFT (or alternative) approaches. As noted in a very recent study by Neese\textsuperscript{1}, the relatively poor performance of DFT for some of the hyperfine couplings might be connected to the wrong behavior of the state-of-the-art exchange-correlation potentials close to the nucleus where they show an unphysical divergence.\textsuperscript{2} The connection between the performance of DFT and the relative size of spin polarization contributions to the HFCCs established became a motivation for a detailed analysis of mechanisms of EPR hyperfine coupling in 3d metal complexes (Chapter 7).

The study reported in here does not include scalar relativistic and spin-orbit effects, except for a rough semi-empirical estimate of SO contributions to HFCCs for some of the complexes. Recently, the zero order regular approximation for relativistic effects (ZORA) has been employed for the calculation of EPR parameters for Ni
complexes by Stein et al.\(^3\) The authors discuss in detail the relation between their results for [Ni(CO)\(_3\)H] and the nonrelativistic results obtained for this complex in the following paper. A detailed evaluation of the density functional approach in the ZORA formalism has been reported recently by Belanzoni et al.\(^4\) In the spin-orbit coupled equations, only spin-restricted density functionals have been applied as the current implementation of the ZORA approach does not yet allow the simultaneous inclusion of spin-orbit and spin-polarization effects.\(^4\) An approach that would allow such simultaneous inclusion is currently being developed in our group.
References


A Critical Validation of Density Functional and Coupled-Cluster Approaches for the Calculation of EPR Hyperfine Coupling Constants in Transition Metal Complexes

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Received: July 7, 1999; In Final Form: September 27, 1999

The performance of various density functional approaches for the calculation of electron paramagnetic resonance (EPR) hyperfine coupling constants in transition metal complexes has been evaluated critically by comparison with experimental data and high-level coupled-cluster results for 21 systems, representing a large variety of different electronic situations. While both gradient-corrected and hybrid functionals allow the calculation of isotropic metal hyperfine coupling constants to within ca. 10–15% for the less critical cases (e.g., ScO, TiN, TiO, VO, MnO, MnF), none of the functionals investigated performs well for all complexes. Gradient-corrected functionals tend to underestimate the important core–shell spin polarization. While this may be improved by exact-exchange mixing in some cases, the accompanying spin contamination may even lead to a deterioration of the results for other complexes. We also identify cases, where essentially none of the functionals performs satisfactorily. In the absence of a "universal functional", the functionals to be applied to the calculation of hyperfine couplings in certain areas of transition metal chemistry have to be carefully selected. Desirable, improved functionals should provide sufficiently large spin polarization for core and valence shells without exaggerating it for the latter (and thus introducing spin contamination). Coupling anisotropies and coupling constants for ligand nuclei are also discussed. The computationally much more demanding coupled cluster (CCSD and CCSD(T)) methods, which have been applied to a subset of complexes, show good performance, even when a UHF reference wave function is moderately spin-contaminated.

1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy represents one of the most powerful experimental tools for studying the molecular and electronic structure of compounds containing unpaired electrons. Since the early days of this technique, a large number of EPR spectra for transition metal complexes have been measured. A wealth of experimental data on electronic g-tensors and hyperfine coupling constants (HFCCs) is thus available.1–8 Quantitative theoretical studies of HFCCs have, however, concentrated largely on organic molecules or on other light main group systems. This is understandable, as the accurate inclusion of electron-correlation effects is mandatory for quantitative calculations of electron–nuclear hyperfine interactions. To achieve this in traditional post-Hartree–Fock ab initio calculations is far from trivial, and such treatments are not easily applicable to larger transition metal complexes. CAS–SCF and MR–SDCI calculations have been done on ScO, TiN, and VN by Mattar et al.9–11 as well as on VO, (x = 1, 2, 3) by Knight et al.12 To our knowledge, no other transition metal systems have been treated at comparable levels.

Recent developments in density functional theory (DFT) do in principle provide an alternative, as DFT includes electron correlation approximately, at moderate computational cost. A number of Kohn–Sham DFT studies on transition metal HFCCs have appeared, using local-spin-density approximations (LSDA), generalized-gradient approximations (GGA), as well as hybrid functionals including exact exchange. Hyperfine parameters have been computed for VN by Mattar and Doleman,11 for TiN and TiO by Engels et al.,13 for CuC2H2 and Cu(CO) by Barone et al.,14,15 for a ruthenium complex by Arntts et al.,16 for TiF3 by Belanzoni et al.17,18 and by van Lenthe et al.,19 and for a series of molybdenum(V) oxyhalide anions by Swann and Westmoreland.20 During the course of the present study, Knight et al. reported DFT results on MO (M = Sc, Y, La).21 A number of earlier calculations employed the Xα method.22–24 Reasonable agreement between experiment and theory for the isotropic HFCCs has been found when significant metal s-character in the singly occupied molecular orbitals (SOMOs) leads to a dominance of direct contributions to the spin density at the nucleus. The description is expected to be considerably more complicated when spin-polarization effects become large, a situation that should apply for many transition metal systems.1

In the studies mentioned, only a limited number of exchange–correlation functionals and basis sets have been employed, and only a relatively small set of molecules and electronic structure situations was encompassed. Further systematic studies are thus needed, if one wants to be able to judge in detail the ability of the available DFT approaches to describe HFCCs for transition metal systems. Here we present a critical validation study, including twenty-one first-row transition metal complexes and eight different state-of-the-art exchange–correlation potentials ψxc. Throughout this work, we have learned much about the mechanisms of spin polarization and related phenomena for HFCCs in transition metal complexes. These interpretational aspects will be covered in more detail elsewhere25 (including numerical results), but will be touched upon briefly in this work whenever needed for an understanding of the performance of different functionals.

After outlining roughly the nonrelativistic theoretical formalism of hyperfine couplings in section 2 (mainly to connect to the rather different types of experimental information available), we will discuss problems connected with the selection of
experimental data (section 3). Information on molecular structures, basis sets, and theoretical approaches used is given in section 4. After a description of coupled cluster results for a subset of the complexes (section 5), which we employ as reference data, basis set effects are examined in section 6. Then the performance of different exchange–correlation functionals is compared systematically for the metal HFCCs (section 7), followed by a brief discussion of ligand HFCCs (section 8). A number of general conclusions are provided in section 9.

2. Theoretical Formalism

The theory of EPR hyperfine couplings is covered in detail in text books,13–8,26 and we summarize only those points which are important for the comparison between computed and experimental quantities. The hyperfine coupling parameters describe the interactions of unpaired electrons with various magnetic nuclei. The $3 \times 3$ hyperfine interaction tensor $A$ can be separated into its isotropic and anisotropic (dipolar) components.6 In the first-order approximation (neglecting spin–orbit effects; cf. discussion in section 4), isotropic hyperfine splittings $A_{	ext{iso}}(N)$ are equal to the Fermi contact term $A_{	ext{FC}}$ and they are related to the spin densities $\rho_{\text{iso}}^{\alpha\beta}(R_N)$ at the corresponding nuclei by:

$$A_{\text{iso}}(N) = A_{\text{FC}} = \frac{4\pi}{3} \beta \sum g_N g_e \langle S_Z \rangle^{-1} \rho_{N}^{\alpha\beta} \tag{1}$$

where $\beta$ is the Bohr magneton, $\beta_N$ the nuclear magneton, $g_e$ the free electron $g$-value (2.002 319 31). The $g$-value of the nucleus $N$ is given by $g_N = \mu_N / I_N$ ($\mu_N$ is the nuclear magnetic moment of nucleus $N$ in units of $\beta_N$, and $I_N$ is the total nuclear spin for that nucleus). $\langle S_Z \rangle$ is the expectation value of the $z$-component of the total electronic spin. The spin density $\rho_{\text{iso}}^{\alpha\beta}$ at the position of nucleus $N$ ($R_N$) can be expressed as:

$$\rho_{N}^{\alpha\beta} = \sum_{\mu,\nu} P_{\mu,\nu}^{\alpha\beta} \langle \phi_{\mu} | \delta(R_N) | \phi_{\nu} \rangle \tag{2}$$

where $P_{\mu,\nu}^{\alpha\beta}$ is the spin density matrix. We will in the following abbreviate $\rho_{\text{iso}}^{\alpha\beta}$ by $\rho_{N}$.

The components $T_{\alpha\beta}$ of the anisotropy tensor are in the first-order approximation given by:

$$T_{\alpha\beta}(N) = \frac{1}{2} \beta \sum g_N g_e \langle S_Z \rangle^{-1} \sum_{\mu,\nu} P_{\mu,\nu}^{\alpha\beta} \langle \phi_{\mu} | \delta(R_N) - 3 r_{\mu,\nu} r_{N}^{\alpha\beta} | \phi_{\nu} \rangle \tag{3}$$

where $r_{\mu,\nu} = r - R_N$. $T$ is always traceless and may be brought to diagonal form. For magnetic nuclei with an electronic environment of axial symmetry (i.e., those located on an at least 3-fold symmetry axis), it has the form $(-A_{\text{dip}}, -A_{\text{dip}}, 2A_{\text{dip}})$, where $A_{\text{dip}}$ is the so-called dipolar coupling constant. From the experimental tensor components ($A_1$, $A_2$, $A_3$), $A_{\text{iso}}$ and $A_{\text{dip}}$ may then be extracted via $A_{\text{iso}} = (A_1 + 2A_2)/3$, $A_{\text{dip}} = (A_2 - A_3)/3$. Another terminology is used in gas-phase spectroscopy studies.30

The high-resolution spectra of linear molecules can be described in terms of five parameters $(a, b, c, d, e)$, of which $b$ and $c$ are related to $A_{\text{iso}}$ and $A_{\text{dip}}$ as $A_{\text{iso}} = (b + c/3)$ and $A_{\text{dip}} = c/3$.

All transition metal nuclei in the present study are at sites of axial symmetry. Although this is not the case for all ligands, experimentalists in the field prefer to use the “$A_{\text{dip}}$” terminology, even if it is not justified by symmetry. This is often due to the fact that the dipolar ligand splittings are small, and two different “perpendicular” components are not observed in the spectra (at least for complexes such as those considered here, where the unpaired spin density is mainly localized on the metal). See section 4 for comments on spin–orbit corrections to the hyperfine couplings.

3. Selection of Experimental Data

The selection of the molecules used in this study was determined mainly by the availability of experimental data on small systems having a well-resolved hyperfine structure for the metal and, if possible, also for the ligands. We have included examples for all first-row transition metals. Some pairs of isoelectronic molecules have been selected to compare different transition metals in similar electronic surroundings. In the following we will comment on the interpretation of the measured data and on the expected accuracy of different experimental techniques.

Gas-Phase Data. For all diatomic oxides and nitrides, and for MnH, literature hyperfine parameters from high-resolution gas-phase molecular spectroscopy have been used. The relative positions of the energy levels were obtained either directly by monitoring of the absorption/emission (“pure” microwave rotational spectroscopy) or indirectly (through fluorescence or molecular beam deflection).30 The hyperfine parameters have been determined from the analysis of the level splittings. The accuracy of such measurements is usually very high, sometimes in the kHz range for microwave optical double resonance.27–29

In most of the gas-phase investigations, the interactions between molecules represent relatively small perturbations which usually affect only the widths of the spectral lines; in molecular beam studies such interactions are completely absent.30 This makes the gas-phase data most reliable for comparison with our computed data on isolated molecules. Moreover, in these gas-phase experiments, the sign of the HFCCs is known.

Condensed-Phase EPR Data. For the remaining systems, the hyperfine parameters had to be taken from condensed-phase EPR spectroscopy. Different trapping sites (mostly inert-gas matrices, but also host crystals and frozen solutions) are thus involved. Obviously, the environment can influence the values of the hyperfine parameters, in particular of the isotropic coupling constants,31 due to both structural and electronic effects. This complicates the comparison of our calculated data with experiment.

In those few cases where EPR results are available on the same complex from both gas- and condensed-phase measurements, the HFCCs differ typically by a few percent, up to ca. 10% in extreme cases. Thus, e.g., the gas-to-matrix shift for $A_{\text{iso}}$(V) of VO is less than 3% of the absolute value (data available are 798 MHz in Ne matrix,12 796 MHz in Ar matrix,32 and 778 MHz in the gas phase33). The situation is similar for ScO (cf. matrix values of 2008–2018 MHz34,21 vs gas-phase value of 1947 MHz28 for $A_{\text{iso}}$(Sc)). Larger gas-to-matrix shifts have been found for MnO (7%; cf. 448 MHz in matrix35 vs 480 MHz in the gas phase36) and MnH (11%; see ref 37). For charged species, counterion effects may be considerable and have to be kept in mind as a potential source of errors.

In view of these environmental effects, we cannot aim at a better agreement with condensed-phase experiments than ca. 10–15%. Furthermore, the theoretical values should best be compared with the whole range of accurate experimental data available. This is most important for complexes with very small isotropic coupling constants, since these are particularly sensitive to the influence of the surroundings. We note also that the computed structures do not include any rovibrational corrections. On the other hand, the experimental structures also have to be viewed with some error bars. Structural aspects contribute thus
Gauss, they have been converted to MHz by multiplying with those cases where the experimental data have been reported in discussed in the footnotes to the tables.

...for an... 44 the observed hyperfine structure. 58 The structure parameters are summarized in Table 1.

...to an MP2 optimization with one f-function (mp2/6-31g) basis set.51 Basis set 51 was used for [Cr(CO) 4 ] and [Fe(CO) 5 ] in agreement with the observed hyperfine structure. 58 The structure parameters are summarized in Table 1. [Cu(CO) 3 ] is a weakly bonded complex with significant dispersion contributions to the bonding. Here the DFT optimizations are known to overestimate the Cu–C distance, and we have therefore resorted to an MP2 optimization with one f-function (α = 3.525) added to the metal basis set.

...theoretical arguments have to be considered. For example, the sign of A_{dp} may be estimated from the type of the singly occupied molecular orbital (SOMO) present. Chemically similar complexes may be expected to have the same signs of A_{ip} and A_{dp}, etc.

In this study, those signs of A_{ip} and A_{dp} are given in the tables (if not known experimentally), for which the resulting value of A_{dp} is as close as possible to our theoretical value. This choice is a natural one, since the calculation of the anisotropic coupling parameters is much less sensitive to the theoretical approach, and thus reasonable agreement with experiment is usually found. In the majority of cases, the resulting sign turned out to be consistent with that adopted in the experimental papers. For several particular cases, the choice of sign is further discussed in the footnotes to the tables.

4. Computational Details

Molecular structures used for the hyperfine structure calculations were taken from experiment where available or have otherwise been optimized in unrestricted Kohn–Sham calculations with the B3LYP functional (using the Gaussian 94 program).59 The optimizations employed small-core effective-core potentials (ECPs) and (8s7p6d)/[6s5p3d] GTO valence basis sets for the ligand atoms (a (4s1p)/[2s1p] hydrogen core potential is used for MnH and [Ni(CO)H]). The resulting structure parameters are summarized in Table 1. [Cu(CO) 3 ] is a weakly bonded complex with significant dispersion contributions to the bonding. Here the DFT optimizations are known to overestimate the Cu–C distance, and we have therefore resorted to an MP2 optimization with one f-function (α = 3.525) added to the metal basis set.

The following symmetry restrictions have been used in the optimizations: D_{4h} symmetry was used for TiF 3 and MnO 3 and for [Cu(CO) 3 ] and [Co(NO) 3 ] . The trigonal planar structures are consistent with hyperfine data46–47 and IR spectra.48,49 D_{5h} symmetry has also been established theoretically for TiF 3 by Belanzoni et al.17 [Co(CO) 3 ] and [Ni(CO) 3 ] have C_{3v} symmetry, respectively.50,51 T_{d} symmetry was used for [Cr(CO) 4 ] and [Mn(CN) 4 ] , again in agreement with experimental evidence.52,53 C_{4v} symmetry has been imposed for [Mn(CO) 3 ] and [Fe(CO) 3 ] , consistent with the EPR spectra.54,55 DFT optimizations performed by Rosa et al.56 for [Mn(CO) 3 ] and by Ricca et al.57 for [Fe(CO) 3 ] have provided structural parameters close to ours. Our optimizations for [Mn(CN) 4 ] , starting from the experimental C_{2v} structure of [Mn(CN) 4 ] ,58 converged to a regular square pyramid (C_{4v}), in agreement with the observed hyperfine structure.58 The structural uncertainties in the comparison between calculation and experiment.

...the solid-state EPR spectrum, only absolute values of the hyperfine tensor components (e.g., A_{||} and A_{sub} for an axially symmetric center) can be determined. Additional information can be obtained, e.g., from the signs of the components of the nuclear quadrupolar tensor, so that the sign of A_{||} and/or A_{sub} may be deduced. Another possibility is to compare A_{||} and A_{sub} from the solid-state measurement with the A_{sub} result obtained via EPR in a solution. Unfortunately, such information is usually not available, and four combinations of A_{sub} and A_{dp} are possible. To decide which of them is the correct one, theoretical arguments have to be considered. For example, the sign of A_{dp} may be estimated from the type of the singly occupied molecular orbital (SOMO) present. Chemically similar complexes may be expected to have the same signs of A_{ip} and A_{dp}, etc.

In this study, those signs of A_{ip} and A_{dp} are given in the tables (if not known experimentally), for which the resulting value of A_{dp} is as close as possible to our theoretical value. This choice is a natural one, since the calculation of the anisotropic coupling parameters is much less sensitive to the theoretical approach, and thus reasonable agreement with experiment is usually found. In the majority of cases, the resulting sign turned out to be consistent with that adopted in the experimental papers. For several particular cases, the choice of sign is further discussed in the footnotes to the tables.

All values of the hyperfine parameters are given in MHz. In those cases where the experimental data have been reported in Gauss, they have been converted to MHz by multiplying with a factor of 2.80238 (g/γ_e).
ture of [Mn(CN)₅NO]²⁻ was optimized in C₄ᵥ symmetry, starting from experimental structure of Pink and Billing. In discussions of the electronic structure of the complexes, we generally refer to the conventional orientation for a given point group.

The all-electron DFT calculations (cf. below for the basis sets) of the hyperfine structure were done with the Gaussian 94 program. Unless noted otherwise, unrestricted Kohn–Sham calculations were carried out. We have compared eight different combinations of exchange and correlation potentials (νₓ[ρ] and νᵧ[ρ], respectively), abbreviated as BLYP, BP86, BPW91, B3LYP, B3PW91, BHLYP, BHP86, and BHPW91. The first three combine Becke’s GGA functional for exchange (60) with integration grids (int 

| TABLE 2: Available Experimental g-Tensor Components |
|----------------|----------------|
| molecule       | g⊥             | g∥             |
| ScO²⁺          | 2.0018(3)      | 2.0018(3)      |
| TiF₄           | 1.8808         | 1.9902         |
| VO²⁺           | 1.9800         | 2.0020         |
| [Cr(CO)₅]⁺     | 1.9986         | 1.9986         |
| MnH            | 2.001         | 2.002²⁺        |
| MnO            | 1.995         | 2.002²⁺        |
| MnF            | 2.0084        | 2.0036         |
| MnF₂           | 1.999         | 2.002²⁺        |
| [Mn(CN)₅(NO)]⁻ | 2.003         | 2.003          |
| [Mn(CN)₅]⁻     | 2.043         | 2.004          |
| [Fe(CO)₅]⁺     | 2.0832        | 2.008          |
| [Ni(CO)₅]H     | 2.0797        |                |
| [Cu(CO)₅]      | 2.0002        | 2.0008         |

* See footnotes to Tables 8 and 10 for references. The g-values were usually estimated from the spectra without considering second-order effects. The g-value of the free electron is 2.0023. Reference 21. Reference 12. "Assumed in the experimental work." Reference 35.

As a medium-size metal basis set for use in larger systems, we have constructed a (1s5p1d6f/9s7p4d) basis. Our starting point was the DZ basis of Schafer et al. to which we added the most diffuse functions (a 1s2p1d set) from the ECP valence IGLO-III basis sets were used for the main group atoms.

Basis-set convergence was tested for several of the smaller complexes. To this end, we used a larger (21s15p10d3f) [13s10p6d2f] metal basis, constructed from the atomic natural orbital (ANO) basis sets of Roos et al. as follows: the 1s-, 2p-, 3p-, and 3d-ANO coefficients were used to contract s-functions 1–12, p-functions 1–10, p-functions 5–12, and d-functions 1–10, respectively. To this we added, in an uncontracted fashion, s-functions 10–21, p-functions 8–15, and d-functions 6–10. Finally, the 3f set of Bauschlicher et al. has been added in a 21 contraction. For both the smaller and larger metal basis sets, more flexible contractions have furthermore been tested (section 5).

As a somewhat larger basis for the first-row main group atoms, we have constructed a (14s8p3d1f/8s6p3d1f) set, starting from the cc-pV5Z basis. To the contracted sets of s-functions 1–11 and p-functions 1–8, s-functions 8–14 and p-functions 4–8 have been added in an uncontracted way, as well as three d-functions and one f-function from the cc-pVQZ basis.

The results we give have been obtained with the default integration grids (int = fingrid option) of the Gaussian 94 program. For various complexes we have also tested larger angular and radial grids (results not shown). The effect of different grids was generally below 1% of the computed HFCCs, even with the largest, uncontracted basis sets.

The present calculations do not include relativistic corrections. Scalar relativistic effects on the isotropic metal HFCCs may be estimated roughly from hydrogen-like multiplicative correction factors to magnetic s-type hyperfine integrals. These range from 1.036 for Sc to 1.072 for Cu. This suggests that the neglect of scalar relativistic effects may lead maximally to an underestimate of ρ₀ by ca. 4–7% within the first transition metal row (in the case of a pure s-type SOMO). The influence on

Using our DFT results for A_{FP} (we chose the BPW91 data), together with experimental values of the g-tensor components (Table 2), we may thus approximately estimate the spin–orbit

\[ A_{\|} = A_{FC} + \left[ \frac{2}{7} \Delta g_{\perp}^2 - \frac{1}{2} \Delta g_{\|} \right] \]

\[ A_{\perp} = A_{FC} + \left[ \frac{2}{7} \Delta g_{\perp}^2 + \frac{15}{14} \Delta g_{\perp} \right] \]
contributions to the hyperfine parameters from eq 6. The values of δ were obtained from the Mulliken population analysis of the SOMO composition. The formulas given here may be used for any axially symmetric system with the SOMO dominated by the metal d2 orbital. This approach is used for TiF3, [Mn(CO)5], [Fe(CO)5]3+, [Ni(CO)5]2+, and [Co(CO)4]. We use related formulae to estimate the spin–orbit contributions for [Mn(CN)3]NO2−, where the SOMO is a metal d5 orbital. In essentially all other cases, deviations of the g-tensors from the free-electron g-value are sufficiently small to expect negligible spin–orbit effects on the HFCCs (no experimental g-tensor is available for CuO; for this complex we expect significant SO effects, cf. section 7). We should also note that the assumption of the d2 orbital dominating the SOMO is not entirely appropriate for [Mn(CO)5] and [Ni(CO)5]2+ (significant 4p character has to be considered), which may lead to a significant error in the estimate (see section 7).

5. Coupled-Cluster Results

The CCSD and CCSD(T) calculations carried out on a subset of complexes (ScO, VO, MnO, MnF2, MnH, TiF3, MnO3, and CuO) should provide benchmark data for the validation of the more economical DFT approaches. The results are summarized in Table 3. Both the standard 9s7p4d and the more flexible 15s10p6d2f metal basis sets were used for the diatomics (see also section 6), together with the IGLO–III basis for the ligand atoms. With the available computational resources we could not use the larger basis set for MnF2, TiF3, or MnO3 (for the latter two complexes, even the CCSD(T) calculations with the smaller basis exceeded our available resources). While the larger basis should be essentially saturated in the important range of the outermost core shells (cf. section 6), it is probably still incomplete with respect to higher angular-momentum functions necessary for the explicit description of electron correlation.

### Table 3: Coupled-Cluster Results (in MHz)

<table>
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<tr>
<th>molecule</th>
<th>9s7p4d</th>
<th>15s10p6d2f</th>
<th>exp†</th>
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<td></td>
<td>RCCSD</td>
<td>UCCSD</td>
<td>UCCSD(T)</td>
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<tr>
<td>Aiso(M)</td>
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<td></td>
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<tr>
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<tr>
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<tr>
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<td>Aiso(X)</td>
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</tr>
<tr>
<td>ScO</td>
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<td>−10.6</td>
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<tr>
<td>MnH</td>
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<td>11.8</td>
<td></td>
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<tr>
<td>TiF3</td>
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<td>6.1, −24.0</td>
<td>18.7, 5.9, −24.6</td>
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<tr>
<td>MnO3</td>
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<td>27.0, −35.8, 62.8</td>
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<tr>
<td>CuO</td>
<td>57.6</td>
<td>55.9</td>
<td></td>
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<table>
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<tr>
<th>&lt;$S^2&gt;$</th>
<th>cc/$&lt;S^2&gt;$</th>
<th>UHF</th>
<th>nominal &lt;$S^2$</th>
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<tbody>
<tr>
<td>0.750</td>
<td>0.750/0.756</td>
<td>0.750/0.755</td>
<td>0.750/0.755</td>
</tr>
<tr>
<td>0.781</td>
<td>0.782/0.753</td>
<td>0.787/0.752</td>
<td>0.785/0.752</td>
</tr>
<tr>
<td>0.792</td>
<td>0.790/0.753</td>
<td>0.795/0.752</td>
<td>0.795/0.752</td>
</tr>
<tr>
<td>0.800</td>
<td>0.800/0.753</td>
<td>0.805/0.752</td>
<td>0.805/0.752</td>
</tr>
<tr>
<td>0.810</td>
<td>0.810/0.753</td>
<td>0.815/0.752</td>
<td>0.815/0.752</td>
</tr>
<tr>
<td>0.820</td>
<td>0.820/0.753</td>
<td>0.825/0.752</td>
<td>0.825/0.752</td>
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<tr>
<td>0.830</td>
<td>0.830/0.753</td>
<td>0.835/0.752</td>
<td>0.835/0.752</td>
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<td>0.840</td>
<td>0.840/0.753</td>
<td>0.845/0.752</td>
<td>0.845/0.752</td>
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<td>0.850</td>
<td>0.850/0.753</td>
<td>0.855/0.752</td>
<td>0.855/0.752</td>
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<tr>
<td>0.860</td>
<td>0.860/0.753</td>
<td>0.865/0.752</td>
<td>0.865/0.752</td>
</tr>
<tr>
<td>0.870</td>
<td>0.870/0.753</td>
<td>0.875/0.752</td>
<td>0.875/0.752</td>
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</tbody>
</table>

† Cf. footnotes to Tables 8 and 10 for sources of experimental data.
Disregarding CuO for the moment, the results of the largest CCSD(T)/15s10p6d2f calculations for the isotropic metal coupling constants are only ca. 4–5% below experiment. For the smaller absolute value in MnH, the deviation is ca. 13% (again the computational result is too low). A similar underestimation of the experimental metal HFCCs was also found in the few available previous post-Hartree-Fock studies.9–12 These results suggest that the coupled-cluster calculations underestimate electron correlation, mainly because of basis-set incompleteness, and therefore may overestimate spin polarization to some extent. Of course we have to remember that scalar relativistic effects and rovibrational corrections have not been considered (cf. section 4). CuO differs from the other cases, as both basis-set extension and inclusion of triple excitations leads to more negative $A_{\text{iso}}$ (Cu) and thus to inferior agreement with experiment (although still better than with DFT methods, see below). The discrepancy is probably related to the neglect of spin–orbit corrections (see discussion in section 7).

Comparison of CCSD(T) and CCSD results indicates that the perturbative inclusion of triple excitations is particularly notable for MnF$_2$ and VO, where the positive triples contribution brings the results closer to experiment (note that for VO the triples contribution is less pronounced with the larger basis set). In all other cases, the influence of triple excitations is small. We note that the inclusion of triple excitations brings our CCSD(T) data for VO into better agreement with experiment than the SDCI and MRCl results of Knight et al. (ca. 685–692 MHz with different basis sets, which are comparable to the ones used here).12

Use of the smaller 9s7p4d metal basis leads to a reduction of $A_{\text{iso}}$ (M) by ca. 9% for MnH, by ca. 5% for MnO, by ca. 3% for CuO, and by only ca. 1% for VO and ScO. While this is in part due to some error compensation, it indicates already that the 9s7p4d basis provides a good compromise between computational effort and accuracy. This is confirmed in the DFT calculations (see below). We expect that a larger basis should bring the result for MnF$_2$ closer to the Ne matrix value. The CCSD results for TiF$_3$ and MnO$_3$ with the 9s7p4d metal basis are already in good agreement with experiment (cf. Table 3). Even for the latter system, the coupled cluster wave function corrects quite efficiently the significant spin contamination of the UHF reference (cf. $<S^2>$ values in Table 3; this behavior of the CC approach was discussed before).77,78 Despite the remaining contamination, the RCCSD and UCCSD results for $A_{\text{iso}}$ (Mn) are already quite close. Differences are still apparent for $A_{\text{iso}}$ (Mn) and for the ligand HFCCs. Spin contamination of the UHF reference wave function for MnO and MnF$_2$ is lower, and thus the agreement between RCCSD and UCCSD results is even closer. This indicates the relative stability of the CC approach with respect to the quality of the reference wave function.77,78 A more detailed analysis of different reference wave functions is beyond the scope of the present study.

The small dipolar coupling constants for the metals are reproduced rather accurately for most systems. The less favorable agreement for MnF$_3$ might be due to matrix effects (cf. Table 8), whereas the description of CuO is generally more complicated, probably due to spin–orbit effects (cf. above and section 7). Except for the latter complex, the dependence of $A_{\text{iso}}$ (M) on triple excitations and basis set is only moderate, as one might expect. Agreement of the CC results with available experimental ligand isotropic and anisotropic HFCCs may also be considered reasonable in most cases, in view of their smallness in absolute terms (note the significant error bars on the experimental result for VO).

<table>
<thead>
<tr>
<th>TABLE 4: Basis-Set Dependence of the HFCC (MHz) in Mn$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>basis</td>
</tr>
<tr>
<td>(15s1l6d)/(9s7p4d)$^a$</td>
</tr>
<tr>
<td>9s7p4d + 1s$^c$</td>
</tr>
<tr>
<td>9s7p4d + 2s$^c$</td>
</tr>
<tr>
<td>9s7p4d + 3s$^c$</td>
</tr>
<tr>
<td>15s1l6d uncontr.$^d$</td>
</tr>
<tr>
<td>(21s15p10d3f)/(13s10p6d2f)$^e$</td>
</tr>
<tr>
<td>13s10p6d2f (all p-orb. uncontr.)</td>
</tr>
<tr>
<td>13s10p10d2f (all d-orb. uncontr.)</td>
</tr>
<tr>
<td>13s10p6d2f + 1s$^c$</td>
</tr>
<tr>
<td>13s10p6d2f + 2s$^c$</td>
</tr>
<tr>
<td>13s10p6d2f + 3s$^c$</td>
</tr>
<tr>
<td>13s10p6d2f + 4s$^c$</td>
</tr>
<tr>
<td>13s10p6d2f + 5s$^c$</td>
</tr>
<tr>
<td>21s15p10d3f (all s-orb. uncontr.)</td>
</tr>
<tr>
<td>21s15p10d3f uncontr.$^d$</td>
</tr>
<tr>
<td>exp$^f$</td>
</tr>
</tbody>
</table>

$^a$ B3PW91 results. $^b$ Standard 9s7p4d basis. $^c$ Outermost core s-functions added in an uncontracted way, see text. $^d$ Fully uncontracted. $^e$ All s-functions uncontracted. Kasai, P. H. Acc. Chem. Res. 1971, 4, 329. Ar-matrix isolation. $^f$ Reference 45 reports a value of 771(14) MHz.

6. Basis-Set Study

While the basis-set dependence of the hyperfine parameters for light main group atoms and molecules has already been investigated in detail,13,15,79,80 systematic basis-set studies are lacking for transition metal systems, except for a comparison of different STO basis-sets for TiF$_3$ by Belanzoni et al.17 For several small systems, we have therefore studied the GTO basis-set convergence at the DFT level.

Table 4 examines the B3PW91 results for $A_{\text{iso}}$ in the 7Mn$^+$ cation, using a variety of basis sets. For this high-spin cation with d$^8$s$^1$ configuration, the large positive direct contribution to the HFCC due to the single s-type SOMO should be partially compensated by negative contributions from spin polarization of the core shells, due to the five d-type SOMOs.81 A better description of this spin polarization should thus reduce the HFCC. From tests with still larger basis sets, we expect the fully uncontracted 21s15p10d3f basis to be converged to within better than ca. 10 MHz. Comparison of the resulting 797 MHz to the 980 MHz obtained at the restricted B3PW91 level (with the same basis) suggests a total spin-polarization contribution of ca. –183 MHz. Remaining differences to experiment (note the two different experimental values available in the literature; footnotes e,f to Table 4) are expected to be largely the result of deficiencies in the exchange–correlation potential, vxc. Contraction of the basis to 13s10p6d2f increases the HFCC by ca. 43 MHz. Starting from this contraction, we may now examine the influence of partial decontraction. Changes in the p- and d-basis have negligible effects. However, if we add s-function 9 (α = 316.3768) in an uncontracted way, 30 MHz of the 43 MHz contraction error have been eliminated. Adding s-exponents 8 (α = 727.3039) and 7 (α = 1755.212) reduces the HFCC by another 8 and 4 MHz, respectively, giving 798.5 MHz for the resulting 15s10p6d2f basis, i.e., almost the value obtained with the fully uncontracted basis (further addition of uncontracted s-functions has thus very little effect). Our MO analyses indicate that this is mainly due to a decrease in the direct SOMO contribution, possibly due to a better description of the nodal structure of the 4s-orbital.

We may also analyze the results obtained with our smaller 9s7p4d standard basis constructed for use in larger systems. Employing this basis fully uncontracted to 15s1l6p6d, the expected basis-set limit HFCC (for the B3PW91 functional used)
is underestimated by ca. 70 MHz (Table 4). This is most
TABLE 6: Dependence of Metal HFCCs (in MHz) on the Metal Basis-Set for Selected Systems

<table>
<thead>
<tr>
<th>molecule</th>
<th>BP86</th>
<th>B3LYP</th>
<th>B3PW91</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9s7p4d³</td>
<td>526.8</td>
<td>507.3</td>
<td>505.7</td>
</tr>
<tr>
<td>9s7p4d +3s³</td>
<td>507.3</td>
<td>505.7</td>
<td>505.7</td>
</tr>
<tr>
<td>15s11p6d (uncontr.)</td>
<td>510.9</td>
<td>488.2</td>
<td>505.7</td>
</tr>
<tr>
<td>13s10p6d²</td>
<td>562.5</td>
<td>557.7</td>
<td>543.3</td>
</tr>
<tr>
<td>13s10p6d² +2s³</td>
<td>539.9</td>
<td>534.8</td>
<td>518.2</td>
</tr>
<tr>
<td>21s15p10d3f (uncontr.)</td>
<td>531.5</td>
<td>527.5</td>
<td>513.7</td>
</tr>
<tr>
<td>9s7p4d 12s7p4d</td>
<td>520.8</td>
<td>518.2</td>
<td>516.3</td>
</tr>
<tr>
<td>12s7p4d 15s10p6d²</td>
<td>510.9</td>
<td>488.2</td>
<td>505.7</td>
</tr>
<tr>
<td>13s10p6d² +2s³</td>
<td>534.5</td>
<td>529.2</td>
<td>516.3</td>
</tr>
<tr>
<td>21s15p10d3f</td>
<td>531.5</td>
<td>527.5</td>
<td>513.7</td>
</tr>
</tbody>
</table>

* Experimental data: A_isd(Mn) = 479.861(100) MHz, A_adf(Mn) = −16.066(59) MHz (gas-phase measurement, ref 36). ^ (15s11p6d/[9s7p4d],
Three outermost core s-functions added, see text. A_fully uncontracted. * (21s15p10d3f)/[13s10p6d²]. Larger ligand basis, see Computational
Methods. ^ Two outermost core s-functions added, see text.

TABLE 7: Nuclear g-Values

<table>
<thead>
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<th>isotope</th>
<th>g-value</th>
</tr>
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<tbody>
<tr>
<td>⁴⁵Sc</td>
<td>1.35883</td>
</tr>
<tr>
<td>⁴⁷Ti</td>
<td>−0.31538</td>
</tr>
<tr>
<td>⁵¹V</td>
<td>1.47100</td>
</tr>
<tr>
<td>⁵³Cr</td>
<td>−0.31567</td>
</tr>
<tr>
<td>⁵⁵Mn</td>
<td>1.37960</td>
</tr>
<tr>
<td>⁵⁷Fe</td>
<td>0.18084</td>
</tr>
<tr>
<td>⁵⁹Co</td>
<td>1.31886</td>
</tr>
<tr>
<td>⁶¹Ni</td>
<td>−0.49987</td>
</tr>
<tr>
<td>⁶³Cu</td>
<td>1.48187</td>
</tr>
<tr>
<td>⁶⁵H</td>
<td>5.58556</td>
</tr>
<tr>
<td>⁶⁷C</td>
<td>1.40480</td>
</tr>
<tr>
<td>⁶⁹N</td>
<td>0.40375</td>
</tr>
<tr>
<td>⁷⁰O</td>
<td>−0.75748</td>
</tr>
<tr>
<td>⁷¹F</td>
<td>5.25760</td>
</tr>
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7. Performance of Different Exchange—Correlation Functionals for Metal HFCCs

General Trends. We will start by discussing some general trends before going into more detailed analyses for specific groups of complexes. Table 8 gives isotropic metal HFCCs, Table 9 the dipolar couplings for all 21 molecules and for the eight functionals of this study, in comparison with experiment. The dipolar couplings give us further insight, as they depend less on subtle details of spin polarization but more on the overall quality of our wave functions. Additional insight on spin contamination is provided by the <S²> expectation values, which are also included in Table 9. ¹²
Figures 1–7 show graphically for groups of related complexes the spin-density at the metal nuclei, and for all functionals, normalized to the number of unpaired electrons. Two general trends hold with very few exceptions: (i) For a given exchange
TABLE 8: Dependence of Isotropic Metal HFCCs on the Exchange—Correlation Functional (in MHz)

<table>
<thead>
<tr>
<th></th>
<th>BLYP</th>
<th>BP86</th>
<th>B3LYP</th>
<th>B3PW91</th>
<th>BHLYP</th>
<th>BHP86</th>
<th>BHPW91</th>
<th>exp*</th>
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</thead>
<tbody>
<tr>
<td>2ScO</td>
<td>2043.5</td>
<td>1979.6</td>
<td>1933.5</td>
<td>2032.3</td>
<td>2030.2</td>
<td>1904.7</td>
<td>1983.1</td>
<td>1847.7</td>
</tr>
<tr>
<td>2TiN</td>
<td>-587.0</td>
<td>-569.0</td>
<td>-556.6</td>
<td>-584.3</td>
<td>-554.2</td>
<td>-569.6</td>
<td>-540.7</td>
<td>-528.0</td>
</tr>
<tr>
<td>2TeO</td>
<td>-257.5</td>
<td>-251.0</td>
<td>-246.3</td>
<td>-252.8</td>
<td>-242.4</td>
<td>-241.9</td>
<td>-233.2</td>
<td>-227.0</td>
</tr>
<tr>
<td>2VN</td>
<td>1437.6</td>
<td>1393.5</td>
<td>1357.8</td>
<td>1388.9</td>
<td>1315.4</td>
<td>1168.9</td>
<td>1124.6</td>
<td>1081.7</td>
</tr>
<tr>
<td>2VO</td>
<td>847.8</td>
<td>821.0</td>
<td>811.9</td>
<td>829.5</td>
<td>795.2</td>
<td>795.0</td>
<td>763.3</td>
<td>753.4</td>
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<td>2MnO</td>
<td>543.1</td>
<td>526.8</td>
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<td>521.8</td>
<td>507.5</td>
<td>528.5</td>
<td>509.8</td>
<td>504.7</td>
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<td>2MnF</td>
<td>313.0</td>
<td>294.2</td>
<td>283.5</td>
<td>240.7</td>
<td>214.1</td>
<td>144.9</td>
<td>118.5</td>
<td>109.0</td>
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<td>2MnH</td>
<td>501.9</td>
<td>480.6</td>
<td>473.9</td>
<td>470.5</td>
<td>443.6</td>
<td>422.3</td>
<td>397.4</td>
<td>391.5</td>
</tr>
<tr>
<td>2MnF</td>
<td>380.0</td>
<td>380.0</td>
<td>385.0</td>
<td>331.8</td>
<td>329.6</td>
<td>277.1</td>
<td>271.8</td>
<td>276.3</td>
</tr>
<tr>
<td>2TiF</td>
<td>-218.0</td>
<td>-216.6</td>
<td>-211.6</td>
<td>-192.2</td>
<td>-186.1</td>
<td>-157.8</td>
<td>-151.9</td>
<td>-149.4</td>
</tr>
<tr>
<td>2MnO</td>
<td>2042.4</td>
<td>2009.3</td>
<td>1987.2</td>
<td>1735.5</td>
<td>1675.9</td>
<td>1187.6</td>
<td>1141.5</td>
<td>1111.7</td>
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<td>2Cr(CO)4</td>
<td>21.9</td>
<td>23.8</td>
<td>25.2</td>
<td>26.9</td>
<td>30.8</td>
<td>34.5</td>
<td>38.4</td>
<td>40.4</td>
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<td>2Fe(CO)5</td>
<td>1.1</td>
<td>0.0</td>
<td>-0.6</td>
<td>-3.2</td>
<td>-5.3</td>
<td>-9.3</td>
<td>-11.7</td>
<td>-12.3</td>
</tr>
<tr>
<td>2Mn(CN)N2</td>
<td>-134.3</td>
<td>-145.8</td>
<td>-153.8</td>
<td>-223.6</td>
<td>-259.2</td>
<td>-304.5</td>
<td>-351.7</td>
<td>-364.1</td>
</tr>
<tr>
<td>2Mn(CN)N2</td>
<td>-160.1</td>
<td>-170.4</td>
<td>-176.0</td>
<td>-250.1</td>
<td>-275.0</td>
<td>-306.7</td>
<td>-348.5</td>
<td>-358.5</td>
</tr>
<tr>
<td>2Ni(CO)4(H)</td>
<td>24.4</td>
<td>23.5</td>
<td>33.3</td>
<td>33.9</td>
<td>51.3</td>
<td>54.8</td>
<td>56.0</td>
<td>9.0(2)*</td>
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<tr>
<td>2(Co(CO)4),</td>
<td>-6.4</td>
<td>-11.3</td>
<td>-15.7</td>
<td>-61.4</td>
<td>-75.4</td>
<td>-175.4</td>
<td>-210.0</td>
<td>-219.7</td>
</tr>
<tr>
<td>2CuO</td>
<td>-651.8</td>
<td>-640.0</td>
<td>-678.1</td>
<td>-755.2</td>
<td>-776.4</td>
<td>-732.4</td>
<td>-676.4</td>
<td>-717.3</td>
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<td>2Cu(CO)2</td>
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<td>-7.1</td>
<td>4.7</td>
<td>13.0</td>
<td>45.0</td>
<td>68.8</td>
<td>67.9</td>
</tr>
</tbody>
</table>


**Figure 1.** Spin density $\rho_{a-b}$ at the metal nuclei in $^{2}$ScO, $^{2}$TiO, $^{2}$TiN, and $^{2}$VN, normalized to the number of unpaired electrons. Dependence on $\nu_{c1}$.

**Figure 2.** Spin density $\rho_{a-b}$ at the metal nuclei in $^{2}$VO and $^{2}$MnO, normalized to the number of unpaired electrons. Dependence on $\nu_{c1}$.
the absolute value of the HFCC but also on other features we species), whereas for others this range may be on the order of percent of the value of the HFCC (e.g., for ScO, TiN, TiO, or VO; note that previous studies have concentrated on such features). We will discuss in more detail below. In comparison with experimental results (Table 8), or with the coupled-cluster results (Table 3), unfortunately we cannot single out any functional which would be superior to the others. The performance of a given functional is very different for different classes of complexes. Thus, while

**TABLE 9: Dependence of Dipolar Metal HFCCs on the Exchange–Correlation Functional (in MHz)**

<table>
<thead>
<tr>
<th>molecule</th>
<th>BLYP</th>
<th>BP86</th>
<th>BPW91</th>
<th>B3LYP</th>
<th>B3PW91</th>
<th>BHLYP</th>
<th>BHP86</th>
<th>BHPW91</th>
<th>exp∧n nominal (S²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>²ScO</td>
<td></td>
<td></td>
<td></td>
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a See corresponding footnotes to Table 8 for the sources of the experimental data. b EPR in Ne and Ar matrix, respectively. c Not observed (zero due to symmetry). d EPR using different solid matrices.

**Figure 3.** Spin density ρωαβ at the metal nuclei in ²TiF₃ and ³MnO₂, normalized to the number of unpaired electrons. Dependence on νxc.
of organic molecules, no "universal functional" appears to be
85

[Mn(CN)4 N]+.

Figure 6. Spin density $\rho^{\alpha\beta}$ at the metal nuclei in $[\text{Mn(CO)}_5]$ and
$[\text{Fe(CO)}_5]^\cdot$, normalized to the number of unpaired electrons. Dependence on $\nu_{xc}$.

Figure 7. Spin density $\rho^{\alpha\beta}$ at the metal nuclei in $[\text{Mn(CN)}_2]\text{NO}^\cdot$ and
$[\text{Mn(CN)}_2]\text{N}^\cdot$, normalized to the number of unpaired electrons. Dependence on $\nu_{xc}$.

of spin contamination. Let us therefore discuss the results in
more detail, and relate them to the electronic structure of the
molecules in question.

ScO, TiN, TiO, VN, and VO. This first group of systems
exhibits large positive spin density at the metal nucleus, resulting
from the dominant participation of the metal 4s orbital in the
SOMO, or in one of the SOMOs. ScO and TiN are the simplest
representatives. Here the $\sigma$-type SOMO has predominantly metal
4s character, with some 3d and 4p admixture (it is polarized away from the ligand). TiO and VN have in addition
one 3d-type SOMO. The dominance of the direct SOMO contribution to the HFCCs explains the relatively low dependence on $\nu_{xc}$ (Figures 1, 2, Table 8). The treatment of dynamical correlation via $\nu_{xc}$ appears to influence the HFCCs mainly via the shape of the SOMO. We
find the SOMO to become more diffuse along the series LYP
$<\text{P86} <\text{PW91}$ (valence-shell spin polarization is also affected somewhat by $\nu_{xc}$). Addition of exact exchange also renders the SOMO somewhat more diffuse and reduces the HFCC slightly
(the spin-polarization contributions are also affected but are not
very pronounced).

VN is exceptional within this group, due to the significant
onset of spin contamination upon inclusion of exact exchange
(in contrast to the isoelectronic TiO$^\cdot$). This leads to a much
erare dependence of the HFCC on the exchange functional,
and finally to a significant deterioration of the results with BH-
type hybrid functionals. This is confirmed by the results for $A_{\text{iso}}(M)$ (Table 9). The relatively low coupling anisotropy is
mainly due to the 3d$^2$-type SOMO and depends relatively little on $\nu_{xc}$ for ScO, TiN, TiO, and VO. In contrast, for VN the
admixture of exact exchange reduces the absolute value of $A_{\text{iso}}(M)$ significantly, in parallel with the drastic increase in $\Delta S^2$ (Table 9). Unfortunately, no experimental $A_{\text{iso}}(M)$ is available for
this system.

$\text{TiO}$ and $\text{TiN}$ have been studied recently by Engels et al.,
using the PWPB6 functional and medium-sized basis sets. For
TiN, their results differ only by ca. 1% from our BP86 value,
despite their ca. 0.03 Å larger Ti$-$N distance. Our own test
calculations for TiN at the structure used by Engels et al. indicate
very small changes ($< 1$ MHz), i.e., a small dependence of the
isotropic metal HFCC on bond length. Recently, B3LYP
calculations for ScO have been performed by Knight et al.
Their value given for $A_{\text{iso}}(\text{Sc})$ was 1877.5 MHz, ca. 8% lower than the value in Table 8, ca. 6% lower than our result with the
larger 15s10p6d2f basis (cf. Table 6), but in excellent agreement
with our B3PW91 results. Indeed, we have meanwhile been informed that Knight et al. erroneously reported their B3PW91
data as B3LYP results.

Except for VN, the dipolar coupling constants (Table 9) are
small and increase slightly in absolute value with increasing
exchange-mixing in the functional. While this trend is
partly related to an increasing participation of the metal 4p
orbital in the SOMO, spin polarization should not be disregarded
completely. Thus, e.g., a restricted B3PW91 calculation on ScO
gives $A_{\text{iso}}(\text{Sc}) = +12.8$ MHz, quite different from the unrestricted result of $+20.0$ MHz. This should be compared to the
RB3PW91 and UB3PW91 results for the isotropic HFCC of
$+1910.6$ MHz and $+1948.8$ MHz, respectively. Thus, on a
relative basis, spin polarization in ScO is more important for
$A_{\text{iso}}(\text{Sc})$ than for $A_{\text{iso}}(\text{Sc})$!

$\text{MnO}$, $\text{MnF}_2$, $\text{MnF}$, $\text{MnH}$. In going to higher spin multiplici-
ties, we may compare $^4\text{MnO}$ to $^2\text{VO}$. MnO has two additional
SOMOs, antibonding orbitals with metal-3d and 4p$_z$ character. Due to the large number of d-type

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ties, we may compare $^4\text{MnO}$ to $^2\text{VO}$. MnO has two additional
SOMOs, antibonding orbitals with metal-3d and 4p$_z$ character. Due to the large number of d-type
SOMOs, spin-polarization effects via the core shells are more pronounced. At first sight surprisingly, the BHLYP hybrid functional gives a somewhat larger spin density than B3LYP. This is most likely connected to the significant spin contamination upon exact-exchange mixing (cf. Table 9). The net dependence on \( v_{\text{ex}} \) may still be considered moderate, with an overall range of less than 10% of the absolute HFCC. The somewhat larger dependence on \( v_{\text{xc}} \) and the spin contamination are also apparent from the somewhat larger variations in \( A_{\text{dip}}(M) \) compared to the above species (Table 9).

As related high-spin systems, but with lower net \( p_N \), we may compare \(^7\)MnF, \(^7\)MnH, and \(^6\)MnF (cf. Figure 3, Table 8). \(^6\)MnF\(_2\) differs from the related \(^5\)MnO by the symmetrical arrangement of two ligands in this linear two-coordinate complex. As a result, the single \( \sigma \)-type SOMO (which is accompanied by two \( 3d_x \) and two \( 3d_y \)-type SOMOs) has larger \( 3d_z^2 \) and less \( 4s \) character than for \(^5\)MnO and is significantly \( \text{Mn}^\text{--F} \) antibonding. The isotropic HFCC is therefore lower, and its significantly larger dependence on \( v_{\text{xc}} \) is mainly due to valence-shell spin polarization. The overall range of \( A_{\text{dip}}(M) \) values is thus larger than the relatively low HFCC itself. Comparison with experiment suggests the BH-type hybrid functionals to provide the best description (Table 8). Spin contamination is generally low. The absolute value of \( A_{\text{dip}}(M) \) is very small and thus difficult to describe accurately. Moreover, it changes significantly from Ne to Ar matrix (Table 9). Remember that this system was also one of the more difficult examples in the coupled cluster calculations (section 5, Table 3).

\(^7\)MnF and \(^7\)MnH differ from \(^5\)MnO and \(^6\)MnF\(_2\) mainly by having two rather than one singly occupied \( \sigma \)-type orbitals. The metal \( 4s \) orbital contributes in an \( \text{Mn}^\text{--X} \) bonding way to one of these SOMOs, in an antibonding fashion to the other one (both orbitals are again dominated by the \( 3d_z^2 \) orbital). As for \(^6\)MnF\(_2\), inclusion of exact exchange influences mainly the SOMO and valence-shell spin-polarization contributions in both systems, while the total core polarizations are almost unaffected. The overall dependence on \( v_{\text{xc}} \) is quite large for \(^\text{Mn}^\text{--H} \) (but not as large as for \(^6\)MnF\(_2\)), somewhat lower for \(^7\)MnF (cf. Figure 3). The choice of \( v_{\text{xc}} \) influences both core and valence shell contributions. For \(^7\)MnH these changes cancel each other so that the overall dependence on \( v_{\text{xc}} \) is low, similar to \(^6\)MnF\(_2\) but in contrast to \(^7\)MnF. The comparison with experiment would suggest BH-type functionals to perform best for \(^7\)MnH. On the other hand, all functionals give results within ca. 13% from experiment for \(^7\)MnF. Spin contamination does not seem to be a problem for \(^6\)MnF\(_2\), \(^7\)MnF, or \(^7\)MnH, in contrast to the BH-type results for \(^5\)MnO (Table 9).

For these four manganese systems, \( A_{\text{dip}}(M) \) is very small and caused mainly by the \( 3d_x \), \( 3d_y \) and \( 3d_z^2 \) character of the \( \sigma \)- and \( \delta \)-type SOMOS. It is notable that the effect of spin polarization is again not negligible (cf. above). For example, the dipolar coupling of \(-1.57 \text{ MHz} \) for \(^5\)MnO at the unrestricted BHPW91 level is changed to \(-20.2 \text{ MHz} \) at the restricted level. Similarly, we obtain \(+2.4 \text{ MHz} \) for \( A_{\text{dip}}(\text{Mn}) \) in \(^5\)MnF\(_2\) at the unrestricted, \(-5.9 \text{ MHz} \) at the restricted BHPW91 level.

**TiF\(_3\) and \(^5\)MnO.** Two related molecules with relatively large positive spin densities at the nuclei, but with a significant dependence on \( v_{\text{ex}} \) are TiF\(_3\) and \(^5\)MnO (cf. Figure 4, Table 8). For both systems, the SOMO is dominated by the metal \( 3d_z^2 \) orbital, interacting with the ligand hybrid orbitals in an antibonding way. Some \( 4s \) character is mixed in. The composition of the SOMO is similar for both complexes ( Mulliken population analyses, using the BLYP functional, give a \( 4s/3d_z^2 \) population ratio of 0.18/0.76 for TiF\(_3\) and of 0.13/0.67 for \(^5\)MnO). The larger \( p_N \) of \(^5\)MnO is thus due to the much larger effective charge on the metal. The sensitivity to \( v_{\text{xc}} \) is already significant for TiF\(_3\), but all functionals do still give results within ca. 15% of the experimental value. DFT calculations of Belanzenzi et al.\(^{17}\) (with the BP86 functional and STO basis sets) gave \(-233.9 \text{ MHz} \) for \( A_{\text{dip}}(\text{Ti}) \), somewhat larger than our \(-216.6 \text{ MHz} \) with the same functional. This difference arises mainly from their shorter LSDA Ti--F bond length (1.756 Å vs our 1.780 Å). Using their shorter distance, we obtain \(-231.0 \text{ MHz} \), i.e., closer agreement with their value (note the negative \( g^\text{N} \)-\( \text{Ti} \)), Table 7). This indicates a much larger structural dependence of \( A_{\text{dip}}(\text{Ti}) \) compared to our above discussion for TiN, probably due to presence of core--shell spin-polarization contributions.

In view of the significant deviations of the g-tensor from the free-electron value (Table 2), TiF\(_3\) is one of the cases where spin--orbit effects have to be considered. Indeed, here we are in the fortunate situation that explicit DFT calculations of these spin--orbit contributions are available, both within a perturbation--theoretical approach,\(^{17}\) and using the explicitly relativistic two-component zero-order-regular-approximation (ZORA) scheme.\(^{19}\) Using the BP86 functional, both approaches gave very small positive spin--orbit (pseudocontact) contributions to \( A_{\text{dip}}(\text{Ti}) \) (ca. \(-3 \text{--6 MHz} \)), whereas the spin--orbit contributions to \( A_{\text{dip}}(\text{Ti}) \) are negative (between \(-2.3 \text{ MHz} \) and \(-2.8 \text{ MHz} \)) and significant relative to the small dipolar coupling. Our own simple semiempirical estimate of the spin--orbit corrections (section 4, eq 6) gives \(+3.4 \text{ MHz} \) for the pseudocontact term and \(-2.1 \text{ MHz} \) for \( A_{\text{dip}} \) in good agreement with the explicit calculations. The addition of the latter value to the computed \( A_{\text{dip}} \) does not improve the agreement with experiment, but it has to be noted that the matrix does affect the results nonnegligibly (cf. Table 9).

For \(^5\)MnO\(_3\), the \( v_{\text{ex}} \) dependence of \( A_{\text{iso}} \) is particularly pronounced (Table 8 and Figure 4), and is complicated by significant spin contamination (cf. \( \delta^2 \)) and the large dependence of \( A_{\text{dip}}(\text{Mn}) \) on \( v_{\text{ex}} \), Table 9). The results for \(^5\)MnO\(_3\) exemplify a dilemma that arises also in other cases (see below): While some admixture of exact exchange increases spin polarization and thus may improve the agreement with experiment relative to the "pure" GGA results, it may lead at the same time to considerable spin contamination (we note that the spin contamination is connected to valence-shell spin polarization.). Thus, despite the superficial similarity with the isoelectronic TiF\(_3\), the demands on the functional are much higher for the more covalent, highly oxidized \(^5\)MnO\(_3\) (cf. also the VN vs TiO comparison above). One could argue that the B3-type functionals do still provide a reasonable description of the wave function for \(^5\)MnO\(_3\) (with moderate but nonnegligible spin contamination). However, the unusually large variations in \( A_{\text{dip}}(M) \) (Table 9) speak against this. Note that the coupled cluster results for \( A_{\text{iso}}(\text{Mn}) \) (Table 3) agree well with experiment (they are slightly too negative).

[**Mn(CN)\(_4\)]\(^2-\) and [**Cr(CO)\(_4\)]\(^2-\). As two further high-spin systems, we may examine the two isoelectronic, tetrahedral ions [**Mn(CN)\(_4\)]\(^2-\) and [**Cr(CO)\(_4\)]\(^2-\). The five SOMOS correspond to all five metal d orbitals, corresponding to the \( t_2 \) and \( e \) irreducible representations in \( T_d \) symmetry. Due to the absence of any direct s-type SOMO contribution, \( p_N \) is entirely caused by spin polarization and is negative for both systems (see Figure 5; the positive \( A_{\text{dip}}(\text{Cr}) \) is due to the negative \( g^\text{N} \)-\( \text{Cr} \), cf. Table 7). Spin polarization of the core shells by the d-type SOMOS dominates (and provides negative \( p_N \)) and is partly compensated by valence-shell spin polarization. Therefore, the dependence
on \( n_{eC} \) is particularly large, and it is rather similar for these isoelectronic systems (Figure 5). Even with BH-type hybrid functionals, which provide the best agreement with experiment, the spin polarization apparently is still underestimated slightly. The coupling anisotropy is zero, due to symmetry, and spin contamination is relatively small for all functionals (Table 9).

\[ \text{[Mn(CO)3]} \text{ and [Fe(CO)3]}. \]

Let us now turn to low-spin complexes. For the isoelectronic low-spin \( \text{d}^3 \) complexes \( ^2\text{[Mn(CO)3]} \text{ and [Fe(CO)3]}^3 \), the SOMO exhibits metal 3d, and \( \alpha \)-bonding with respect to the axial M-CO bond in these square pyramidal \( (C_{4v}) \) complexes. The metal 4s contribution to the SOMO is small. As the small positive direct SOMO contribution to \( A_{sO} (\text{M}) \) (ca. +60 MHz and ca. +14 MHz for \( M = \text{Mn, Fe} \), respectively) is furthermore cancelled partly by negative core–shell spin-polarization contributions, very small isostropic HFCCs result for these low-spin systems. As a consequence, the description is difficult and the dependence on \( n_{eC} \) (particularly on \( n_{eC} \)) is large on a relative scale (Figure 6). This holds in particular for the iron complex. In other words, a larger effective charge at the metal appears to increase the sensitivity to the functional (as found above for other isoelectronic pairs, e.g., VN vs TiO or MnO vs TiF). Based on the comparison to experiment, it is difficult to select any particular functional that would be preferable over the others (the BH-type hybrids might seem to be less preferable, although spin contamination is not very pronounced). We estimate spin–orbit corrections (cf. section 4) of ca. +21.2 MHz for \( A_{sO} (\text{Mn}) \) and of ca. +12.8 MHz for \( A_{sO} (\text{Mn}) \) in [Mn(CO)3], as well as ca. +5.3 MHz for \( A_{sO} (\text{Fe}) \) and ca. −3.0 MHz for \( A_{sO} (\text{Fe}) \) in [Fe(CO)3]. The correction for the manganese complex may be overestimated, as the coefficient of the 3d, orbital in the SOMO is small (\( d_z^2 = 0.43 \), cf. eq 6) and the neglected contribution from the 4p, orbital may be large.

\[ \text{[Mn(CN)5NO]}^2 \text{ and [Mn(CN)5N]}^- \text{.} \]

The two \( C_{4v} \) symmetrical systems \( ^2\text{[Mn(CN)5NO]}^2 \) and \( ^2\text{[Mn(CN)5N]}^- \) (a low-spin \( \text{d}^5 \) and a \( \text{d}^6 \) complex, respectively) both have a single metal 3d, type SOMO. They also share the unfortunate problem of significant spin contamination, in particular with hybrid functionals (Table 9). Significant core–shell spin polarization dominates the observed negative isostropic HFCCs. This is augmented by valence-shell spin polarization, mainly involving metal \( d_y \) and \( d_z^2 \) orbitals. These \( d \)-orbitals contribute to the \( \pi \)-components of the Mn–N triple bond in the \( \text{d}^1 \) system, and to both Mn–N \( \pi \)-bonding and \( \pi \)-antibonding MOs in the \( \text{d}^5 \) complex. Low-lying excited states involving these \( \pi \) and \( \pi^* \) orbitals are mainly responsible for the spin contamination (i.e., the spin contamination is connected to significant valence-shell spin polarization, as found above for MnO).

Spin contamination is already nonnegligible for the GGA functionals, increases for the B3-type hybrids, and becomes dramatic for the BH-type hybrids. As a consequence, the computed \( A_{sO} \) values appear to be still reasonable for the GGA but deteriorate significantly for the hybrid functionals (with the exception of the B3-type hybrid results for [Mn(CN)5N] ). The isotropic HFCCs are not sufficiently negative with the GGA, are in closer agreement with experiment for the B3-type hybrids, but become much too negative with the BH-type hybrids (Figure 7). We have to conclude that the reasonable \( A_{sO} \) results with the B3-type hybrids are at least in part fortuitous, due to spin contamination. None of the functionals investigated here is thus really adequate to describe all features of the hyperfine coupling in these two complexes. We also note that SCF convergence to a global minimum in parameter space (i.e., in the MO coefficients) was difficult with several of the functionals, in particular for [Mn(CN)3N] . It appears that low-lying local minima exist. We have therefore used tighter convergence criteria on the density matrix for these systems than the Gaussian 94 default values (i.e., \( 10^{-8} \) au instead of \( 10^{-4} \) au root-mean-square deviation).

The pure GGA functionals give three positive occupied orbital energies for [Mn(CN)3NO] (no positive eigenvalues are obtained with the BH-type hybrids), indicating that the isolated dianion might not be stable with respect to electron loss (this holds also for the [Mn(CN)3] dianion discussed above). However, we believe that, in connection with the finite basis set, this affects the HFCC results negligibly compared to the more serious problem of spin contamination.

Due to the significant deviations of the g-tensor components from the free-electron value (Table 2) in [Mn(CN)3NO] , we have considered spin–orbit corrections. Our simple estimate gives a pseudocontact term of ca. +6.4 MHz and a spin–orbit contribution to \( A_{sO} \) of −2.8 MHz. Spin–orbit effects are estimated to be small for [Mn(CN)3N] (cf. g-tensor in Table 2).

\[ \text{[Ni(CO)3H]} \text{ and [Co(CO)4]} \text{.} \]

The SOMO of these two trigonal pyramidal \( (C_{3v}) \) \( \text{d}^5 \) complexes is of \( \alpha \) symmetry and composed of metal 3d, and 4p, contributions, with overall axial metal–ligand \( \sigma \)-antibonding character. In both cases, the SOMO has very little metal 4s character and thus gives only small direct contributions to \( \rho_N \). These are furthermore compensated partially by the negative core–shell spin polarization. As a result, the isotropic HFCCs are low. Possibly due to the partial 4p, character of the SOMO, the dipolar couplings are relatively large (in analogy to the low-spin \( \text{d}^5 \) complexes [Mn(CO)3] and [Fe(CO)3] discussed above).

At first sight, \( A_{sO} \) in [Co(CO)4] would seem significantly too large with GGA (and B3-type) functionals (Table 9), despite the relatively small spin contamination. However, in view of the very large g-shifts (Table 2), spin–orbit corrections are expected to be particularly significant for this complex. Indeed, our simple estimate (eq 6, section 4) provides a large correction of −42.2 MHz to \( A_{sO} (\text{Co}) \). This would bring both the GGA results and the B3-type hybrid results into good agreement with experiment, whereas the BH-type hybrid results would then be too low. The reduction of the dipolar couplings by inclusion of exact exchange is again accompanied by significant spin contamination, and we do not expect these BH-type functionals to provide a reliable description for this system. In view of its smallness, the isotropic HFCC (Table 8) is difficult to describe. Considering also the estimated spin–orbit correction to \( A_{sO} (\text{Co}) \) of +69.5 MHz may suggest that even the B3-type hybrid results are still insufficiently negative. On the other hand, the BH-type hybrid results clearly overshoot the negative spin–polarization contributions dramatically.

Both spin contamination and the dependence of \( A_{sO} \) on \( n_{eC} \) are less pronounced for [Ni(CO)3H]. The GGA results would seem to agree best with experiment for \( A_{sO} (\text{Ni}) \), whereas the BH-type hybrid results are clearly too negative (and are accompanied by spin–contamination, Table 9). Our estimated spin–orbit correction of +16.4 MHz to \( A_{sO} (\text{Ni}) \) would change this picture but may be too large, as the metal 4p, orbital contributes significantly to the SOMO (the 3d, contribution to the SOMO is particularly low for this complex, with \( d_z^2 = 0.28 \), cf. eq 6). The estimated spin–orbit correction to \( A_{sO} (\text{Ni}) \) (pseudocontact term) of −26.8 MHz may thus also be too large. In view of these uncertainties about the magnitude of the spin–orbit corrections, either GGA or B3-type hybrid functionals might
be closest to the experimental isotropic HFCC (Table 8), whereas the BH-type hybrids give in any case too large values.

**CuO.** The $d^9$ complex $^3$CuO differs from the previous cases by exhibiting a hole in a degenerate ($\pi$-type) MO. In other words, the one-particle description of the X$^2\Sigma$ ground state of CuO assigns three electrons to the $4\sigma$ MO (the two components are built from the O 2$p_\pi$, Cu 3$d_{xz}$, Cu 4$p_\pi$, and from the O 2$p_\pi$, Cu 3$d_{yz}$, and Cu 4$p_\pi$ orbitals, respectively).\(^{39}\) It is thus clear that a cylindrically symmetrical wave function in a single-determinant framework may be obtained only by using fractional occupations (i.e., 0.5 electrons in each of the two MOs). The integer occupation of one of the two degenerate $4\sigma$ MOs would, e.g., not provide an axially symmetrical hyperfine tensor. On the other hand, one may average calculations with different integer occupations (similar considerations pertain to Kohn–Sham calculations on certain degenerate states of open-shell atoms\(^{90,94}\)). The results for $A_{\text{iso}}(\text{Cu})$ obtained by this averaging procedure are given in Table 9 (the coupled cluster results in Table 3 were obtained in the same manner). As we were not able to enforce appropriate fractional occupations within the Gaussian 94 program, we resorted to calculations using the BP86 functional and the deMon code\(^{31,90}\) to compare integer and fractional occupations (using the same basis set but in addition auxiliary basis sets to fit charge density and exchange–correlation potential\(^{91,96}\)). Indeed, the dipolar couplings obtained with fractional occupations differed by less than 6 MHz from averaged results with integer occupations (the isotropic couplings also changed by less than 5 MHz). This seems to justify the averaging procedure.

Due to the absence of metal $4s$ orbital contributions to the SOMO, the isotropic metal HFCC arises exclusively from spin polarization. Interestingly, the $\nu_c$ dependence for a given $\nu_c$ is $\rho_N(B) > \rho_N(BH) > \rho_N(B3)$. On the other hand, we find a significant decrease of $A_{\text{iso}}(\text{Cu})$ from B to B3 to BH functionals. The latter trend is due to the shift of single-electron density from Cu to O with admixture of exact exchange. For the isotropic HFCCs, stronger core–shell spin polarization accounts for the more negative value with B3-type relative to B-type functionals. Further dramatic decrease of the spin density on Cu reverses the trend and gives a less negative $A_{\text{iso}}(\text{Cu})$ with BH-type functionals.

The $A_{\text{iso}}(\text{Cu})$ results are too negative for all functionals, whereas the variation between the functionals is smaller than the discrepancy with respect to experiment. Note that even the coupled cluster calculations give too negative $A_{\text{iso}}(\text{Cu})$ when considering the trend upon enlarging the basis set (Table 3). Moreover, spin contamination seems to be small. The difference with respect to experiment is thus probably not mainly a problem of describing the spin polarization well. There are three other possible reasons which might account for the too negative isotropic HFCCs, of which we suspect the latter to be decisive: multireference character of the wave function, errors in the bond length, relativistic effects.

**Multireference Character of the Wave Function.** Our coupled cluster wave functions give no large coefficients for configurations other than the given reference configuration. We note also that the single-reference coupled-pair-functional (CPF) calculations by Langhoff and Bauschlicher appear to describe the ground state of CuO adequately (whereas CISD calculations without corrections for higher order excitations perform poorly).\(^{91}\) Thus, CuO is probably not a priori a multireference case. Moreover, spin contamination is small. This speaks against significant problems of describing the wave function with the current approaches.

**Bond Length Errors.** The isotropic HFCC is extremely dependent on the Cu–O bond length. Shortening the bond by only 0.005 Å (from 1.729 to 1.724 Å) changes $A_{\text{iso}}(\text{Cu})$ from −776 MHz to −747 MHz, i.e., by ca. 4% (B3PW91 result). Together with the above results for TiN and TiF$_3$, this suggests that the dependence of the isotropic HFCCs on bond length increases with an increasing importance of spin polarization (a more systematic study of the interdependence between structural changes and HFCCs in transition metal complexes is beyond the scope of the present study but should be pursued in the future). On the other hand, the experimental bond distance of 1.729 Å appears to be reliable and has been confirmed experimentally\(^{92}\) and theoretically.\(^{93}\)

**Relativistic Effects.** Scalar relativistic effects should lead to a larger (negative) spin density at the nucleus and would thus be expected to lead to more negative values for $A_{\text{iso}}(\text{Cu})$. Spin–orbit effects are difficult to judge, as unfortunately no experimental g-tensor information is available. Our preliminary perturbation–theoretical calculations of the g-tensor indicate a large positive $\Delta g_{\perp}$. Thus, we may expect significant spin–orbit contributions to the HFCCs, and we believe that this is the most likely reason for the discrepancies between calculation and experiment.

$[\text{Cu}(\text{CO})_3]$. Finally, we look at a very different bonding situation. The wave function in $[\text{Cu}(\text{CO})_3]$ is derived from the $3d^{10}4p^1$ configuration of Cu, and the SOMO is composed of the Cu 4$p_\pi$ orbital and $\pi$-type ligand orbitals. The isotropic metal HFCC is thus exclusively due to spin polarization. Interestingly, $\rho_{\text{sd}}(\text{Cu})$ is positive, whereas we have seen above that core–shell spin polarization due to 3d-type SOMOs always contributes negatively to $\rho_{\text{sd}}(\text{M})$. Thus, the situation resembles more that known for main-group $\pi$-type radicals, with the (slight) difference that we have a very polarizable M-shell below the 4$p_\pi$-type SOMO. The description for $[\text{Cu}(\text{CO})_3]$ is thus considerably more difficult than for Cu(C$_2$H$_4$) or Cu(CO) studied previously with DFT methods by Barone et al.,\(^{14,15}\) where large positive direct contributions from a metal $4s$-type SOMO dominate.

Spin contamination is minor, and the dipolar couplings depend relatively little on the functional (however, the BH-type hybrids give ca. 6–7 MHz lower values, cf. Table 9). The experimental $A_{\text{iso}}(\text{Cu})$ is underestimated. It is possible that this is due to an overestimate of the Cu–C bond length even by the MP2 optimizations used (cf. Table 1). This would be consistent with our finding that test calculations at the larger DFT optimized bond length (also Table 1), give ca. 8 MHz lower dipolar couplings. In other words, structural errors are more likely for this weakly bound complex than for the other systems.

Looking at the isotropic metal HFCC (Table 8), we see that we obviously underestimate core–shell spin polarization with the pure GGA functionals. Even the sign of the HFCC is wrong. The agreement with experiment is improved somewhat with B3-type hybrids, and even more significantly with the BH-type hybrids, without any apparent spin contamination problem. The situation may thus be comparable to that for $\pi$-type organic radicals.\(^{15}\) We also see a surprisingly large difference between the BHLYP functional and the BHP86 and BHPW91 functionals (likely due to the description of the SOMO).

8. **Ligand HFCCs**

As this work concentrates on complexes with the SOMO mainly localized on the metal, the spin densities at the ligand nuclei are about 1–2 orders of magnitude smaller than those at the metal nuclei. This places of course considerable demand...
on the computational approach to describe the subtle delocalization of spin density to the ligands, as well as spin-polarization effects. We should also mention again that relativistic effects, which are not considered here, may have a nonnegligible influence on the small ligand HFCCs (cf. section 4). The metal HFCCs are our main interest in this work, but we may nevertheless note some trends in the computed ligand HFCCs.

Table 10 summarizes the isotropic ligand HFCCs, Table 11 the dipolar couplings. Concerning the dependence of the isotropic HFCCs on \( \nu_5 \), we note trends very similar to above for the metal HFCCs. Thus, the spin densities \( \rho_{\text{iso}} \) at the ligand nuclei (when including their signs) exhibit often the \( \nu_5 \) dependence \( \rho_{\text{iso}}(\text{LYP}) \geq \rho_{\text{iso}}(\text{B3LYP}) \geq \rho_{\text{iso}}(\text{BPW91}) \) for a given \( \nu_5 \) and typically the \( \nu_5 \) dependence \( \rho_{\text{iso}}(\text{B}) \geq \rho_{\text{iso}}(\text{B3}) \geq \rho_{\text{iso}}(\text{B86}) \) for a given \( \nu_5 \) (the negative \( \Delta \rho \) needs to be kept in mind, cf. Table 7). A notable exception to this trend is provided by the inverse dependence on \( \nu_5 \), i.e., \( \rho_{\text{iso}}(\text{B}) \geq \rho_{\text{iso}}(\text{B3}) \geq \rho_{\text{iso}}(\text{B86}) \) in the high-spin complexes MnO, MnF, and MnF in the case of splitting in CuO and Cu(CO)\(_3\). Exceptions to the abovementioned trends are also notable when significant spin contamination is connected to orbitals with large contributions on the ligand (see, e.g., results for VN, MnO, [\( \text{Co(CO)}_4 \)], and for the axial nitrogen in [\( \text{Mn(CN)}_4 \text{N}^+ \)] (cf. Table 10). The relative sensitivity of the results to \( \nu_5 \) vs \( \nu_c \) is of course different than it was for the metal HFCCs, as the relevant spin-polarization effects are now those around the ligand nuclei.

As for the isotropic metal HFCCs, the isotropic ligand HFCCs are made up of direct SOMO and indirect spin-polarization contributions. The latter are missing for MnH, where the single hydrogen 1s-\( \text{AO} \) is directly involved in two of the SOMOs (cf. section 7). The \( \Delta \rho_{\text{iso}}(\text{H}) \) in MnH is thus a relatively simple measure of the localization of the two \( \sigma \) type SOMOs at the H nucleus. Interestingly, the dependence of this \( \Delta \rho_{\text{iso}}(\text{H}) \) on \( \nu_5 \) is similar to that of the metal HFCCs in ScO and TiN, which are also dominated by direct SOMO contributions (but with much larger overall \( \Delta \rho \); cf. section 7). The significant difference between LYP and the two other correlation functionals is particularly notable for \( \Delta \rho_{\text{iso}}(\text{H}) \) in MnH. This may suggest that the description of dynamical correlation is critical for the charge distribution within the two \( \sigma \) type SOMOs.

A similar dependence on \( \nu_c \) is apparent for the \( ^{13} \text{C} \) HFCCs in [\( \text{Mn(CN)}_4 \text{N}^+ \)] and [\( \text{Cr(CO)}_4 \text{N}^+ \)], but for a different reason: The SOMO contributions are affected very little, and it is valence-shell spin polarization which changes with \( \nu_c \) (core polarizations at carbon are negligible). Experimental data are available only for [\( \text{Cr(CO)}_4 \text{N}^+ \)]. The hybrid functionals appear to give better
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<td>3[Fe(CO)4]y</td>
<td>5.0</td>
<td>3.6</td>
<td>4.9</td>
<td>3.5</td>
<td>3.0</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3[Fe(CO)4]z</td>
<td>5.0</td>
<td>3.6</td>
<td>4.9</td>
<td>3.5</td>
<td>3.0</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Individual T_e components are given for nonaxial tensors. * Experimental values are taken from the sources cited in the footnotes to Tables 8 and 10. * In Ne or Ar matrix, respectively. * Hyperfine tensor components are given in order: (1) along the metal—ligand bond, (2) normal to the metal—ligand bond, in the molecular plane, and (3) along the molecular z-axis. * Anisotropy experimentally not well defined, cf. discussion in ref 18. * Hyperfine tensor components are given in order: (1) along the metal—ligand bond, (2) normal to the metal—ligand bond and parallel to the xy plane, and (3) perpendicular to directions 1 and 2.
agreement with experiment than pure GGAs. A relatively large dependence on $\nu_c$ is also apparent for MnF$_2$ and MnF$_3$.

A large dependence on $\nu_c$ is seen for the isotropic $^{13}$C HFCCs of the axial ligands in $[^3\text{Mn(CO)}_5]$ and $[^3\text{Fe(CO)}_5]$]. The exchange–correlation potential affects mainly the valence-shell spin polarization, and the direct SOMO contribution. The (smaller) dependencies on $\nu_c$ and $\nu_e$ for VO, TiN, and TiF$_3$ are also due to the valence-shell polarization and to SOMO contributions. Particularly large dependence on $\nu_c$ is found in all cases with significant spin contamination problems, e.g., for MnO$_3$. Thus, the very large dependence of $A_{\text{iso}}(\text{O})$ in MnO$_3$ on $\nu_c$ is probably an artifact of the large spin contamination with BH-type hybrid functionals (cf. section 7 and Table 9).

Other examples are $^{13}$C and nitrosyl $^{14}$N HFCCs in [Mn(CN)$_5$NO]$^{2-}$, $^{13}$C and nitride $^{14}$N HFCCs in [Mn(CN)$_5$N]$^{-}$, and $^{13}$C HFCCs in [Co(CO)$_4$] (Table 10).

For most of the present systems, the theoretical values for $A_{\text{dirp}}$ of the ligands are very small, and often results with different functionals differ by less than 1 MHz. Agreement with the sparse experimental data appears reasonable in these cases. A larger dependence on $\nu_c$ is seen for TiF$_3$, MnO$_3$, and MnF$_2$ (and also for cases with large spin contamination, cf. above). Thus, the ligand dipolar couplings in $^9$MnO and $^9$MnF$_2$ increase when adding exact exchange.

9. Conclusions

The present study shows that the quantitative calculation of hyperfine coupling constants for transition metal systems is still a challenge to quantum chemistry, more so than for organic radicals. None of the density functionals investigated here may be considered to provide acceptable results for the whole range of transition metal species studied. For a number of particularly difficult systems, essentially none of the functionals provides satisfactory results.

There are various reasons why the HFCCs of transition metal systems present such difficulties. One of them is the very delicate core–shell spin polarization, which is in many cases the dominant pathway to create spin density at the metal nucleus. Even for an isolated transition metal atom (consider Mn$^+$ in section 5), we may understand why this type of spin polarization is so difficult to describe by present-day functionals. The spin polarization is mainly due to exchange interactions between singly occupied metal 3d orbitals and the outermost doubly occupied 3s- and 2s-type core shells. It is clear that these exchange interactions are strongly nonlocal (specific examples will be discussed elsewhere$^{25}$ and thus difficult to account for with approaches derived from the local density approximation.$^{94}$ It is also clear that the description of such subtle spin-polarization effects is very different from the energy quantities that are currently used to fit the free parameters in the exchange–correlation functionals. The description of spin polarization is already nontrivial for organic $\pi$-radicals.$^{13,15,83}$ The spin polarization mechanisms in transition metal complexes are even more variable, and they involve not only the valence shell but also to a large extent the outermost core shells of the metal.

A second difficulty is connected to spin contamination. In several of the examples studied here, spin contamination became significant when exact exchange was mixed into $\nu_c$. This led to a significant deterioration of the results. In some cases where spin polarization was underestimated at the GGA level, and where exact-exchange mixing would thus have been desirable to increase it, the dramatic onset of spin contamination made it impossible to improve the results with hybrid functionals. In some of the “limiting cases” discussed toward the end of section 7, spin contamination is already significant with pure GGA-type functionals. The spin contamination for the hybrid functionals is closely related to the well-known bias of unrestricted Hartree–Fock wave functions for higher spin multiplicities. Obviously, the spin contamination may be very pronounced for transition metal complexes (particularly so for 3d-metals) due to the presence of low-lying excited states.

It is not clear how the magnitude of the spin polarization could be increased while avoiding significant spin contamination.$^{99}$ However, one may speculate that improved functionals might give increased core–shell spin polarization without exceedingly large valence-shell spin polarization (and thus spin contamination). Obviously, the description of valence spin polarization is also not trivial, even in cases with low spin contamination (cf. section 7). It seems likely that the desired functional would have to incorporate significantly less than 50% exact exchange. Generally, hyperfine coupling constants, in particular for transition metal systems, may turn out to be a particularly fruitful testing ground for new DFT (or alternative) approaches. In addition to the appreciable literature on organic molecules,$^{13,15,31}$ the hyperfine coupling constants of the 21 complexes studied in the present work should be useful as a benchmark set against which to calibrate new methods.

On the other hand, we should not judge even the present situation too pessimistically. For a significant number of complexes, the ca. 10–15% agreement with experimental isotropic metal HFCCs we are hoping for has been achieved with essentially all of the functionals (e.g., for ScO, TiN, TiO, VO, MnO, or MnF). In other subsets of molecules, the analysis of the electronic structure suggests the range of functionals (GGAs, B3-type, or BH-type hybrids) that might be most appropriate (as shown by the various examples discussed in this work). Careful selection of functionals is thus still expected to allow useful chemical applications in many areas, even though such an approach is obviously not completely satisfactory from a theoretical point of view. We expect that spin contamination is less pronounced for 4d or 5d transition metal complexes, and thus the choice of functional may also be somewhat less critical (on the other hand, relativistic effects will definitely have to be considered for heavy-atom systems, and we are presently developing approaches to do so).

The coupled cluster calculations we carried out for a subset of systems appear to be less influenced by such problems. Even in cases of significant spin contamination the results appeared to remain relatively stable. On the other hand, the computational effort involved presently makes such coupled-cluster approaches prohibitive for larger systems. Even for those di-, tri-, and tetraatomic complexes studied here, the large demand on the computational resources has not allowed us to truly saturate the basis sets with regard to higher angular momentum functions. There remains thus an urgent need for more economical approaches, and more accurate density functionals might offer the most practical route for improvement.

The present calculations also show conclusively that spin-polarization effects are nonnegligible for the metal dipolar couplings. This contrasts to the situation for main group compounds, where it is usually sufficient to take account of the direct SOMO spin densities to obtain good results for dipolar couplings.$^{13}$ The importance of spin polarization for transition metal dipolar hyperfine couplings arises from the presence of strongly polarizable semicore $p$-type orbitals (mainly the $3p$ orbitals for first-row transition metals), which have a very similar radial extent as the valence $d$-type SOMO orbitals. The importance of spin polarization for dipolar coupling constants...
of the metal had already been noted by Belanizoni et al., in their careful study of TiF$_3$. In view of the importance of spin polarization, the widely used simplified models that derive the $d$ or $s$ character of the SOMO directly from the dipolar coupling constants should be viewed with caution in transition metal systems. More detailed analyses of spin-polarization mechanisms for transition metal hyperfine coupling constants will be given elsewhere.  

Acknowledgment. This work has been supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie. Part of this work benefited also from the graduate college “Moderne Methoden der magnetischen Resonanz” at Universität Stuttgart. We are grateful to Vladimir G. Malkin, Olga L. Malkina (Bratislava), Pavel Kubíček (Brno), and Dominik Munzar (Stuttgart) for helpful discussions. Jürgen Gauss (Mainz) kindly provided assistance with the ACES-II code. We also thank Evert-Jan Baerends (Amsterdam) for a preprint of ref 18 and Ernest R. Davidson for informing us about an error in ref 21 (cf. section 7).

References and Notes

EPR Hyperfine Coupling Constants


(73) Cf. Extensible Computational Chemistry Environment Basis Set Database, Version 1.0; Molecular Science Computing Facility: Pacific Northwest Laboratory.
(81) We note that the metal 3s-shell provides a positive core—shell spin-polarization contribution to the metal HFCC, whereas the 2s-shell provides an even larger negative contribution. This is consistent with previous interpretations, see refs 1 and 3. Compare also: Freeman, A. J.; Watson, R. E. In Magnetism; Rado, G. T., Suhl, H., Eds.; Academic Press: New York, 1965; Volume IIa, p 167. Watson, R. E.; Freeman, A. J. in Hyperfine Interactions; Freeman, A. J., Fraenkel, R. D., Eds.; Academic Press: New York, 1967; p 53, as well as refs 23 and 24.
(82) These $<\tau^2>$ values pertain to the Kohn—Sham wave function, i.e., to the noninteracting reference system rather than to the real system. Such data are nevertheless expected to give a reasonable and useful representation for the real system as well (see, e.g., Baker, J.; Scheiner, A.; Andzelm, J. Chem. Phys. Lett. 1993, 216, 380).
(84) Note, however, that there may be significant differences even between different GGA functionals.13,15,31,83
(85) Note however, that for $\pi$-type radicals spin polarization is important.13—15,83 Indeed, it appears that in many cases even B3LYP underestimates this spin polarization. See also, e.g., Carmichael, I. J. Phys. Chem. A 1997, 101, 4633.
(87) Davidson, E. R., personal communication.
(94) In this study we have concentrated on GGA exchange functionals derived from Becke’s 1986 ansatz. Some differences may already be expected when using other GGA approaches.13,79
(95) In principle, one might remove the spin contaminants by spin projection techniques. However, the justification for doing so is doubtful. For a lucid discussion, see e.g., Chipman, D. M. Theor. Chim. Acta 1992, 82, 93.
The only justification for our concepts is that they serve to represent the complex of our experience; beyond this they have no legitimacy.

Albert Einstein (1879-1955)

6 Density Functional Calculations of Electronic $g$-Tensors for Transition Metal Complexes: A Validation Study

Introduction

The electronic $g$-tensor is a characteristic part of any EPR spectrum and can provide information on the identity, as well as electronic and molecular structure of the paramagnetic species present. The fundamental physical laws that determine the $g$-tensor are well understood. However, serious computational difficulties had largely prevented a rigorous first-principles prediction of this quantity. Thus, in contrast to the treatment of EPR hyperfine coupling constants that already do have an appreciable history of first principles theoretical treatments, quantitative calculations of electronic $g$-tensors by nonempirical quantum chemistry have become possible only very recently. The first accurate calculations at the HF and multireference configuration interaction (MRCI) levels of theory are due to Lushington et al. $^{1,2}$ Vahtras and coworkers$^3$ have employed HF and multiconfigurational self-consistent-field (MCSCF) linear response functions. Recently, two different DFT implementations of $g$-tensor calculations within the Amsterdam density-functional code have been reported by Schreckenbach and Ziegler$^4$ and by van Lenthe et al.$^5$

The following paper reports an alternative DFT implementation of electronic $g$-tensors within the deMon code including all relevant perturbation operators. A main feature of the new approach is the use of two types of accurate yet efficient approximations to the full one- and two-electron molecular spin-orbit operators. The new method has been validated on a number of species, including a detailed analysis of different contributions to $g$-shifts. The author of this thesis contributed to the paper by performing validation calculations on a set of 3$d$-transition metal complexes. The
The corresponding results are summarized in Table 10, Figure 2, and the relevant discussion in Part 6 ("Further Validation Calculations") of the paper. The two sections given below, Results and Conclusions, refer to the work done by the author of this thesis.

Results

Table 10 in the following paper gives results obtained with the VWN functional, and, in addition to the accurate atomic mean-field treatment of the \( \Delta g_{SO/OZ(1e)} \) and \( \Delta g_{SO/OZ(2e)} \) terms, contains also results that neglect the \( \Delta g_{SO/OZ(2e)} \) terms altogether. Additional results obtained by the author that have not been included in the paper are presented in Table 5.1. The latter table contains information on the effect of the density functional (VWN/BP86) and inclusion of the “SOS-DFPT” correction on the \( g \)-tensor components.

In contrast to the good performance for main-group species (cf. Figure 1 of the paper), the results obtained for 3\( d \) transition metal complexes are less satisfactory. The graphical comparison of the theoretical and experimental results in Figure 2 indicates that the proper inclusion of the two-electron SO terms deteriorates the agreement with experiment significantly. The two-electron terms reduce the overall \( g \)-shifts by ~40-50\%, so that a linear fit with slope 0.59 is obtained when including both the one-electron and the two-electron terms in the calculation. This observation corresponds strikingly to observations obtained recently by Bühl et al.,\(^6,7\) when testing GGA-DFT approaches in calculations of nuclear shieldings of 3\( d \) transition metal nuclei. UDFT-GIAO calculations with GGA functionals gave slopes of ~0.6 in comparison with experiment. This corresponds to a significant underestimate of the paramagnetic contributions to shielding. Bühl found that the slope could be improved to almost 1.0 by using hybrid functionals (B3LYP or B3PW91).\(^7\) In view of the close similarity of nuclear shielding tensor and electronic \( g \)-tensor, we expect that the origin of the failure of the GGA functionals in both cases is related, and that the inclusion of Hartree-Fock exchange should improve the performance also for the \( g \)-tensor.
Table 5.1 Comparison of Computed and Experimental $\Delta g$-Tensor Components (ppt) for a Series of 3d Transition Metal Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>VWN, UDFT, with $\Delta g_{SO/OZ(2e)}$</th>
<th>VWN, SOS-DFPT$^b$, with $\Delta g_{SO/OZ(2e)}$</th>
<th>VWN, UDFT, with $\Delta g_{SO/OZ(2e)}$</th>
<th>VWN, SOS-DFPT$^b$, without $\Delta g_{SO/OZ(2e)}$</th>
<th>BP86, UDFT, with $\Delta g_{SO/OZ(2e)}$</th>
<th>BP86, SOS-DFPT$^b$, without $\Delta g_{SO/OZ(2e)}$</th>
<th>Exp.$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiF$_3$</td>
<td>-28.3</td>
<td>-23.2</td>
<td>-79.4</td>
<td>-61.8</td>
<td>-62.1</td>
<td>-50.7</td>
<td>-111.3</td>
</tr>
<tr>
<td>Mn(CN)$_2$NO$_2^-$</td>
<td>-1.9</td>
<td>-1.4</td>
<td>-1.2</td>
<td>-0.3</td>
<td>-5.2</td>
<td>-4.2</td>
<td>-10.1</td>
</tr>
<tr>
<td>TiF$_3$</td>
<td>-1.2</td>
<td>-1.2</td>
<td>-1.8</td>
<td>-1.8</td>
<td>-1.9</td>
<td>-1.9</td>
<td>-11.1</td>
</tr>
<tr>
<td>Mn(CO)$_5$</td>
<td>-0.9</td>
<td>-1.0</td>
<td>-1.2</td>
<td>-1.3</td>
<td>-1.7</td>
<td>-1.7</td>
<td>-3.7</td>
</tr>
<tr>
<td>[Fe(CO)$_5$]$^{1-}$</td>
<td>-0.9</td>
<td>-0.9</td>
<td>-0.6</td>
<td>-0.6</td>
<td>-1.0</td>
<td>-1.0</td>
<td>-1.5</td>
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<td>0.0</td>
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<td>-0.8</td>
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<td>-1.2</td>
<td>-0.5(3)</td>
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<tr>
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<td>-0.1</td>
<td>-0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>-0.5(3)</td>
</tr>
<tr>
<td>Ni(CO)$_3$H</td>
<td>4.3</td>
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<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
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<td>2.5</td>
<td>2.0</td>
<td>1.8</td>
<td>1.9</td>
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<td>8.1</td>
<td>7.4</td>
<td>3.6</td>
</tr>
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<td>27.8</td>
<td>24.7</td>
<td>28.8</td>
</tr>
<tr>
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<td>34.8</td>
<td>40.7</td>
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<td>28.4</td>
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<td>46.5</td>
<td>48.7</td>
</tr>
<tr>
<td>Cu(NO$_3$)$_2$</td>
<td>28.2</td>
<td>26.3</td>
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<td>45.1</td>
<td>42.2</td>
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<tr>
<td>Cu(NO$_3$)$_2$</td>
<td>31.0</td>
<td>28.9</td>
<td>49.3</td>
<td>46.0</td>
<td>50.8</td>
<td>47.4</td>
<td>49.9(5)</td>
</tr>
<tr>
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<td>31.5</td>
<td>55.4</td>
<td>49.9</td>
<td>55.4</td>
<td>50.4</td>
<td>48.7</td>
</tr>
<tr>
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<td>39.8</td>
<td>36.5</td>
<td>65.0</td>
<td>59.7</td>
<td>67.1</td>
<td>61.6</td>
<td>65.1</td>
</tr>
<tr>
<td>[Fe(CO)$_5$]$^{1-}$</td>
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<td>43.0</td>
<td>89.3</td>
<td>78.8</td>
<td>77.9</td>
<td>70.2</td>
<td>81.0, 77.4</td>
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<tr>
<td>Co(CO)$_4$</td>
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<td>68.3</td>
<td>137.5</td>
<td>118.7</td>
<td>120.7</td>
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<tr>
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<td>116.3</td>
<td>105.8</td>
<td>183.0</td>
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<td>183.6</td>
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<td>165.5</td>
<td>180.2</td>
<td>165.8</td>
<td>285.2</td>
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</table>

$^a$UDFT-IGLO / SOS-DFPT-IGLO with AMFI approximation for $\Delta g_{SO/OZ(2e)}$, 9s7p4d metal basis, BIII basis on ligands, BII on remote atoms in Cu(acac)$_2$. $^b$Including the correction term in the Loc.1 approximation. $^c$For references to the literature, see last column of Table 10 of the paper.
Conclusions and outlook

In contrast to the good performance of our DFT approach for main-group species, the present results for a rather diverse set of 3d transition metal complexes indicate that the paramagnetic contributions are underestimated significantly. We expect that the use of exchange-correlation functionals that include some exact exchange will enable more accurate calculations. The present version of our code does not allow the inclusion of the Hartree-Fock exchange. However, hybrid functionals have recently been implemented in a new code of our group. Initial test calculations indicate improved performance for the calculation of g-tensors of the same series of 3d transition metal complexes.
References


Density Functional Calculations of Electronic g-Tensors Using Spin–Orbit Pseudopotentials and Mean-Field All-Electron Spin–Orbit Operators

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Received March 20, 2000. Revised Manuscript Received June 29, 2000

Abstract: Modern density-functional methods for the calculation of electronic g-tensors have been implemented within the framework of the deMon code. All relevant perturbation operators are included. Particular emphasis has been placed on accurate yet efficient treatment of the two-electron spin–orbit terms. At an all-electron level, the computationally inexpensive atomic mean-field approximation is shown to provide spin–orbit contributions in excellent agreement with the results obtained using explicit one- and two-electron spin–orbit integrals. Spin–orbit contributions account for up to 25–30% of the two-electron terms and may thus be non-negligible. For systems containing heavy atoms we use a pseudopotential treatment, where quasirelativistic pseudopotentials are included in the Kohn–Sham calculation whereas appropriate spin–orbit pseudopotentials are used in the perturbational treatment of the g-tensors. This approach is shown to provide results in good agreement with the all-electron treatment, at moderate computational cost. Due to the atomic nature of both mean-field all-electron and pseudopotential spin–orbit operators used, the two approaches may even be combined in one calculation. The atomic character of the spin–orbit operators may also be used to analyze the contributions of certain atoms to the paramagnetic terms of the g-tensors. The new methods have been applied to a wide variety of species, including small main group systems, aromatic radicals, as well as transition metal complexes.

1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is one of the most important experimental techniques of studying compounds containing unpaired electrons. Typical applications encompass biological systems, paramagnetic defects in extended solids, transition metal complexes, or simple organic radicals (e.g., in zeolites). The recent development of high-field EPR spectroscopy (at frequencies of 95 GHz or higher) has significantly widened the scope of the method and of the information that may be extracted. In particular, in modern solid-state EPR experiments the components of the electronic g-tensor may frequently be resolved. Interpretation of these experiments by quantum chemical calculations has thus become highly desirable. However, in contrast to the treatment of EPR hyperfine coupling constants that already do have an appreciable history of first principles theoretical treatments, quantitative calculations of electronic g-tensors by the machinery of nonempirical quantum chemistry have become possible only very recently (for semiempirical calculations, cf. refs 3 and 4; see also ref 5).

The first accurate calculations at the Hartree–Fock (HF) and multireference configuration interaction (MRCI) levels of theory are due to Lushington et al.6,7 Vahtras and co-workers8 have employed HF and multiconfiguration self-consistent-field (MCSCF) linear response functions. These ab initio implemen-


10.1021/ja000984s CCC: $19.00 © 2000 American Chemical Society
Published on Web 09/13/2000

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tations include essentially all perturbation operators—at the Breit—Pauli level of treating spin–orbit coupling—which are thought to be relevant for the electronic g-tensor. Thus, at least for systems containing only light elements, it is in principle possible to converge to the experimental results, by using larger and larger basis sets and by improving the treatment of electron correlation. However, obviously such calculations are at present largely restricted to relatively small systems; as the accurate inclusion of electron correlation becomes very demanding with increasing size of the system.

In case of the NMR shielding tensor, which is conceptually related to the electronic g-tensor, it has recently been shown that density-functional theory (DFT) provides a valuable alternative to post-HF treatment, by approximately including electron correlation at lower computational cost. Indeed, a recent state-of-the-art DFT implementation of g-tensor calculations, reported by Schreckenbach and Ziegler (SZ), was based on their previous NMR chemical shift implementation (using gauge-including atomic orbitals, GIAOs) in the Amsterdam density-functional (ADF) program. A different DFT-GIAO implementation (but also in the ADF code), using the two-component zero-order regular approximation (ZORA) to account for spin–orbit (SO) coupling and scalar relativity, has been reported by van Lenthe et al. Two-component UHF approach has been implemented by Jayatilaka.

Here we report an alternative DFT implementation of electronic g-tensors within the deMon code. Our method differs from SZ mainly in the way we deal with spin–orbit coupling. SZ used an effective Kohn–Sham potential to model approximately the two-electron SO terms. This treatment does not include the spin–orbit–orbit terms, and it also involves a number of other approximations. We have recently shown for calculations of SO corrections to NMR chemical shifts that (1) a mean-field one-center approximation to the full two-electron SO integrals gives results in excellent agreement with an exact treatment, at a small fraction of the computational effort; (2) spin–orbit pseudopotentials (spin–orbit effective-core potentials, SO-ECPs) do also provide a good approximation to the full SO operator, in a valence-only treatment, and they allow easily the simultaneous treatment of SO and scalar relativistic effects. Our new g-tensor code is based on these efficient and accurate “atomic” treatments of SO coupling. This leads to a number of advantages in the calculations, as well as in the subsequent interpretation of the results, as we will demonstrate.

2. Methods

We define the g-tensor as

\[ \mathbf{g} = g_{\mathbf{e}} \mathbf{1} + \Delta \mathbf{g} \]  

and focus on g-shifts (\( \Delta g \)) relative to the free electron g-value. Throughout this work, g-shifts are given in ppm for main group radicals and in ppt (parts-per-thousand) for most transition metal systems (more significant digits are typically not available from experiment anyway).

The second-order theory for calculating \( \Delta g \) within a one-component approach has been presented in several recent reports of modern quantum chemical implementations. Hence, we limit ourselves to recapitulating only the relevant points and give the final expressions used in our present DFT calculations. Here we investigate radicals with double electronic ground states only. We look for terms bilinear in the magnetic field \( \mathbf{B}_0 \) and effective electron spin \( s \) in the molecular energy expression \( E \); hence, the Cartesian \( \mu \) component of \( \Delta g \) is

\[ \Delta g_{\mu \nu} = \frac{1}{\mu_B} \frac{\partial^2 E}{\partial B_{\mu \nu} \partial \mathbf{S}} \bigg|_{\mathbf{B}=0} \]  

We shall employ atomic units based on the SI system, where the Bohr magneton \( \mu_B = {\hbar \over 2} \).

The main contributions to the \( \Delta g \) tensor up to \( \mathcal{O}(s^2) \) (i.e., the fine-structure constant) arise from the SO coupling Hamiltonian

\[ H_{SO} = \frac{\alpha^2}{4} \sum_{\mathbf{r} \mathbf{M}} \left( \sum_{\mathbf{a}} s_{\mathbf{a}M} \right)^2 - \sum_{\mathbf{r}} \left( \mathbf{B}_{0 \mathbf{r}} \cdot \mathbf{s} + 2 \mathbf{B}_{0 \mathbf{r}} \times \mathbf{r} \right) \]  

where \( z_{\mathbf{a}} \) is the charge of nucleus \( M \), \( s \) the spin of electron \( i \), \( \mathbf{i}_M = (\mathbf{r}_i - \mathbf{R}_M) \) the angular momentum of electron \( i \) with respect to the position of nucleus \( M(\mathbf{R}_M) \), and \( \mathbf{B}_0 = (\mathbf{r}_i - \mathbf{R}_M) \) the corresponding angular momentum with respect to the position of electron \( j(\mathbf{r}_j) \). Here, \( \mathbf{B}_{0 \mathbf{r}} = \mathbf{B}_0 \times (\mathbf{r}_i - \mathbf{R}_M) \) is the vector potential at \( \mathbf{r}_i \), corresponding to the external magnetic field. We note that at the present level of accuracy of both the theory and experiment, it is not necessary to distinguish between \( g_e \) and the \( g \)-factor associated with the SO interaction. The field-independent part of \( H_{SO} \) (arising from the \( -i \mathbf{V} \) terms in eq 3) couples, in double perturbation theory, with the orbital Zeeman (OZ) interaction

\[ H_{OZ} = -\sum_{\mathbf{r} \mathbf{M}} \mathbf{I}_{\mathbf{M}} \cdot \mathbf{B}_0 \]  

to the sum-over-states density-functional perturbation theory (SOS-DFT) expression for the paramagnetic part of \( \Delta g \)

\[ \Delta g_{SO,SOZ} = \frac{\alpha^2}{2} \sum_{\mathbf{a}} \sum_{i \mathbf{M} j \mathbf{N}} \left\{ \langle \psi_i^\mathbf{M} | H_{SO,SOZ} | \psi_j^\mathbf{N} \rangle \langle \psi_i^\mathbf{M} | \mathbf{I}_{\mathbf{M}} \cdot \mathbf{B}_0 | \psi_j^\mathbf{N} \rangle - \langle \psi_i^\mathbf{M} | \mathbf{I}_{\mathbf{M}} \cdot \mathbf{B}_0 | \psi_j^\mathbf{N} \rangle \langle \psi_i^\mathbf{M} | H_{SO,SOZ} | \psi_j^\mathbf{N} \rangle - \langle \psi_i^\mathbf{M} | H_{SO,SOZ} | \psi_j^\mathbf{N} \rangle \langle \psi_i^\mathbf{M} | \mathbf{I}_{\mathbf{M}} \cdot \mathbf{B}_0 | \psi_j^\mathbf{N} \rangle \right\} \]  

Here, \( \psi_i^\mathbf{M} \) and \( \psi_j^\mathbf{N} \) are unperturbed occupied and virtual \( \alpha/\beta \) MOs, respectively. \( \epsilon_i^\mathbf{M} \) and \( \epsilon_j^\mathbf{N} \) are the corresponding Kohn–Sham eigenvalues, and \( \Delta E_{\mathbf{M} \mathbf{N}} \) is the “SOS-DFT correction” (Loc.1 in the present paper) imposed on the energy denominators. We refer to the original papers for details. Leaving the \( \Delta E_{\mathbf{M} \mathbf{N}} \) term out corresponds to the uncoupled DFT (UDFT) approximation. \( H_{SO} \) denotes the \( \mathbf{a} \)-component of the spin-free part of the field-free SO Hamiltonian (the prefactors \( 2 \epsilon_i^\mathbf{M} / \hbar \) of \( H_{SO} \) of eq 3 have been absorbed in the prefactor of eq 5). While the

present formulae are written in terms of a common gauge origin, the choice of individual-gauges-for-localized-orbitals (IGLO) can be trivially read from the nuclear shielding formulae of ref 22.

As mentioned above, an accurate treatment of spin–orbit coupling is particularly critical for quantitative g-tensor calculations. We base our implementation on our latest version of the deMon-NMR module for calculating the SO contribution to the nuclear shielding tensor and use three different types of SO integrals in the present calculation: (1) from the full microscopic one- and two-electron SO Hamiltonian of eq 3 using the EAGLE code, (2) from the effective one-electron one-center mean-field approximation for both one- and two-electron SO integrals as implemented in the AMFI software, and (3) from spin–orbit potentials of the Pitzer-Winter form. The second alternative is a very accurate approximation of the first (as shown below), and allows calculations of much larger molecular systems due to eliminating the need to compute and store a large number of two-electron integrals. Since $g$ is largely a valence property, SO-ECPs can be used to reduce the computational effort further by removing the core electrons and to take into account scalar relativistic effects when used in connection with Kohn–Sham valence pseudo-orbitals optimized in the presence of corresponding quasirelativistic ECPs. Furthermore, the implementation allows mixed usage of AMFI and SO-ECP integrals on different atomic centers of the molecule. Hence, it is possible to perform an atomic break-down of the calculated $\Delta g_{\text{SO(2e)}}$ contributions.

To obtain a consistent account for all the important terms up to $O(\alpha^2)$, one has to additionally consider the bilinear terms of the Breit–Pauli Hamiltonian:

$$H_{\text{RMC}} = -\frac{1}{4} g^2 e \sum_{\mu \nu} p^{\mu, \nu}_c \cdot B_0$$

the so-called kinetic energy correction to the spin–Zeeman interaction (taken up to $O(B_0)$, with $p = -i \nabla$), and the part of the SO Hamiltonian arising from the magnetic field dependence of the SO Hamiltonian (the $A_0$-dependent terms in eq 3). After taking the appropriate expectation values, the former leads to a diagonal (isotropic) contribution

$$\Delta g_{\text{RMCAvo}} = -\frac{1}{2} g^2 e \sum_{\mu \nu} \sum_{\alpha \beta} P^{\alpha \beta} \langle \mu | \psi^{\alpha, \beta} | \nu \rangle$$

where

$$P^{\alpha \beta} = \sum_{\mu \nu} \sum_{\alpha \beta} p^{\mu \nu}_c \cdot B_0 \langle \mu | \psi^{\alpha, \beta} | \nu \rangle$$

is the spin density matrix in the atomic orbital ($\mu, \nu$) basis and $c$ are the MO coefficients. The latter term causes diamagnetic gauge correction contributions, whose one-electron term reads

$$\Delta g_{\text{RGC(lo),av}} = \frac{1}{4} g^2 e \sum_{\mu \nu} \sum_{\alpha \beta} \delta_{\alpha \beta} (r_{\mu} \cdot r_{\nu}) - r_{\mu \nu} r_{\nu \mu} Z_{\mu \nu}$$

In the present calculations we neglect the corresponding and analogous two-electron contribution $\Delta g_{\text{SO(2e)}}$ due to its general smallness (see refs 7 and 12) and the lack of a computationally efficient approximation thereto.

### 3. Computational Details

#### 3.1. Structures.

For small main group radicals, we used better comparison with the results of Schreckenbach and Ziegler (SZ) their DFT-optimized structures. Similarly, we employed the DFT (VWN)-optimized structures of Patchkowski and Ziegler (PZ) for a set of MXY$_4$ transition metal complexes. Most of the structures of 3d complexes are those reported in a recent study of hyperfine couplings for these systems (mostly DFT-optimized, in a few cases experimental). Additional 3d complexes are the three vanadyl complexes $[\text{N,N'-ethylenebis}-(\text{o}-\text{tert-butyl})-\text{p}-\text{methylsalicyldimino})\text{oxovanadium(IV)}]$, bis(1-isopropyl-o-ethylsalicyldiminate)oxovanadium(IV), and bis(1-methyl-o-tert-butyl-salicyldiminate)oxovanadium(IV), for which experimental structures were used. Structures of $\text{Cu(acac)}_2$ and $\text{Cu(NO)}_2$, and of phenoxyl radicals have been fully optimized with the Gaussian98 code at the gradient-corrected, unrestricted DFT level (BP86 functional) with either local density (VWN) or gradient-corrected (GGA) functionals. We mainly used BP86, but PP86 and PW91 functionals were also tested. In most calculations, in particular in our comparison with the results of


(37) d-Type polarization functions have been taken from: Gaussian Basis Sets for Molecular Calculations, Huizenga, S., Ed.; Elsevier: New York, 1984.


Calculations of Electronic g-Tensors

For simple main-group radicals and with those of PZ for some d¹ transition metal systems, we will concentrate on the BP86 results. The calculations were performed in two separate steps, (1) the Kohn–Sham SCF calculation, and (2) the computationally inexpensive perturbation calculation, based on the Kohn–Sham orbitals of the previous step. This two-step procedure makes it easy to alter the parameters of the perturbation calculation only, for example, to test different options to treat the gauge problem, different SO operators, or for analysis purposes.

As we employ exchange-correlation functionals that do not depend on the current density, the resulting perturbation calculations are uncoupled (UDFT). In NMR chemical shift calculations on main group compounds with low-lying excited states, it was found previously, that the simple correction term \( \Delta E_{\text{corr}} \) in eq 5 may be used to reduce the paramagnetic contributions to the shielding tensors, thereby improving in most cases the agreement with experiment.17,22 In the case of the electronic g-tensor, we find that the accuracy of the experimental data available does typically not allow us to judge whether this SOS-DFPT correction term is beneficial to the agreement between theory and experiment. We will thus concentrate on the UDFT results and give SOS-DFPT results for comparison only in a few examples.

Unless noted otherwise, results are reported with the IGLO procedure. For the heavier main-group compounds and the square pyramidal d¹ complexes, the Pipek-Mezey localization45 converged better and was used instead. The \( \alpha \) and \( \beta \) MOs were localized separately. For analyses in terms of canonical MOs, a common gauge origin at the center of mass has been employed. g-Tensor calculations are known to be less gauge-dependent than, for example, NMR chemical shift computations, and we find that the IGLO and common gauge results typically do not differ much.

All-electron basis sets used for the 3d metals were \((15s11p6d)/(9s7p4d)\) sets designed previously for hyperfine calculations.39 Basis sets for Mo and Zr were constructed from the primitive set of the well-tempered series of Huzinaga et al.30 by removing the tightest three s-, two p- and four d-functions and adding the two most diffuse p-functions from the ECP basis set.31 The resulting \( 24s19p13d \) sets were used fully uncontracted. Test calculations show that this allows a valid comparison with ECP results. The basis sets BII and BIII (also termed IGLO-II and IGLO-III) of Kutzelnigg et al.41 (based on the earlier work of Huzinaga40) were used for main group atoms. In some cases, smaller DZVP basis sets43 were also studied (either with or without p-polarization functions on hydrogen).

Energy-adjusted ECPs and valence basis sets for 4d and 5d transition metals were the same as those used in the structure optimizations, augmented by appropriate spin–orbit pseudopotentials in the perturbation step of the calculation. Similarly, an ECP treatment of main group atoms (mainly of Kr, Xe, and the halogens) employed the same quasi-relativistic ECPs as the optimizations, together with SO-ECPs.32 The valence basis sets were decontracted and extended to TZ + 2P quality. The fitting procedure of the SO-ECPs used differs slightly from that of the quasi-relativistic ECPs, as they were obtained by a single-electron fit rather than by a multielectron fit.33,35 Moreover, the SO-ECPs used in the present work have been fitted to two-component Wood-Boring or averaged four-component Dirac–Fock energies that do not include the Breit interaction. Thus, they do not cover the spin–orbit–orbit term. Development of improved two-component multielectron-fit ECPs and SO-ECPs adjusted to multiconfiguration Dirac–Fock–Breit energies is presently carried out by Stoll et al.48 and we plan to use these more accurate parameters in our future g-tensor work. In some cases we also used nonrelativistic ECPs in the Kohn–Sham step for interpretation purposes. Gauge factors arising from the use of ECPs in the IGLO treatment have been neglected in the present work.39

4. All-Electron Calculations: The Importance of the Two-Electron SO Terms

For two systems, namely for CO²⁺ and for H₂O⁺, SZ reported individual contributions to the \( \Delta g \) components from their DFT calculations.12 This allows us detailed comparison, in particular regarding the different treatment of the two-electron SO terms (\( \Delta g_{\text{S(O/O2/2e)}} \) terms). Table 1 gives the results for CO²⁺. Table 2 for H₂O⁺. We give results with either (1) the exact (EAGLE) treatment of all one- and two-electron SO integrals, (2) the one-center and mean-field approximation (AMFI) to these integrals, and (3) the results of SZ, using their approximate treatment of the two-electron SO terms via an effective Kohn–Sham SO treatment. We give \( \Delta g_{\text{S(O/O2/2e)}} \) values with either (1) the exact (EAGLE) treatment of all one- and two-electron SO integrals, (2) the one-center and mean-field approximation (AMFI) to these integrals, and (3) the results of SZ, using their approximate treatment of the two-electron SO terms. The agreement with experiment is typically better for the IGLO rather than GIAO treatment due to the different treatment of the two-electron SO terms. The fact that we use IGLO rather than GIAO should not be relevant as we obtain essentially the same results with other choices of gauge origin.

| contribution | exact SO-ECPs | atomic mean-field appr. | SZ
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</tr>
</thead>
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<tr>
<td>( \Delta g_{\text{S(O/O2/2e)}} )</td>
<td>( \Delta g )</td>
<td>( \Delta g )</td>
<td>( \Delta g )</td>
</tr>
<tr>
<td>( \Delta g_{\text{S(O/O2/2e)}} )</td>
<td>85</td>
<td>71</td>
<td>85</td>
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<tr>
<td>( \Delta g_{\text{S(O/O2/2e)}} )</td>
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<td>-</td>
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</tr>
<tr>
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Table 1. Analysis of Different Contributions to g-Tensors (ppm) in CO²⁺
We first note that the agreement between the exact (EAGLE) treatment and the one-center mean-field approximation (AMFI) is excellent, both for the $\Delta_8$ terms (which include the one-center approximation in AMFI but not in EAGLE), and for the $\Delta_{8so}$ terms. Differences are below 7% (typically below 5%) in the two-electron terms, that is, much less for the overall $g$-shifts. This confirms the excellent performance of the atomic mean-field SO approximation, as found in many other types of applications.18,25,50 For systems with heavier atoms, the mean-field approximation is expected to be even more accurate. The computational effort for the atomic mean-field approximation is expected to be even more accurate.

The exact treatment of the two-electron SO integrals with the EAGLE code gives the following results: $\Delta_{g1} = -142$ ppm, $\Delta_{g2} = 3855$ ppm, $\Delta_{g3} = 10422$ ppm. Reference 12. Spin–s–orbit–orbit contribution. Spin–other–orbit–orbit contribution. Gas-phase experiments give $\Delta_{g1} = 200$ ppm, $\Delta_{g2} = 4800$ ppm, $\Delta_{g3} = 18800$ ppm.

As shown already by other workers (see, e.g., refs 6 and 7), the $g$-shift tensors are usually except for very light systems or for very small components dominated by the second-order (paramagnetic) $\Delta_{8so(1e)}$ and $\Delta_{8so(2e)}$ terms, while the first-order (diamagnetic) contributions ($\Delta_{8rmc}$ and $\Delta_{8gc(1e)}$ terms) are small. In both CO$^+$ and H$_2$O$^+$, our $\Delta_{8rmc}$ terms agree quantitatively with the results of SZ. Similarly, the $\Delta_{8gc}$ contributions for these two radicals, as well as for NO$^+$ and MgF, agree excellently with the MRCI results of Lushington.2 The $\Delta_{8gc(1e)}$ corrections are not directly comparable, due to the different choice of gauge origin. Nevertheless, they are close to the results of SZ and agree also with those of Lushington (we find an even better agreement when using a common gauge origin at the center of mass). We neglect the $\Delta_{8gc(2e)}$ corrections. They have been found to be smaller and of the opposite sign to the $\Delta_{8gc(1e)}$ terms, that is, small compared to the paramagnetic terms.7,12 This is expected to cause slight errors for very small components, where the spin–orbit terms are small, but it will not influence much the comparison with experiment.

Interestingly, even the $\Delta_{8so(1e)}$ contributions to the larger components agree with the results of SZ to within better than 5%. Thus, any significant deviation between the overall results must stem from the treatment of the $\Delta_{8so(2e)}$ terms. Indeed, in both systems the two-electron SO contributions recovered by SZ account for only $\sim$50% of our results. As a consequence, the overall $g$-shifts of SZ are generally somewhat larger than ours, as the partial compensation of the one-electron SO terms by the two-electron terms is underestimated. We have tried to find out to what extent the incomplete recovery of the two-electron terms by SZ is due to either (1) the neglect of the SOO terms or (2) to the approximations involved in the effective Kohn–Sham potential used. Tables 1 and 2 show that in both systems, the SOO term accounts for $\sim$25% of the total $\Delta_{8so(2e)}$ terms. Thus, about half of the errors of SZ in the two-electron terms is due to the neglect of the SOO term, the other half must be due to the other approximations mentioned.

Table 2. Analysis of Different Contributions to $g$-Shifts (ppm) in H$_2$O$^+$

<table>
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<tr>
<th>contribution</th>
<th>$\Delta_{g1}$</th>
<th>$\Delta_{g2}$</th>
<th>$\Delta_{g3}$</th>
<th>$\Delta_{g1}$</th>
<th>$\Delta_{g2}$</th>
<th>$\Delta_{g3}$</th>
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<tr>
<td>$\Delta_{8gc(1e)}$</td>
<td>138</td>
<td>172</td>
<td>183</td>
<td>147</td>
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<td>$\Delta_{8gc(2e)}$</td>
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<td>-109</td>
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<tr>
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<td>-312</td>
<td>-310</td>
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<td>-310</td>
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<td>$\Delta_{8so(1e)}$</td>
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<td>10205</td>
<td>-209</td>
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a UDFT results with BP86 functional. Our results with basis BIII and IGLO gauge. Results of SZ with STO basis and GIAO gauge. Mean-field and one-center approximation. The exact treatment of the two-electron SO integrals with the EAGLE code gives the following results: $\Delta_{g1} = -142$ ppm, $\Delta_{g2} = 3855$ ppm, $\Delta_{g3} = 10422$ ppm. Reference 12. Spin–same–orbit contribution. Spin–other–orbit contribution. Gas-phase experiments give $\Delta_{g1} = 200$ ppm, $\Delta_{g2} = 4800$ ppm, $\Delta_{g3} = 18800$ ppm.

Table 3. $g$-Tensor Components (ppm) for Some Light Main Group Radicals

<table>
<thead>
<tr>
<th>Component</th>
<th>this work</th>
<th>SZ</th>
<th>Lushington (MRCI)</th>
<th>exp.</th>
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<td>$\Delta_{g3}$</td>
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<td>13824</td>
<td>16019</td>
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<td></td>
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<td>$\Delta_{g2}$</td>
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a UDFT-BP86 results. Basis BIII, UDFT-IGLO, AMFI approximation. UDFT-GIAO. Multireference configuration interaction results. Experimental data as quoted in refs. 7, 12.

Calculations of Electronic $g$-Tensors

Figure 1. Comparison of calculated and experimental $g$-shift tensor components (ppm) for first-row compounds (cf. Tables 3, 9; Only components with $|\Delta g|$ $>$ 1000 ppm have been included).

Obviously, the importance of errors in the two-electron SO terms for the overall $g$-shifts depends on the relative importance of the $\Delta g_{SO/OZ(2e)}$ contributions. In CO$^+$ and H$_2$O$^+$, the two-electron terms amount to $\sim$35% of the absolute magnitude of the $\Delta g_{SO/OZ(1e)}$ terms (with opposite sign). We find this to be the general behavior for compounds containing atoms from at most the second period. Our results for other systems containing heavier main group atoms indicate that the importance of the two-electron terms decreases to $\sim$20%, 10%, 7% for the third, fourth and fifth period, respectively (see, e.g., results for TiF$_3$; X = Cl, Br, I, in Table 4). The same percentages were found previously in both DFT$^{16}$ and MCSCF calculations$^{51}$ of SO corrections to NMR chemical shifts. Thus, the accurate treatment of the two-electron terms becomes somewhat less important for compounds of heavier main group elements. For light main group, for example, organic radicals, the two-electron SO terms are particularly critical. The SOO term accounts for $\sim$20% of the two-electron SO terms also for the heavier main group compounds (cf. Table 4).

The relative importance of the different terms changes when transition metals are involved. This is demonstrated for the simple 3d and 4d complexes TiF$_3$ and ZrH$_3$ in Table 5. In both cases, the spin density is mainly localized on the metal, and the SO coupling at the metal dominates the $g$-tensor. For the titanium complex, the $\Delta g_{SO/OZ(2e)}$ contributions amount to $\sim$47% and $\sim$55% of the magnitude of the $\Delta g_{SO/OZ(1e)}$ terms for $\Delta g_{||}$ and $\Delta g_{\perp}$, respectively. For the ZrH$_3$ 4d model complex the fractions are $\sim$34% and $\sim$31%, respectively. In both cases, the two-electron contributions are thus of considerably larger relative importance than with main group elements of the same row (cf. $\sim$13% for Br, $\sim$7% for I). This is probably related to the more pronounced penetration of the valence d-orbitals of the transition metals into the core.$^{52}$

Another difference compared to the main group case is seen with the SOO term, which for both TiF$_3$ and ZrH$_3$ accounts for only $\sim$10$-$12% of the $\Delta g_{SO/OZ(2e)}$ contribution, that is, it is only about half as important as in the main group cases we have looked at above. Good agreement with the perturbational UKS results (obtained with the SZ code) of van Lenthe et al.$^{14}$ for TiF$_3$ may be obtained by reducing our $\Delta g_{SO/OZ(2e)}$ contributions by $\sim$50%. This suggests that the main difference is in their incomplete treatment of the two-electron terms. On the other hand, their restricted Kohn$-$Sham (ROKS) calculations (both perturbational and two-component treatment) give much larger $\Delta g_{\perp}$ than the UKS treatment, i.e., spin polarization does seem to be important. Here the ROKS data are closer to experiment, probably due to error compensation, cf. section 6.

The previous examples were relatively simple, as the spin$-$orbit coupling arose mainly from one (the heaviest) atom, and from only a few molecular orbitals. Obviously, things may be much more complicated, if several heavy atoms are involved, and if several MOs may contribute. As an illustration, Table 6 compares the analyses for the two square pyramidal complexes CrOF$_4^-$ and CrOCl$_4^-$ in the case of CrOF$_4^-$, things are still relatively straightforward. The $\Delta g_{SO/OZ(2e)}$ terms amount to about half of the $\Delta g_{SO/OZ(1e)}$ terms ($\sim$51% for $\Delta g_{||}$, $\sim$45% for $\Delta g_{\perp}$), and the SOO term to about 11$-$14% of the $\Delta g_{SO/OZ(2e)}$ contribution. However, in the case of CrOCl$_4^-$, $\Delta g_{\perp}$ behaves “normally” ($\sim$45% magnitude of the two-electron terms, $\sim$10% fraction of SOO terms), but $\Delta g_{||}$ is atypical. Here the $\Delta g_{SO/OZ(2e)}$ terms are very small ( $\sim$2%; with $\sim$35% SOO contribution). An MO analysis (section 7) indicates that at least two occupied MOs contribute significantly to $\Delta g_{||}$, with opposite signs.

Table 4. Analysis of Different Contributions to $g$-Shifts (ppm) in CF$_3$X$^-$ (X = Cl, Br, I)$^a$

| CF$_3$X$^-$ | $\Delta g_{||}$ | $\Delta g_{\perp}$ |
|------------|----------------|----------------|
| all-el.$^a$ | $\Delta g_{SO/OZ(1e)}$ | 130 | 96 |
| all-el.$^a$ | $\Delta g_{SO/OZ(2e)}$ | $-315$ | $-315$ |
| all-el.$^a$ | $\Delta g_{SO/OZ(1e)}$ | $-482$ | 17891 |
| all-el.$^a$ | $\Delta g_{SO/OZ(2e)}$ | 134 | $-3474$ |
| all-el.$^a$ | (SO$^+$, SOO$^+$) | (93°, 41°) | ($-2768^\circ$, $-707^\circ$) |
| total all-el.$^a$ | $\Delta g_{||}$ | $-532$ | 14198 |
| ECP-QR(Cl)$^{b,c}$ | $\Delta g_{||}$ | $-390$ | 12961 |
| ECP-QR(Br)$^{b,d}$ | $\Delta g_{||}$ | $-609$ | 14573 |
| ECP-QR(I)$^{b,e}$ | $\Delta g_{||}$ | $-610$ | 15112 |
| exp.$^a$ | $\Delta g_{||}$ | $-200$ | 4700 |
| CF$_3$Br$^-$ | $\Delta g_{||}$ | 141 | 401 |
| CF$_3$I$^-$ | $\Delta g_{||}$ | 130 | 96 |
| CF$_3$I$^-$ | $\Delta g_{SO/OZ(1e)}$ | $-313$ | $-313$ |
| CF$_3$I$^-$ | $\Delta g_{SO/OZ(2e)}$ | $-475$ | 57833 |
| CF$_3$I$^-$ | (SO$^+$, SOO$^+$) | 151 | $-5663$ |
| CF$_3$I$^-$ | (SO$^+$, SOO$^+$) | (117°, 34°) | ($-458^\circ$, $-1080^\circ$) |
| total all-el.$^a$ | $\Delta g_{||}$ | $-470$ | 52258 |
| ECP-QR(Cl)$^{b,c}$ | $\Delta g_{||}$ | $-353$ | 53680 |
| ECP-QR(Br)$^{b,d}$ | $\Delta g_{||}$ | $-635$ | 67273 |
| ECP-QR(I)$^{b,e}$ | $\Delta g_{||}$ | $-637$ | 70229 |
| exp.$^a$ | $\Delta g_{||}$ | $-1300$ | 18990 |

$^a$ UDFT-IGLO results with BP86 functional and AM1 approximation. All-electron results with basis BII. $^b$ Spin$-$same$-$orbit terms only. $^c$ Spin$-$other$-$orbit terms only. $^d$ Quasirelativistic ECP/SO-ECP and TZ$+$P valence basis on all halogen atoms, BII on C. $^e$ DFT-GIAO, ref 12. $^f$ Without scalar relativistic effects. $^g$ With scalar relativistic effects. $^h$ In tetramethylsilane matrix (Hasegawa, A.; Williams, F., Chem. Phys. Lett. 1977, 46, 66). These anions are expected to experience increasing interactions with the environment from X = Cl through X = I. Therefore, the experimental data are probably not well-suited to be compared with calculations on the isolated anions.


$^{52}$ The fact that the 3d shell is the first shell with $l = 2$ and thus particularly compact, may be responsible for the particularly large $\Delta g_{SO/OZ(2e)}$ contributions for 3d systems (similar arguments apply to the 2p shell).
Table 5. Analysis of Different Contributions to g-Shifts (ppm) in TiF₃ and ZrH₃

<table>
<thead>
<tr>
<th>contribution</th>
<th>Δgᵣ</th>
<th>Δg⊥</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ₆₀(Cl₁)</td>
<td>+203</td>
<td>+371</td>
</tr>
<tr>
<td>Δ₆₆₀mc</td>
<td>−320</td>
<td>−320</td>
</tr>
<tr>
<td>Δ₆₀(SO₂Cl₁)</td>
<td>−1924</td>
<td>−58669</td>
</tr>
<tr>
<td>Δ₆₀(SO₂Cl₂)</td>
<td>+907</td>
<td>+32043</td>
</tr>
<tr>
<td>(SSO₂⁶, SOO₂⁶) (+783, +124⁴)</td>
<td>(+28199⁴, +3844⁴)</td>
<td></td>
</tr>
<tr>
<td>total all-el.</td>
<td>−1124</td>
<td>−26577</td>
</tr>
<tr>
<td>ECP-NR(Zr)⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>van Lenthe UKS⁶</td>
<td>−1700</td>
<td>−42800</td>
</tr>
<tr>
<td>van Lenthe ROKS⁵</td>
<td>+100</td>
<td>−73300</td>
</tr>
<tr>
<td>van Lenthe 2-comp.⁰</td>
<td>−1000</td>
<td>−97900</td>
</tr>
<tr>
<td>exp.</td>
<td>−1110⁰</td>
<td>−11190⁰</td>
</tr>
<tr>
<td></td>
<td>−3700⁰</td>
<td>−123700⁰</td>
</tr>
</tbody>
</table>

Table 6. Analysis of Different Contributions to g-Shifts (ppm) in CrOF₄⁻ and CrOCl₄⁻

<table>
<thead>
<tr>
<th>contribution</th>
<th>Δgᵣ</th>
<th>Δg⊥</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ₆₀(Cl₁)</td>
<td>+549</td>
<td>+472</td>
</tr>
<tr>
<td>Δ₆₆₀mc</td>
<td>−701</td>
<td>−701</td>
</tr>
<tr>
<td>Δ₆₀(SO₂Cl₁)</td>
<td>−27513</td>
<td>−39331</td>
</tr>
<tr>
<td>Δ₆₀(SO₂Cl₂)</td>
<td>+14073</td>
<td>+17741</td>
</tr>
<tr>
<td>(SSO₂⁶, SOO₂⁶) (+1247¹⁴, +1602¹⁴)</td>
<td>(+15216⁴, +2525⁴)</td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>−13592</td>
<td>−21811</td>
</tr>
<tr>
<td>PZ³</td>
<td>−19000</td>
<td>−29000</td>
</tr>
<tr>
<td>exp.</td>
<td>−43000</td>
<td>−32000</td>
</tr>
</tbody>
</table>

---

Δ₆₀(SO₂Cl₂) contributions from these two MOs compensate each other to a large extent. Thus, obviously the importance of the two-electron terms, as well as the relative contributions from the SSO and SOO terms to them may differ significantly from system to system, and for different tensor components within one system. It is therefore not justified to use a simple scaling procedure to correct for a neglect of certain two-electron SO terms.

We may again ask to what extent the differences of our results relative to those of Ziegler et al. are due to their incomplete treatment of the Δ₆₀(SO₂Cl₂) terms. If we simply reduce our two-electron terms by half, we obtain roughly −20000 ppm and −30000 ppm for Δgᵣ and Δg⊥, respectively, in CrOF₄⁻, in much better agreement with the results of Patchkovski and Ziegler. The same procedure applied to CrOCl₄⁻ produces more negative Δg⊥ (≈ −25000 ppm), whereas Δgᵣ is not affected much, due to the smallness of the two-electron terms in this case.

5. ECP Calculations: Validation of Spin–Orbit Pseudopotentials

Table 7 compares all-electron (AE) and pseudopotential (ECP/SO-ECP) treatments of Δg components for NF₂, KrF, XeF, and MoOF₆⁻. Table 3 includes the same comparison for CF₂X⁻ (X = Cl, Br, I), and Table 5 for ZrH₃. The results of Ziegler et al., with an approximate treatment of the Δ₆₀(SO₂Cl₂) terms, are included in Tables 4 and 7 as well, and experimental data are given for completeness. However, at least the data for KrF, XeF, and particularly those for the anions CF₂X⁻, are probably influenced significantly by environmental effects (cf. below).

We will thus only compare the different theoretical approaches. For easier comparison, the ECP calculations use ECPs and SO-ECPs only for the heaviest atoms, whereas the all-electron AMFI treatment is kept for the lighter atoms (as discussed in section 2, this combination of methods is allowed, due to the atomic nature of the SO operators involved).

As the SO-ECPs used here have been adjusted to atomic calculations that did not include the Breit interaction, they do not cover the SOO term. The ECP results might therefore be expected to slightly overestimate the Δ₆₀(SO₂Cl₂) contributions, typically by 10–15% for NF₂, by less than half of this for the heavier main group and transition metal species (cf. section 4). On the other hand, the direct comparison between all-electron and ECP–NR results has to be viewed with some caution, as the use of nonrelativistic ECPs with the relativistically adjusted SO-ECPs is not consistently consistent.

Inspecting the data of Tables 5 and 7, the ECP–NR results are found to be both high or low relative to the all-electron data. However, agreement is found generally within a few percent. The differences are significantly smaller than, for example, differences between local or gradient-corrected density functionals, and also smaller than differences relative to the approximate treatment of the SO integrals by SZ. This indicates that the combination of ECPs in the Kohn–Sham step with SO-ECPs in the perturbation treatment provides a useful valence-only approximation to the all-electron calculations. In all cases, our g-shifts are lower than those of SZ.

Comparison of the ECP–NR and ECP-QR results for KrF and XeF (Table 7) suggests an increase of Δg⊥ due to scalar...
relativistic effects (more so for XeF than for KrF). This is consistent with the increase of the \( g \)-shifts upon inclusion of scalar relativistic effects by SZ (at the first-order Breit-Pauli level). Moreover, the relative increase is of comparable magnitude, suggesting that the comparison of NR-ECP and QR-ECP results provides a reasonable estimate of the influence of scalar relativistic effects.

In the case of the anions CF\(_2\)X\(^-\) (X = Cl, Br, I; Table 4), the ECP calculations use quasirelativistic ECPs and SO-ECPs for X (no appropriate nonrelativistic ECPs have been available for comparison). The QR-ECP results for \( \Delta g_{ij} \) in CF\(_2\)Cl\(^-\) are \( \sim 9\% \) lower than the all-electron results. In contrast, the QR-ECP calculations give \( \sim 3\% \) and \( \sim 8\% \) larger values for CF\(_2\)Br\(^-\) and CF\(_2\)I\(^-\), respectively, probably in part due to the inclusion of scalar relativistic effects in the ECP calculations (cf. comparison between nonrelativistic and relativistic results of SZ). Again, our \( \Delta g_{ij} \) components are somewhat smaller than those of SZ. The experimental data were obtained in a solid matrix of tetrachloroethylene and are probably not strictly comparable to the free-anion calculations. The increasing discrepancy from Cl through X = I may be due either (1) to potential problems with the perturbation treatment of SO coupling for the heavier halogens, as suggested by SZ, or (2) to an increasingly diffuse nature of the SOMO (which corresponds to a \( \sigma^* \) (C–X) MO and does exhibit small positive energies in our Kohn–Sham calculations) and thus increasing interactions with the environment. The second possibility, which we find more likely, could be tested by calculations that simulate the matrix environment. This is beyond the scope of the present study.

ECP and all-electron results for the 4d model system ZrH\(_3\) may be compared in Table 5. The ECP–NR calculations give \( \sim 7\% \) too positive \( \Delta g \). Scalar relativistic effects appear to reduce further significantly the absolute value. In contrast, for the more complicated 4d complex MoOF\(_4\) (Table 7), the scalar relativistic effects appear to be modest.

### Table 7. Comparison of All-Electron and ECP/SO-ECP Results for \( g \)-Shift Components (ppm)\(^a\)

<table>
<thead>
<tr>
<th>X</th>
<th>( \Delta g_{11} )</th>
<th>( \Delta g_{22} )</th>
<th>( \Delta g_{33} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF(_2)Cl(^-)</td>
<td>–246</td>
<td>49494</td>
<td></td>
</tr>
<tr>
<td>CF(_2)Br(^-)</td>
<td>–184</td>
<td>127288</td>
<td></td>
</tr>
<tr>
<td>CF(_2)I(^-)</td>
<td>–91</td>
<td>130003</td>
<td></td>
</tr>
</tbody>
</table>

### Table 8. Comparison of First-Order Corrections (ppm) from All-Electron and ECP/SO-ECP Calculations\(^a\)

<table>
<thead>
<tr>
<th>X</th>
<th>( \Delta g_{\text{RMC}} )</th>
<th>( \Delta g_{\text{SOC}(1\text{e})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF(_2)Cl(^-)</td>
<td>–209</td>
<td>195,270</td>
</tr>
<tr>
<td>CF(_2)Br(^-)</td>
<td>–118</td>
<td>220,412</td>
</tr>
<tr>
<td>CF(_2)I(^-)</td>
<td>–229</td>
<td>219,403</td>
</tr>
</tbody>
</table>

\(^a\) UDFT-BP86 results. Basis sets and ECPs as in Tables 3, 5, and 7. \( \Delta g_{\text{SOC}(1\text{e})} \) terms with common gauge at center of mass. \( \Delta g_{11}, \Delta g_{22}, \) and \( \Delta g_{33} \) for NF\(_2\), \( \Delta g_0 \) and \( \Delta g_1 \) for the other compounds.
ROHF and MCSCF calculations of Engström et al. They found

Table 9. Effects of Basis Sets and Functionals on Computed $g$-Shift Components (ppm) for Phenoxyl Radicals

<table>
<thead>
<tr>
<th>basis</th>
<th>$\Delta g_{10}$</th>
<th>$\Delta g_{11}$</th>
<th>$\Delta g_{22}$</th>
<th>$\Delta g_{33}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenoxyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VWN, UDFT</td>
<td>DZVP$^a$</td>
<td>3136</td>
<td>-139</td>
<td>363</td>
</tr>
<tr>
<td>VWN, UDFT</td>
<td>DZVP</td>
<td>4429</td>
<td>-150</td>
<td>2145</td>
</tr>
<tr>
<td>VWN, UDFT</td>
<td>BII</td>
<td>4505</td>
<td>-85</td>
<td>2249</td>
</tr>
<tr>
<td>VWN, UDFT</td>
<td>BIII</td>
<td>4543</td>
<td>-83</td>
<td>2292</td>
</tr>
<tr>
<td>PP86, UDFT</td>
<td>BII</td>
<td>3388</td>
<td>-91</td>
<td>2125</td>
</tr>
<tr>
<td>PW91, UDFT</td>
<td>BII</td>
<td>3548</td>
<td>-89</td>
<td>2117</td>
</tr>
<tr>
<td>BP86, UDFT</td>
<td>DZVP$^a$</td>
<td>2333</td>
<td>-146</td>
<td>319</td>
</tr>
<tr>
<td>BP86, UDFT</td>
<td>DZVP</td>
<td>3355</td>
<td>-160</td>
<td>2031</td>
</tr>
<tr>
<td>BP86, UDFT</td>
<td>BII</td>
<td>3405</td>
<td>-91</td>
<td>2171</td>
</tr>
<tr>
<td>BP86, UDFT</td>
<td>BIII</td>
<td>3461</td>
<td>-85</td>
<td>2170</td>
</tr>
<tr>
<td>BP86, SOS-DFPT$^b$</td>
<td>BIII</td>
<td>2980</td>
<td>-85</td>
<td>2133</td>
</tr>
<tr>
<td>ROHF$^c$</td>
<td>cc-pVDZ</td>
<td>24200</td>
<td>150</td>
<td>5200</td>
</tr>
<tr>
<td>MCSCF$^d$</td>
<td>cc-pVDZ</td>
<td>2500</td>
<td>200</td>
<td>2400</td>
</tr>
<tr>
<td>t-Bu-substituted phenoxyl$^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VWN, UDFT</td>
<td>DZVP</td>
<td>2721</td>
<td>42</td>
<td>1834</td>
</tr>
<tr>
<td>BP86, UDFT</td>
<td>DZVP</td>
<td>2314</td>
<td>-4</td>
<td>1734</td>
</tr>
<tr>
<td>BP86, SOS-DFPT$^b$</td>
<td>DZVP</td>
<td>2093</td>
<td>-7</td>
<td>1721</td>
</tr>
<tr>
<td>exp.</td>
<td></td>
<td>2297</td>
<td>70</td>
<td>1960</td>
</tr>
<tr>
<td>tyrosyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VWN, UDFT</td>
<td>DZVP</td>
<td>4263</td>
<td>-167</td>
<td>2177</td>
</tr>
<tr>
<td>BP86, UDFT</td>
<td>DZVP$^a$</td>
<td>3264</td>
<td>-181</td>
<td>2064</td>
</tr>
<tr>
<td>BP86, SOS-DFPT$^b$</td>
<td>DZVP</td>
<td>2827</td>
<td>-195</td>
<td>2037</td>
</tr>
<tr>
<td>exp. (E. coli RNR$^{g}$)</td>
<td>DZVP</td>
<td>2670</td>
<td>-300</td>
<td>1900</td>
</tr>
<tr>
<td>exp. (S. typh. RNR$^{g}$)</td>
<td></td>
<td>2848 (±70)</td>
<td>-200</td>
<td>2000</td>
</tr>
<tr>
<td>exp. (N–Ac–L–TyrO$^{h}$)</td>
<td></td>
<td>3200 (±200)</td>
<td>-200</td>
<td>2000</td>
</tr>
</tbody>
</table>

$^a$ DFT results with IGLO gauge and AMFI approximation. $^b$ Without polarization functions on hydrogen. $^c$ Including correction term in Loc.1 approximation. $^d$ Results with common gauge at center of mass. $^e$ Only a limited number of digits were given. $^f$ Results for 2,4,6-tris-$t$-Bu-C$_6$H$_2$O.


Scheme 1. Three Phenoxyl Radicals Studied

![Scheme 1](image)

and $\Delta g_{33}$ components change relatively little in going from DZVP to the larger BII and BIII basis sets (this holds for both VWN and BP86 functionals). Only the DZVD basis, that is, omission of polarization p-functions on hydrogen, leads to a rather dramatic deterioration of the results, mainly for $\Delta g_{22}$. Closer inspection indicates that without the polarization functions, too much spin density is accumulated on the hydrogen atoms and withdrawn from the heavy atoms. In going from the local VWN to the gradient-corrected BP86 functional, the $g$-shifts decrease moderately but nonnegligibly. On the other hand, differences between different GGA functionals (BP86, PP86, PW91) are small. This is our general experience and the reason for concentrating mostly on one functional (BP86) throughout this work. An only modest dependence on the functional was also noted by Ziegler and co-workers, and similar conclusions pertain to NMR chemical shift calculations on main-group nuclei.

We may compare our results for the phenoxyl radical to the ROHF and MCSCF calculations of Engström et al. They found that electron correlation is extremely important for the description of the $g$-tensor of the phenoxyl radical. This may be seen from the dramatically overestimated $\Delta g_{22}$ and $\Delta g_{33}$ components at the ROHF level (Table 9). Much lower $g$-shifts were obtained at the MCSCF level (Table 9). Our DFT results (e.g., UDFT-IGLO with BP86 functional and BIII basis) are much closer to the MCSCF than to the ROHF data but give ~65% larger $\Delta g_{33}$ than the former.

The good agreement with the experimental result for the 2,4,6-tris-$t$-Bu-C$_6$H$_2$O radical has been taken as evidence for the good quality of the CASSCF wave function for the phenoxyl radical. While the substituted radical was too large to be studied at the MCSCF level, our DFT approach is easily applicable also to the larger system. Interestingly, the computed $g$-shifts are considerably reduced by the substitution (Table 9). In particular, $\Delta g_{33}$ is much lower. On the other hand, our computed results for the tyrosyl radical are much closer to those for the unsubstituted phenoxyl radical. tert-Butyl substituents in ortho position have obviously a rather significant effect on the spin density within the system (in particular on that for oxygen, which dominates the $g$-tensor; cf. below), but the amino acid moiety in para position of the tyrosyl radical oxygen atom affects the spin density distribution much less. Thus, while the free phenoxyl radical is not a very good model to study quantitatively the $g$-tensor of the 2,4,6-tris-$t$-Bu-C$_6$H$_2$O radical, it serves as a very good model for the biologically relevant tyrosyl system (as previously concluded from spin-density calculations). Notably, the present DFT approach reproduces rather accurately the experimental differences between the two substituted radicals. This suggests that substituent influences on the $g$-tensor in aromatic radicals may now be studied with good accuracy. We note in passing that, in contrast to the ring


protons, the neglect of polarization p-functions on the t-butyl hydrogens on the 2,4,6-tris-t-Bu-C₆H₄O radical has a negligible effect on the computed g-shifts.

In addition to our UDFT-IGLO results with various functionals and basis sets, Table 9 also includes SOS-DFPT results with the BP86 functional. As is well-known from NMR chemical shift calculations, the SOS-DFPT correction term reduces to some extent the paramagnetic contributions and thus the overall shift components.17,22,56 No experimental data are available to judge the performance of the different approaches for the free phenoxyl radical. For the 2,4,6-tris-t-Bu-C₆H₄O radical, the UDFT and SOS-DFPT results with the BP86 functional bracket the experimental value for Δg₃2, whereas Δg₂₂ is underestimated slightly in both calculations. The latter point is probably a basis set effect, cf. the basis set study for the free phenoxyl radical. For the 2,4,6-tris-t-Bu-C₆H₄O radical, the advantage of DFT is to treat large systems. Indeed, we are presently studying MCSCF wave functions of ref 54. The advantage of DFT is that the relatively low computational effort, and thus the possibility to treat large systems. Indeed, we are presently studying g-tensors for much larger radicals. This requires also a very efficient treatment of the spin–orbit operators, such as demonstrated in this work.

Less favorable performance of DFT was noted by PZ for g-tensors of transition metal complexes (a number of square pyramidal d¹ complexes were studied, see below) compared to Hartree–Fock calculations with GGA functionals. 57 For a number of 4d¹ and 5d¹ complexes. The agreement of our calculations with experiment is again not satisfactory, actually even somewhat worse than for those of PZ. This is probably due to some error compensation in the results of PZ, related to the incomplete treatment of the SO operators. The paramagnetic contributions to the nuclear shielding of 4d transition metal nuclei are known to be underestimated less dramatically by GGA functionals than in the cases of 3d metals (e.g., the slope for Rh shielding at the GIAO–BP86 level was found to be ~0.857,58). One might thus expect 4d systems to be less critical also for g-tensor calculations. This is not borne out by the limited set of data given in Table 11. More calculations on a larger set of more diverse 4d complexes will be needed to settle this question.

7. Separation of g-Tensors into Atomic Contributions

As already mentioned, our use of a superposition of effective atomic spin–orbit operators does also offer advantages in terms of analyses of g-tensors. In this way we obtain a particularly straightforward separation of the ΔgSO/OZ terms into atomic SO contributions. This is shown as an example for the phenoxyl radical in Table 12. We first note that the relative weights of ΔgSO/OZ(1e) and ΔgSO/OZ(2e) terms, as well as of SOO and SSO contributions to the latter, are essentially just as discussed above for CO²⁺ and H₂O⁺.

The atomic analysis is performed by carrying out a number of separate calculations (which employ the same Kohn–Sham wave function and thus do not require much extra computational effort), in which atomic mean-field SO operators are only used of ⁵⁷Fe, but similar observations apply to ⁵⁹Co.19) UDFT-GIAO calculations with GGA functionals gave slopes of ~0.6 in comparison with experiment, with one extreme outlier (ferrocene).57 This corresponds to a significant underestimate of the paramagnetic contributions to shielding. Bühler found that the slope could be improved to almost 1.0 by using hybrid functionals (B3LYP or B3PW91).58 In view of the close similarity of nuclear shielding and electronic g-tensor, we expect that the origin of the failure of the “pure” GGA functionals in the two cases is related (most likely, the usual functionals do not describe accurately local excitations at the metal59). Thus, the inclusion of Hartree–Fock exchange (and of the resulting coupling terms) should improve the performance also for the g-tensor. In the present version of our code we cannot include Hartree–Fock exchange. However, we are presently implementing a new program which will allow this to be done. Then more accurate calculations of g-tensors should also become possible for transition metal compounds.61 Until then, a simple multiplicative scaling of the SO contributions may be considered as a short-term improvement. This result contrasts somewhat with the conclusions of PZ, based on a less diverse set of complexes. PZ argued that a simple, additive constant shift (different for 3d, 4d, and 5d systems) might be used to correct the computed results.28 We expect less problems for complexes where the spin density is largely concentrated on the ligands. In fact, GGA functionals perform excellently for nuclear shieldings of ligand atoms in transition metal systems.9,10,11

Finally, Table 11 compares our results and those of PZ for a number of 4d¹ and 5d¹ complexes. The agreement of our calculations with experiment is again not satisfactory, actually even somewhat worse than for those of PZ. This is probably due to some error compensation in the results of PZ, related to the incomplete treatment of the SO operators. The paramagnetic contributions to the nuclear shielding of 4d transition metal nuclei are known to be underestimated less dramatically by GGA functionals than in the case of 3d metals (e.g., the slope for Rh shieldings at the GIAO–BP86 level was found to be ~0.857,58). One might thus expect 4d systems to be less critical also for g-tensor calculations. This is not borne out by the limited set of data given in Table 11. More calculations on a larger set of more diverse 4d complexes will be needed to settle this question.
Table 10. Comparison of Computed and Experimental g-Shift Tensor Components (ppt) for a Series of 3d Transition Metal Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>component</th>
<th>without $\Delta g_{SOOZ2e}$</th>
<th>with $\Delta g_{SOOZ2e}$</th>
<th>exp. lit (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiF$_3$</td>
<td>$\Delta g_0$</td>
<td>-1.8</td>
<td>-1.2</td>
<td>b(1)</td>
</tr>
<tr>
<td>Mn(CN)$_3$N$^-$</td>
<td>$\Delta g_0$</td>
<td>9.8</td>
<td>3.9</td>
<td>-3.3</td>
</tr>
<tr>
<td>Mn(CO)$_3$</td>
<td>$\Delta g_0$</td>
<td>-1.2</td>
<td>-0.9</td>
<td>f(1)</td>
</tr>
<tr>
<td>Fe(CO)$_3^+$</td>
<td>$\Delta g_0$</td>
<td>-0.6</td>
<td>-0.9</td>
<td>g(1)</td>
</tr>
<tr>
<td>ScO</td>
<td>$\Delta g_0$</td>
<td>-0.9</td>
<td>0.0</td>
<td>-0.5(3)</td>
</tr>
<tr>
<td>MnO</td>
<td>$\Delta g_0$</td>
<td>4.2</td>
<td>4.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Mn(CN)$_2$NO$^+$</td>
<td>$\Delta g_0$</td>
<td>36.3</td>
<td>17.9</td>
<td>28.8</td>
</tr>
<tr>
<td>Mn(CO)$_3$</td>
<td>$\Delta g_0$</td>
<td>42.6</td>
<td>22.6</td>
<td>40.7</td>
</tr>
<tr>
<td>Cu(acac)$_2$</td>
<td>$\Delta g_{zz}$</td>
<td>50.1</td>
<td>30.6</td>
<td>48.7</td>
</tr>
<tr>
<td>Cu(NO)$_3$</td>
<td>$\Delta g_{zz}$</td>
<td>45.1</td>
<td>30.2</td>
<td>49.9(5)</td>
</tr>
<tr>
<td>Cu(acac)$_2$</td>
<td>$\Delta g_{zz}$</td>
<td>49.3</td>
<td>31.0</td>
<td>49.9(5)</td>
</tr>
<tr>
<td>Ni(CO)$_3$H</td>
<td>$\Delta g_{zz}$</td>
<td>55.4</td>
<td>34.7</td>
<td>48.7</td>
</tr>
<tr>
<td>Fe(CO)$_3^+$</td>
<td>$\Delta g_{zz}$</td>
<td>65.0</td>
<td>39.8</td>
<td>65.1</td>
</tr>
<tr>
<td>Co(CO)$_4$</td>
<td>$\Delta g_{zz}$</td>
<td>89.3</td>
<td>48.7</td>
<td>81.0, 77.4</td>
</tr>
<tr>
<td>Cu(NO)$_3$</td>
<td>$\Delta g_{zz}$</td>
<td>137.5</td>
<td>79.3</td>
<td>126.7</td>
</tr>
<tr>
<td>Cu(acac)$_2$</td>
<td>$\Delta g_{zz}$</td>
<td>183.0</td>
<td>116.3</td>
<td>246.6(3)</td>
</tr>
</tbody>
</table>


...on specific atoms or sets of atoms. The sums of these contributions do in all cases studied correspond closely to the overall $\Delta g_{SOOZ2e}$ results, as they should. The analysis for the phenoxyl radical shows, as expected in this case, that SO coupling at the oxygen atom dominates the $\Delta g_{22}$ and $\Delta g_{33}$ components. The other atomic contributions are much smaller but not always negligible. Thus, for example, contributions from SO coupling at the ortho carbon atoms reduce $\Delta g_{33}$ but enhance $\Delta g_{22}$. We may go one step further and decompose also individual molecular orbital contributions into their atomic SO constituents. Table 12 shows this as an example for the in-plane $\pi_b$ HOMO. The coupling of the $\beta$-part of this MO (cf. Figure 3a) with the unoccupied $\beta$-part of the out-of-plane $\pi_b$ SOMO (Figure 3b) is known to dominate $\Delta g_{33}$ (contributions from several occupied MOs with $\alpha(C=O)$ bonding character dominate $\Delta g_{22}$). This is confirmed by the entry in Table 12. The further
Figure 2. Comparison of calculated and experimental g-shift tensor components (ppm) for 3d transition metal complexes (cf. Table 10).

Table 11. g-Shift Tensor Results (ppm) for Some Square Pyramidal 4d¹ and 5d¹ Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>ECP−SO</th>
<th>PZb</th>
<th>exp.c</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoOF₄⁻</td>
<td>−59</td>
<td>−51</td>
<td>−62</td>
</tr>
<tr>
<td>MoOCl₄⁻</td>
<td>+12</td>
<td>−38</td>
<td>+6</td>
</tr>
<tr>
<td>MoBr₂Cl₂</td>
<td>+119</td>
<td>−29</td>
<td>+142</td>
</tr>
<tr>
<td>MoNCl₂⁻</td>
<td>−35</td>
<td>−6</td>
<td>−47</td>
</tr>
<tr>
<td>WOCl₄⁻</td>
<td>−31</td>
<td>−120</td>
<td>−68</td>
</tr>
<tr>
<td>TcNFO⁻</td>
<td>−43</td>
<td>−15</td>
<td>−41</td>
</tr>
<tr>
<td>TcNCl₂⁺</td>
<td>+47</td>
<td>+8</td>
<td>+43</td>
</tr>
<tr>
<td>TcNB₂Cl⁺</td>
<td>+187</td>
<td>+64</td>
<td>+212</td>
</tr>
<tr>
<td>ReOF₄⁻</td>
<td>−123</td>
<td>−156</td>
<td>−132</td>
</tr>
<tr>
<td>ReOCl₂⁺</td>
<td>+106</td>
<td>−117</td>
<td>+80</td>
</tr>
<tr>
<td>ReOBr₂⁺</td>
<td>+253</td>
<td>−84</td>
<td>+257</td>
</tr>
<tr>
<td>ReNF₂⁺</td>
<td>−189</td>
<td>−57</td>
<td>−187</td>
</tr>
<tr>
<td>ReNCl₂⁺</td>
<td>+46</td>
<td>−7</td>
<td>+9</td>
</tr>
<tr>
<td>ReNBr₂⁺</td>
<td>+185</td>
<td>+40</td>
<td>+174</td>
</tr>
</tbody>
</table>

a This work, UDFT-BP86. Quasirelativistic ECP/UDFT calculations. b UDFT-GIAO, BP86 ref. 28. c Experimental data as compiled in ref 28.

atom decomposition of the HOMO contribution shows again clearly the dominance of oxygen SO coupling, but also the negative contributions from the ortho carbon atoms, which reduce the Δg₃₃ component.

While the dominance of oxygen SO coupling has been obvious in the previous example, Table 13 shows two examples, CrOF₄⁻ and CrOCl₂⁻, in which several atoms contribute nonnegligibly. We may first examine the atomic break-down of the total g-shift components. In both cases, SO coupling from the metal dominates the negative Δg₃₃. In contrast, halogen SO coupling contributes positively to Δg₂₃. While the negative metal contribution is larger and dominates in CrOF₄⁻, the halogen contribution in CrOCl₂⁻ dominates, and a relatively small, positive Δg₂₃ result (experimentally, this component is also small but negative, cf. Table 6).

MO analyses of the g-tensors for these types of C₄v-symmetrical d¹ complexes have already been discussed in detail,²⁸ and we refer the reader to that work for the MO notation. In Table 13, we go a step further and decompose the most important MO contributions into their atomic constituents. The above-mentioned compensation between metal and halogen SO coupling for Δg₃₃ arises in an interesting manner. Metal SO coupling contributes negatively via the SOMO but positively via the b₁ MO, and in the case of CrOCl₂⁻ also via the e MOs. Halogen SO coupling contributes positively through all three MOs. In contrast, metal SO coupling dominates Δg₂₃ mainly via the negative SOMO contribution. These results are just

Table 12. Break-Down of g-Shift Tensor (ppm) for the Phenoxy Radical

<table>
<thead>
<tr>
<th>Complex</th>
<th>Δg₁₁</th>
<th>Δg₂₂</th>
<th>Δg₃₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>41</td>
<td>−1</td>
<td>8178</td>
</tr>
<tr>
<td>C₃₃N(C₆H₅)</td>
<td>0</td>
<td>−1</td>
<td>123</td>
</tr>
<tr>
<td>C₃₃N(C₆H₅)</td>
<td>4</td>
<td>−5</td>
<td>620</td>
</tr>
<tr>
<td>C₃₃N(C₆H₅)</td>
<td>−5</td>
<td>−5</td>
<td>−24</td>
</tr>
<tr>
<td>C₃₃N(C₆H₅)</td>
<td>−1</td>
<td>−1</td>
<td>94</td>
</tr>
<tr>
<td>H (5x)</td>
<td>0</td>
<td>−1</td>
<td>1</td>
</tr>
<tr>
<td>ΔgSO/OZ</td>
<td>40</td>
<td>−14</td>
<td>7752</td>
</tr>
</tbody>
</table>

* UDFT-BP86 calculations with common gauge at center of mass, BIII basis, and AMFI approximation. b Spin−same-orbit contribution. c Spin−other-orbit contribution. D Atomic mean-field SO operators were employed only on the specified atoms in each case (see text).

Figure 3. Display of Kohn−Sham orbitals for the phenoxyl radical as isosurface (±0.1 au). (a) b₁-component of HOMO (b₁). (b) b₂-component of SOMO (b₂). Illustrative examples of the additional insight that is provided by the use of SO operators which are accurate and yet atomic in nature. Analyses of this type should become useful for a large variety of questions related to the interpretation of electronic g-tensors.

8. Conclusions

We have implemented and validated DFT calculations of the electronic g-tensor of EPR spectroscopy including all the relevant perturbation operators and IGLO gauge origins. The main advantage of the present approach lies in the treatment of spin−orbit coupling. To our knowledge, both the all-electron atomic mean-field approximation to the complete Breit−Pauli SO operators and the combination of quasirelativistic ECPs with SO-ECPs have been used here for the first time in g-tensor calculations. Both approximations provide an inexpensive but accurate way to include SO coupling. Agreement of the mean-field SO treatment with the full-blown explicit treatment of all
Table 13. Break-Down of $g$-Shift Tensor (ppt) for CrOX$_4^{-}$ ($X$ = F, Cl)\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>CrOF$_2^{-}$</th>
<th>CrOCI$_2^{-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta \xi$</td>
<td>$\Delta \eta$</td>
</tr>
<tr>
<td>Cr</td>
<td>-25</td>
<td>-21</td>
</tr>
<tr>
<td>X</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>-15</td>
<td>-22</td>
</tr>
<tr>
<td>total $\Delta g_{SO/OZ}$</td>
<td>-15</td>
<td>-22</td>
</tr>
</tbody>
</table>

atomic break-down of dominant MO contributions\textsuperscript{b}

SOMO (b$_2$, “d$_{x^2}$”)

<table>
<thead>
<tr>
<th></th>
<th>CrOF$_2^{-}$</th>
<th>CrOCI$_2^{-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>-34</td>
<td>-20</td>
</tr>
<tr>
<td>X</td>
<td>7</td>
<td>-1</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>-27</td>
<td>-21</td>
</tr>
</tbody>
</table>

$\pi$ (Cr$-$O) MOs (e)

<table>
<thead>
<tr>
<th></th>
<th>CrOF$_2^{-}$</th>
<th>CrOCI$_2^{-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>-3</td>
<td>0</td>
</tr>
<tr>
<td>X</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>-3</td>
<td>0</td>
</tr>
</tbody>
</table>

\textsuperscript{a} UDFT-BP86 results with BII basis, AMFI approximation, and common gauge at the center of mass. Cf. Table 6 for the IGLO results (and for a decomposition into first- and second-order terms). \textsuperscript{b} Atomic mean-field SO operators were employed only on the specified atoms in each case (see text). \textsuperscript{c} Cf. ref 28 for a more detailed discussion of the MO contributions.

In contrast to the good performance for main-group species, the results obtained for transition metal complexes are much less satisfactory. We agree with Patchkowski and Ziegler\textsuperscript{28} in attributing this less favorable performance for transition metal systems to deficiencies in the gradient-corrected functionals. The present results for a rather diverse set of 3d transition metal complexes indicate that the paramagnetic ($\Delta g_{SO/OZ}$) contributions are underestimated systematically. A simple multiplicative scaling of these terms improves the overall agreement with experiment but is certainly not satisfactory from a theoretical point of view. We have also pointed out that similar problems have been observed by Bühl et al. for NMR chemical shifts of transition-metal nuclei.\textsuperscript{57,58} In the latter case, the use of exchange-correlation functionals that include some exact, non-local exchange, enabled much more accurate calculations. We expect this to be the case also for $g$-tensor calculations on systems in which the spin density is mainly localized on a transition metal. We are thus presently implementing a code which will allow such hybrid functionals to be used also for the calculation of $g$-tensors.

A further potential source of errors stems from the first-order perturbation theoretical treatment of SO coupling. This may affect the results for systems with very heavy atoms. Therefore, our ongoing work involves also a two-component relativistic approach that covers SO coupling variationally. Despite the obvious need for further methodological improvements, the present approach should provide a very powerful tool to study electronic $g$-tensors in a large variety of areas ranging from materials research to biochemistry.

Acknowledgment. We thank Drs. H. Stoll (Stuttgart), H.-J. Flad (Leipzig), and P. Pyykkö (Helsinki) for helpful discussions. V.G.M. and O.L.M. gratefully acknowledge financial support from the Slovak Grant Agency VEGA (Grant No. 2/7203/00) and from the COST chemistry program (Project D9/0002/097), and they thank the Computing Center of the Slovak Academy of Sciences for computational resources. J.V. is on leave from the University of Oulu, Department of Physical Sciences, Oulu, Finland, and has been supported by the Marie Curie program (Contract No. ERBFMIBCT982911) of the European Commission. Further support has been provided within the Graduiertenkolleg “Moderne Methoden der magnetischen Resonanz” in Stuttgart (scholarship to B.S. and travel costs), by Deutsche Forschungsgemeinschaft (Heisenberg scholarship to M.K. and Schwerpunktprogramm “Relativistische Effekte in der Chemie und Physik schwerer Elemente”), and by the Fonds der Chemischen Industrie.

Supporting Information Available: Tables S1–S5 give optimized Cartesian coordinates for the phenoxy1, 2,4,6-tris-t-Bu-C$_6$H$_2$O and tyrosyl radicals, as well as for Cu(acac)$_2$ and Cu(NO$_3$)$_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org. 

JA000984S
7 Mechanisms of EPR Hyperfine Coupling in Transition Metal Complexes

Introduction

The density-functional and coupled-cluster study of EPR hyperfine coupling in 21 transition metal complexes (Chapter 5) has not only validated the existing computational methods but also aroused the curiosity of the author to understand the underlying mechanisms of the hyperfine interactions. The problematic performance of DFT for some of the HFCCs has lead us to an analysis of orbital contributions to the hyperfine coupling. Both the striking order observed in the core-polarization contributions and the large variability in the valence-shell polarization became a motivation for a detailed study of mechanisms of EPR hyperfine coupling that is presented in the following paper.

The latter work concentrates on the qualitative aspects of hyperfine coupling in transition metal compounds and attempts to provide a detailed understanding of the different spin polarization mechanisms. The interpretations are based on the molecular DFT calculations of Chapter 5 but are augmented by detailed UHF and ROHF analyses of the relevant exchange, Coulomb, and one-electron integrals for some atomic systems. The author of this thesis performed all of the calculations included in the study, most of the interpretational work, and contributed significantly to the preparation of the manuscript.

Results
The detailed analysis of the spin polarization in atomic systems has shown that the contributions from the metal 2s and 3s orbitals to $A_{\text{iso}}$ and from the metal 2p and 3p orbitals to $A_{\text{dip}}$ have opposite signs due to the orthogonality requirement between orbitals of the same angular momentum. While spin polarization enhances the exchange interaction of the 2s and 2p shells with the singly occupied orbitals, the 3s and 3p orbitals are forced to lose some of their exchange to stay orthogonal to their respective penultimate shell. The core-shell spin-polarization contributions to the isotropic hyperfine couplings have been found to be proportional to the spin population in the metal 3d orbitals and relatively independent of other details of the bonding. The valence-shell spin-polarization, however, depends strongly on the electronic structure of the system. Particularly large valence-shell spin-polarization contributions to both isotropic and dipolar coupling constants are found for systems in which the SOMO overlaps significantly with certain high-lying doubly occupied valence orbitals. These are the same cases in which our previous study found dramatic spin contamination effects to plague unrestricted Kohn-Sham calculations with hybrid functionals. In contrast to the assumptions implicit in many qualitative and quantitative schemes in current use by experimentalists, both core- and valence-shell spin polarization may significantly contribute to transition-metal dipolar coupling constants.

Conclusions and outlook

The present work provides basic insight into the mechanisms of spin polarization in 3d transition metal systems. The results obtained may also be used to pinpoint the weaknesses of certain theoretical approaches for the calculation of HFCCs and hopefully also to develop improved methods. It is the wish of the author to extend the study undertaken in this paper to 4d and 5d systems, including a detailed analysis of valence-shell spin polarization, and of the mechanisms that transfer the spin density to the ligands. In the author’s opinion, this study illustrates that the combination of the DFT approach and qualitative molecular-orbital thinking is a very powerful analytical tool that once again emphasises the great potential of one-electron approximations for understanding chemistry.
Mechanisms of EPR Hyperfine Coupling in Transition Metal Complexes

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Received June 9, 2000. Revised Manuscript Received August 25, 2000

Abstract: A detailed quantum chemical analysis of the underlying principles of hyperfine coupling in 3d transition metal complexes has been carried out. The explicit evaluation of one- and two-electron integrals for some atomic systems has been used to understand the spin polarization of the core shells. While spin polarization enhances the exchange interaction of the 2s and 2p shells with the singly occupied orbitals, the opposite spin polarization of the 3s and 3p shells arises from the required orthogonality to the 2s and 2p shells, respectively.

1. Introduction

The early history of EPR spectroscopy is closely connected to the study of transition metal complexes. Already during the 1950s, the concept of spin polarization was used in the discussion of the hyperfine coupling constants (HFCs) to transition metal nuclei (cf. section 2). Transition metal systems have thus been adequately represented in early, qualitative theoretical studies of EPR hyperfine couplings. In contrast, modern applications of quantum chemical methods to calculate hyperfine couplings more quantitatively have largely concentrated on organic radicals, due to the various practical difficulties presented by the more complicated transition metal systems.

We recently reported a systematic study, in which various density functional theory (DFT) and coupled cluster approaches were critically compared in calculations of hyperfine coupling tensors for a representative set of 21 3d transition metal complexes. Complexes with significant metal 4s orbital contributions to the singly occupied molecular orbital(s) (SOMO) may be treated adequately with essentially any of the state-of-the-art density functionals. In contrast, it is much more difficult to reproduce experimentally derived HFC tensors in systems in which the spin density at the metal arises largely from spin polarization. Gradient-corrected functionals tend to underestimate the important spin polarization of the 2s and 3s core orbitals. While admixture of exact exchange in “hybrid functionals” helps to enhance the core-shell spin polarization in some cases, the related spin contamination may deteriorate significantly the quality of the results in other systems. Overall, no functional was found to perform satisfactorily for all systems, and for some systems, none of the functionals studied was acceptable. The general quantitative study of HFC tensors for transition metal systems remains thus a challenge to quantum chemistry.

A better understanding of the detailed relation between electronic structure and hyperfine couplings should aid in looking for improved approaches for their calculation. Apart from the validation of existing methods, the detailed study of 21 complexes has provided us with considerable qualitative insight into the mechanisms of spin polarization in transition metal systems. As expected, the underlying interactions can be much more variable than those in organic radicals. For example, not only s-type but also p- and d-type metal orbitals may be

10.1021/ja002062v CCC: $19.00 © 2000 American Chemical Society Published on Web 11/15/2000
involved, and both core and valence shells of the transition metal may be polarized significantly. The present work concentrates on these more qualitative aspects of hyperfine coupling in transition metal compounds and attempts to provide a detailed understanding of the different spin polarization mechanisms. Our interpretations are based on the molecular DFT calculations of ref 11 but will be augmented by detailed UHF and ROHF analyses of the relevant exchange, Coulomb, and one-electron integrals for some atomic systems. The geometrical and electronic structures of the molecular complexes studied, as well as the relevant available experimental data, have already been discussed. Therefore, with the exception of few systems that will be discussed in more detail, the reader is referred to ref 11 for further information.

2. The Spin Polarization Model: Previous Work

The general theoretical background of EPR hyperfine coupling is documented in many textbooks. The isotropic hyperfine coupling is directly proportional to the spin density at the point of the corresponding nucleus (\(\rho^0\)), in the following abbreviated as \(\rho_0\). In traditional interpretations, \(\rho_0\) is frequently approximated by the density of the singly occupied orbital(s). However, for the majority of systems studied by EPR spectroscopy, this simple approach is not sufficient. The unpaired electron, by virtue of its different interactions with electrons of different spin, spin-polarizes the electron distribution in the closed shells. This process can add significant spin density at the position of the nuclei. The inadequacy of the spin-restricted theory of the hyperfine interaction has been noted since 1933 for various main-group atoms. In the 1950s, the spin polarization model turned out to be very important for the early qualitative interpretation of EPR spectra for the transition metal ions. In many of these, the unpaired electrons occupy metal d-type orbitals. Although these orbitals have a node at the nucleus, substantial isotropic hyperfine splittings from metal nuclei were observed. Abrahâm et al. suggested that the isotropic hyperfine splitting in Mn\(^{3+}\) resulted from the spin polarization of the outermost occupied core shell (3s in the case of 3d metal ions).

Later, Watson and Freeman showed by UHF calculations for several 3d ions that the polarized 2s shell contributes even more to the hyperfine coupling than the outermost 3s shell, but with the opposite (negative) sign. Polarization of the 1s orbital provided also a negative, albeit very small, spin density at the nucleus. It was concluded that in the 1s and 2s shells, which exhibit radial density maxima at much smaller radii than the 3d orbitals (cf. Figure 1), the \(\alpha\)-spin electrons are “attracted” outward, leaving a region of negative spin density near the nucleus (similar arguments have been used to describe the core polarization in 4d metal complexes). The usual argument given is that exchange reduces the electron repulsion between 2s and the 3d\(^{1}\) SOMO and thus allows these electrons to get closer. This would correspond to an “effective attraction” of like-spin electrons. However, what happens with the 3s orbital? All of its radial maxima are also located closer to the nucleus than the 3d radial maximum (cf. Figure 1). Nevertheless, the 3s shell is polarized in the direction opposite from the 1s and 2s orbitals, as if the 3s orbital were “repelled” from the 3d-type SOMO. Watson and Freeman interpreted this as a result of the large overlap between 3s and 3d shells, leading to “competing tendencies” in the spin polarization. We will show below that the requirement of orthogonality between 2s and 3s shells is responsible for these seemingly paradoxical observations.

In main-group chemistry, spin polarization dominates the hyperfine couplings for some 2p atoms and ions, for some small \(\pi\)-radicals (e.g., NO, CO\(^+\), \(\text{H}_2\text{O}\)), and for the larger class of organic planar \(\pi\)-radicals. In these cases, the spin polarization of the 1s and 2s orbitals is known to transfer spin density to the nuclei. Just as for transition metal ions, spin polarization of the valence orbitals contributes with a positive sign to \(\rho_0\), spin polarization of the core (1s) orbitals with a negative sign.

Unlike for transition metals, the positive outer-shell contributions dominate, providing an overall positive \(\rho_0\). The traditional interpretation of these observations is analogous to the model of Watson and Freeman. The \(\alpha\)-component of the 1s orbital is attracted outward, leaving negative spin density at the nucleus. The 2s orbital, which has its outermost maximum at slightly larger radius than 2p (Figure 2), is attracted inward and thus provides more \(\alpha\)-spin density at the nucleus. This “exchange attraction” of electrons with the same spin is often viewed as a manifestation of Hund’s rule of maximum multiplicity.

In the past, the concept of spin polarization has been used exclusively to rationalize isotropic hyperfine couplings. However, recent theoretical work shows that dipolar hyperfine coupling in transition metal systems may also be influenced significantly by spin polarization. In 3d complexes, large contributions to the metal dipolar coupling may come from the

![Figure 1. ROHF radial distribution functions \(\langle R_{d}(r) \rangle^2 \) for Mn\(^{3+}\).](http://example.com/figure1.png)
contamination is typically very small.\textsuperscript{11} Calculations and analyses of isotropic hyperfine coupling constants (at the Hartree--Fock level) were done with the Gaussian94 program.\textsuperscript{24} Applying the CUBIC program option, the values of the individual orbitals at the transition metal nuclei have been determined and they were used for the analysis of the contributions to $\sigma_{\text{tot}}$. DFT calculations of the dipolar hyperfine coupling constants have additionally been carried out with a modified version of the deMon-EPR code,\textsuperscript{10,25} where a routine for the analysis of the orbital contributions to $A_{\text{dip}}$ has been implemented.

The medium-sized (15s11p6d)/[9s7p4d] metal basis sets constructed in ref 11 (based on the work of Schäfer et al.)\textsuperscript{26} were used together with basis sets BIII of Kutzelnigg et al. (also known as IGLO-III\textsuperscript{27}) for main-group atoms. In the Gaussian94 DFT calculations, the default integration grids (int = finegrid option)\textsuperscript{28} of the program have been used. In deMon calculations, additional auxiliary basis sets (5,5,5,5) for the metal and (5,2,5,2) for the ligand have been used to fit the density and the exchange-correlation potential (in this case, an extra iteration without fit of the potential and with extended grid was carried out after SCF convergence). For the numerical integration in deMon, we have employed a nonrandom FINE angular grid with 128 radial shells.\textsuperscript{10,28}

**Hartree--Fock Analysis of One- and Two-Electron Integrals.** The total energy corresponding to a Hartree--Fock wave function may be written as\textsuperscript{29}

$$E_0 = \sum_{\alpha} h_i^\alpha + \sum_{\beta} h_i^\beta + \frac{1}{2} \sum_{\alpha,\beta} \left( J_{ij}^\alpha - K_{ij}^\alpha \right) + \frac{1}{2} \sum_{\alpha,\beta} \left( J_{ij}^\beta - K_{ij}^\beta \right) + \sum_{\alpha,\beta} f_{\alpha\beta}^\alpha$$  \hspace{1cm} (1)

with $\alpha$ and $\beta$ denoting spin.

The one-electron term

$$h_i^\alpha = \int d\mathbf{r} |\psi_i^\alpha(\mathbf{r})|^2 \left( -\frac{1}{2} \nabla^2 - \sum_{A} Z_A \right) \psi_i^\alpha(\mathbf{r})$$  \hspace{1cm} (2)

represents the average kinetic and nuclear-attraction energy of an electron described by the orbital $\psi_i^\alpha(\mathbf{r})$; the two-electron Coulomb integral

$$J_{ij} = \langle i | j \rangle = \int d\mathbf{r}_i d\mathbf{r}_j |\psi_i(\mathbf{r}_i)|^2 |\psi_j(\mathbf{r}_j)|^2$$  \hspace{1cm} (3)

expresses the classical Coulomb repulsion between the charge

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**Calculations and MO Analyses of HFCCs.** In the following discussion, we will neglect (spin--orbit or scalar) relativistic corrections to the HFCCs (which have been estimated in ref 11). The selection of experimental data for most of the systems used here, and the conversion between different representations of HFCCs, have been summarized in our previous work.\textsuperscript{11} The computed and experimental molecular structures used are also those described in ref 11. We will concentrate on all-electron unrestricted Kohn--Sham calculations, mainly on results obtained with the gradient-corrected BP86\textsuperscript{23} functional. This “pure” generalized gradient approximation has the advantage that spin-polarized 2p and 3p orbitals. This viewpoint will be strengthened and extended to valence-shell contributions by the present work. Note that, for magnetic nuclei in an electronic spin-polarized 2p and 3p orbitals. This viewpoint will be strengthened and extended to valence-shell contributions by the present work. Note that, for magnetic nuclei in an electronic spin-polarized 2p and 3p orbitals. This viewpoint will be strengthened and extended to valence-shell contributions by the present work. Note that, for magnetic nuclei in an electronic spin-polarized 2p and 3p orbitals. This viewpoint will be strengthened and extended to valence-shell contributions by the present work. Note that, for magnetic nuclei in an electronic spin-polarized 2p and 3p orbitals. This viewpoint will be strengthened and extended to valence-shell contributions by the present work. Note that, for magnetic nuclei in an electronic spin-polarized 2p and 3p orbitals. This viewpoint will be strengthened and extended to valence-shell contributions by the present work.

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**References**


Table 1. Spin Densities at the Metal Nuclei (au) for a Series of Manganese Complexes

<table>
<thead>
<tr>
<th>molecule</th>
<th>1s</th>
<th>2s</th>
<th>3s</th>
<th>VS</th>
<th>SOMO</th>
<th>total</th>
<th>exp</th>
<th>3s/2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>6[Mn(CO)3]</td>
<td>0.00</td>
<td>-0.18</td>
<td>0.09</td>
<td>0.04</td>
<td>0.06</td>
<td>0.00</td>
<td>0.00...0.01</td>
<td>-0.50</td>
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<tr>
<td>6MnO</td>
<td>0.01</td>
<td>-0.33</td>
<td>0.18</td>
<td>-0.58</td>
<td>2.54</td>
<td>1.82</td>
<td>1.46</td>
<td>-0.55</td>
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<tr>
<td>7[Mn(CN)3]N</td>
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<td>-0.39</td>
<td>0.20</td>
<td>0.04</td>
<td>0.00</td>
<td>-0.15</td>
<td>-0.25</td>
<td>-0.51</td>
</tr>
<tr>
<td>7[Mn(CN)3]NO</td>
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<td>-0.50</td>
<td>0.24</td>
<td>0.13</td>
<td>0.00</td>
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<td>-0.20</td>
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<td>3.56</td>
<td>2.39</td>
<td>2.17</td>
<td>-0.46</td>
</tr>
<tr>
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<td>-1.60</td>
<td>0.71</td>
<td>0.46</td>
<td>0.00</td>
<td>-0.45</td>
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<td>-0.44</td>
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<td>2.45</td>
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<tr>
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<td>0.76</td>
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<td>5.30</td>
<td>4.31</td>
<td>4.12</td>
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<td>0.79</td>
<td>0.00</td>
<td>0.00</td>
<td>-1.07</td>
<td>-0.76...-1.24'</td>
<td>-0.43</td>
</tr>
</tbody>
</table>

\[ a \] DFT results with the BP86 functional. \[ b \] Contributions from the core-shell spin polarization (1s,2s,3s), valence-shell spin polarization (VS), and singly occupied orbital(s) (SOMO). \[ c \] From ref 11, unless stated otherwise. \[ d \] Kasai, P. H. Acc. Chem. Res. 1971, 4, 329. Ar-matrix isolation. \[ e \] Values obtained in different host crystals; see ref 1.

Table 2. Spin Densities at the Metal Nuclei (au) for a Series of First-Row Transition Metal Complexes

<table>
<thead>
<tr>
<th>molecule</th>
<th>1s</th>
<th>2s</th>
<th>3s</th>
<th>VS</th>
<th>SOMO</th>
<th>total</th>
<th>expr</th>
<th>3s/2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO</td>
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<td>-0.24</td>
<td>0.02</td>
<td>-0.12</td>
<td>2.31</td>
<td>1.99</td>
<td>1.91</td>
<td>-0.08</td>
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<tr>
<td>TiF</td>
<td>0.01</td>
<td>-0.17</td>
<td>0.03</td>
<td>-0.09</td>
<td>1.07</td>
<td>0.86</td>
<td>0.70...0.73</td>
<td>-0.18</td>
</tr>
<tr>
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<td>0.07</td>
<td>-0.27</td>
<td>2.87</td>
<td>2.37</td>
<td>2.23</td>
<td>-0.21</td>
</tr>
<tr>
<td>Cr+</td>
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<td>-1.38</td>
<td>0.42</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.97</td>
<td>-0.30</td>
<td></td>
</tr>
<tr>
<td>[Cr(CO)6]3+</td>
<td>-0.01</td>
<td>-1.20</td>
<td>0.39</td>
<td>0.35</td>
<td>0.00</td>
<td>-0.47</td>
<td>-0.82</td>
<td>-0.33</td>
</tr>
<tr>
<td>Fe+</td>
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<td>-2.30</td>
<td>1.19</td>
<td>0.00</td>
<td>0.00</td>
<td>-1.14</td>
<td>-0.81...-1.05</td>
<td>-0.52</td>
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<tr>
<td>[Fe(CO)5]2+</td>
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<td>-0.33</td>
<td>0.19</td>
<td>0.05</td>
<td>0.10</td>
<td>0.00</td>
<td>-0.02</td>
<td>-0.58</td>
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<tr>
<td>[Co(CO)4]2+</td>
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<td>-0.38</td>
<td>0.23</td>
<td>0.05</td>
<td>0.10</td>
<td>0.00</td>
<td>-0.05</td>
<td>-0.61</td>
</tr>
<tr>
<td>[Ni(CO)4]</td>
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<td>-0.18</td>
<td>0.12</td>
<td>0.00</td>
<td>0.00</td>
<td>-0.06</td>
<td>-0.02</td>
<td>-0.67</td>
</tr>
</tbody>
</table>

\[ a \] DFT results with the BP86 functional. \[ b \] Contributions from the core-shell spin polarization (1s,2s,3s), valence-shell spin polarization (VS), and singly occupied orbital(s) (SOMO). \[ c \] From ref 11, unless stated otherwise. \[ d \] Values obtained in different host crystals; see ref 1.

Below we refer to the sum of all Coulomb integrals from eq 1 as the total Coulomb energy \( E_C \) and to the sum of all exchange integrals from eq 1 as the total (negative) exchange energy \( E_X \). Note that the summations in eq 1 are not restricted to pairs of different spin orbitals. Therefore, the (unphysical) electrostatic interaction of an electron with itself is accounted for in the Coulomb part and again subtracted in the exchange part (ref 32 p 180). This allows a unique orbital breakdown of the total electron repulsion energy into exchange and Coulomb parts. The Coulomb part may be interpreted as a classical electrostatical energy of a charge cloud of density \( \rho(r) \), whereas the exchange part includes all nonclassical effects, (ref 32, pp 34 and 39).

4. Analysis of Contributions to \( \rho_S \)

Table 1 gives a breakdown of the DFT results for the spin density at the metal nucleus into MO contributions in a series of manganese complexes (and in three atomic systems).
This is seen best when comparing the isoelectronic high-spin negative when moving toward the right end of the 3d series. It becomes more polarization of the 3s orbital with increasing nuclear charge. (s) from the SOMO(s) is(are) also given (for cases such as MnH which do not provide the same analysis for other 3d complexes. In addition to the 1s, 2s, and 3s core contributions (i.e., contributions from MOs with predominantly metal core character), we summarize under “valence” contributions arising from the spin polarization of the doubly occupied valence MOs. The direct contribution- (subscripts U and R will indicate unrestricted or restricted contributions, but also to the absolute value of the total range of conditions (out-of-plane bending) has also been reported.

Figure 3. Correlation between Mulliken gross d-orbital spin populations and core-shell spin polarization for a series of manganese complexes. BP86 results.

2 provides the same analysis for other 3d complexes. In addition to the 1s, 2s, and 3s core contributions (i.e., contributions from MOs with predominantly metal core character), we summarize under “valence” contributions arising from the spin polarization of the doubly occupied valence MOs. The direct contribution(s) from the SOMO(s) is(are) also given (for cases such as MnH or MnF₂, where more than one SOMO possesses s-character, their contributions have been summed up). Spin densities derived from experimental hyperfine coupling constants¹¹ are included for comparison.

While contributions from valence-shell spin polarization vary in both their signs and magnitudes, the core contributions depend much less on the detailed bonding situation (compare, e.g., [Mn(CN)₄]²⁻ and MnF₂).³⁴ The negative 2s contributions dominate, whereas the 3s contributions are smaller and positive. The 1s contributions are very small. Both 2s and 3s contributions increase with increasing spin multiplicity of the system. However, the ratio between 3s and 2s (3s/2s ratio in Tables 1 and 2) remains close to −0.5 for all Mn complexes (Table 1). A more detailed analysis indicates that both the 2s and 3s contributions exhibit a remarkable proportionality to the total 3d spin population (Figure 3). Neither the specific bonding situation nor the spin population of the metal 4s orbitals influence the 2s and 3s contributions appreciably. For example, we may compare the 2s and 3s contributions to Rₚₘ for the ⁶Mn atom (−1.78 and 0.78 au), the ⁵Mn⁺ cation (−1.79 and 0.76 au), and the ⁶Mn⁺⁺ cation (−1.85 and 0.79 au).

Interestingly, the 3s/2s ratio is influenced more by nuclear charge than by anything else (Tables 1 and 2). It becomes more negative when moving toward the right end of the 3d series. This is seen best when comparing the isoelectronic high-spin d⁶ ions ⁵Cr³⁺, ⁵Mn²⁺, and ⁴Fe³⁺, for which the 3s/2s ratio is computed to be −0.30, −0.43, and −0.52, respectively. Intuitively, it is not clear whether this is just a consequence of a change in the relative magnitudes of the (spin-averaged) 3s and 2s orbitals at the nucleus or of an increasing spin polarization of the 3s orbital with increasing nuclear charge. As will be shown below, the latter interpretation is to be preferred. In the following, the spatial parts of the spin—orbitals ψ₂(r)(α(ω), ψ₂(r)(β(ω), ψ₃(r)(α(ω), and ψ₃(r)(β(ω)) will be abbreviated as 2s(r), 2p(r), 3s(r), and 2p(r), respectively (subscripts U and R will indicate unrestricted or restricted orbitals). For s-type orbitals, the angular part of the wave function is constant and equal to 1. Therefore, we will in the following refer to the radial wave functions only (hence, the scalar argument r is used, rather than the vector r). A given pair of spin-polarized orbitals 2s(α) and 2s(β) contributes to ρₚ like (2s(α)(0))² − (2s(β)(0))². The function (2s(α)(r))² − (2s(β)(r))² may be divided into two parts corresponding to (i) the polarization of the 2s orbital and (ii) the polarization of the 2p orbital, relative to the corresponding orbitals in the restricted (Hartree—Fock or Kohn—Sham) calculation. We may thus expand the function as

\[
(2s(α)(r))² - (2s(β)(r))² = (2s(α)(r))² + (2s(β)(r))² - 2s(α)(r)\cdot 2s(β)(r) = 4s(α)(r)\cdot 4s(β)(r)
\]

If we denote [2s(α)(r) − 2s(β)(r)] as Δ2s and [2s(α)(r) + 2s(β)(r)] as Δ2p, eq 6 may be rewritten as

\[
(2s(α)(r))² - (2s(β)(r))² = 2s(α)(r)\cdot (Δ2s + Δ2p) - Δ2s²(r)
\]

Both Δ2s(r) and Δ2p(0) are much smaller than 2s(r). The quadratic terms (Δ2s²(r), Δ2p²(r)) may therefore be neglected. Furthermore, to a large extent (Δ2s²(r)) is compensated by (−Δ2p²(r)) (cf. section 5). The left side of eq 7 may thus be approximated as

\[
(2s(α)(r))² - (2s(β)(r))² ≈ 2s(α)(r)\cdot (Δ2s + Δ2p) - Δ2s²(r)
\]

Analogously we obtain for the contribution from the 3s orbitals

\[
(3s(α)(r))² - (3s(β)(r))² ≈ 2s(α)(r)\cdot (Δ3s + Δ3p) - Δ3s²(r)
\]

The ratio between the 3s and 2s orbital contributions is thus to a good approximation

\[
\frac{(3s(α)(r))² - (3s(β)(r))²}{(2s(α)(r))² - (2s(β)(r))²} ≈ \frac{3s(α)(r)\cdot Δ3s(r) - Δ3p(r)}{2s(α)(r)\cdot Δ2s(r) - Δ2p(r)}
\]

Each of the orbital contributions to ρₚ seems proportional to the difference between the restricted and unrestricted orbitals, but also to the absolute value of the restricted orbital. As a consequence, the much larger value of the 2s orbital at the nucleus results in the larger 2s orbital contribution to ρₚ(0), although Δ3s(0) ≈ Δ3p(0) > Δ2s(0) − Δ2p(0). The ratio 3s(0)/2s(0) changes only slightly throughout the 3d series: for Cr⁺, Mn⁺⁺, and Fe³⁺, we obtain the ratios −0.373, −0.377, and −0.383, respectively (BP86 results). In contrast, Δ3s(0) − Δ3p(0)/Δ2s(0) − Δ2p(0) changes from −0.821 for Cr⁺ through −1.138 for Mn⁺⁺, to −1.348 for Fe³⁺ (extracted from ROBP86 and UBP86 results). An interpretation of this trend is given in section 5.

While the valence-shell spin polarization contributions to ρₚ appear to be irregular at first sight, we find a relation between their sign and the character of the SOMO: The valence contribution to ρₚ is positive only when there is no metal 4s admixture into the SOMO (e.g., in ⁶Mn⁺, ⁴[Mn(CN)₄]²⁻, ⁴[Cr(CO)₅]⁺) or when the admixture is very small (³[Cr(CO)₅]), ³[Fe(CO)₅]⁺). In the presence of significant metal 4s contribu-
the associated differences between the UHF and ROHF distributions. The area confined between $[\psi_{3s}(r)]^2 - [\psi_{3p}(r)]^2$ and the $x$ axis may be interpreted as a measure of spin-density redistribution within a given spin-orbital, due to spin polarization. We find that (a) in areas where the spin polarization increases the magnitude of the $\alpha$ spin-orbital, the magnitude of the corresponding $\beta$ spin-orbital is decreased and vice versa; (b) close to the nucleus (within $\sim 0.3$ au), the spin density of the $2\sigma$ orbital decreases whereas that of the $3\sigma$ orbital increases (see Figure 4a,c). The same holds for the relation between the $2\sigma$ and $3\sigma$ curves. Furthermore, the $2\pi$ and $3\pi$ curves, as well as the $2\pi$ and $3\pi$ curves, exhibit the same kind of complementarity in the core region (cf. Figure 4b,d). This suggests that the relation between the $2s$ and $3s$ contributions to $\rho_{\text{core}}$, in particular their opposite sign (as well as the relation between $2p$ and $3p$ contributions to the dipolar coupling, cf. section 7), is due to the orthogonality required between the orbitals of the M and L shells.

To gain deeper insight into this relation, we examine in Table 4 the influence of spin polarization on the values of two-electron integrals between the SOMO(s) and the (spin-polarized) doubly occupied orbitals. We discuss first the exchange integrals. Each of them has been calculated (a) for both electrons occupying ROHF orbitals, (b) for the unpaired electron in a ROHF orbital and the “paired” electron in a UHF orbital, and (c) for both electrons in spin-relaxed (unrestricted) orbitals. This allows us to compare the energy gain/loss due to the spin polarization of the doubly occupied orbital and the effect of the relaxation (contraction) of the SOMO. The spin polarization of the $2s$ and $2p$ orbitals increases their exchange interaction with the SOMO, and the SOMO relaxation enhances this interaction further, so that the exchange stabilization may be understood as a driving force of $2s$ and $2p$ spin polarization. Exchange stabilization correlates with an increase in the overlap of the radial wave functions (Table 4, Figure 4a,b). In the following, we will refer to this type of overlap integral as radial overlap, as opposed to the more common overlap integral defined in eq 5. The exchange of the $2s$ or $3p$ orbitals with the $3d$ SOMO is decreased by core-shell spin polarization and is accompanied by a decrease in the radial overlap (Table 4). Relaxation of the SOMO recovers only part of the radial overlap and of the exchange interaction. Obviously, the redistribution of spin density does not enhance the exchange interaction with the SOMO for all orbitals.

This may be not too surprising, as not only exchange with the SOMO but also Coulomb repulsion with the SOMO, exchange and Coulomb repulsion with the other electrons, and electron–nuclear attraction and kinetic energy change upon going from the ROHF to the UHF wave function. Indeed, the absolute value of the exchange energy is roughly 1 order of magnitude smaller than these other terms. Note, also, that changes in the exchange and Coulomb interactions for the $\alpha$ spin–orbital are partly compensated by the corresponding, complementary changes in the $\beta$ component (Table 4). Spin polarizations of individual orbitals are obviously not independent processes.

What is the driving force for the spin polarization of the $3s$ (and $3p$) orbitals? To understand this we have to be aware that the optimized orbitals for an atom have to be orthogonal. This may be realized (a) by the spin parts, (b) by the angular parts, or (c) by the radial parts of the wave functions. For two $s$-type $\alpha$ spin–orbitals, condition $c$ applies; i.e., the radial functions have to be orthogonal, both for the ROHF and UHF wave functions. In other words, the area between the function $f =...
2s\((r) 3s\((r) r^2\) and the x axis in regions where \(f\) is positive has to be equal to the area in regions where \(f\) is negative. This is demonstrated in Figure 5 for the spin-restricted case. If we now, for example, allow the 2s orbital to be polarized (decontracted to larger \(r\), cf. Figure 4a), the negative area under \(f\) decreases, whereas the positive area increases. The orthonormality between 2s and 3s has been lost. To recover it, the polarization of the 3s orbital must again enhance the negative area and reduce the positive area; i.e., it has to contract. Changes of the 2s and 3s spin–orbitals behave analogously, with opposite directions. The same conditions apply to the 2p and 3p pairs; i.e., their radial functions must also remain orthogonal. This orthogonality does not hold strictly for molecular systems. However, as the nature of the core orbitals does not change much in molecules, we expect that the same mechanisms apply (see further below).

From this we conclude that the 2s orbital is spin-polarized to enhance the exchange interaction with the SOMO. The 3s orbital has to stay orthogonal on 2s, even if this means a reduced exchange interaction with the SOMO. Why does the spin polarization of the 2s orbital dominate? The reason is that the energy gain in the exchange interaction between 2s and the 3d SOMO is much larger than the energy loss due to the exchange interaction between the 3s and the 3d SOMO (Table 4). If we were to optimize the exchange between 3s and the SOMO, the reduced exchange interaction between 2s and the SOMO would overcompensate the gain. This is best illustrated in Figure 4. 2s\(u\) is well separated from 3d and clearly enhances its interaction with the SOMO upon radial expansion (Figure 4a). In contrast, spin polarization of 3s\(u\) is much less effective, as areas with increased and reduced overlap will partly compensate each other (Figure 4c). The same arguments may be applied to the spin polarization of the 2p and 3p orbitals (Figure 4b,d). The polarization of 2s\(u\), 3s\(u\), and 3d\(u\) orbitals is of course not an isolated process but is accompanied by the polarization of all other orbitals of either spin. Besides the exchange interaction, Coulomb repulsion and electron–nucleus attraction also come into play. This will be discussed in more detail below.

The requirement of orthogonality between the 3s and 2s orbitals helps us also to understand better the dependence of their contributions to \(\rho_{PN}\) on nuclear charge. From the orthogonality of 2s\(u\)(\(r\)) and 3s\(u\)(\(r\)) follows:

\[
(2s^u(r)|3s^u(r)\rangle = \langle 2s^u(r)|3s^u(r)\rangle + \langle 2s^u(r)|\Delta 3s^u(r)\rangle + \\
\langle \Delta 2s^u(r)|3s^u(r)\rangle + \langle \Delta 2s^u(r)|\Delta 3s^u(r)\rangle = 0 \quad (11)
\]

The first term in the middle of (11) vanishes, since the ROHF 2s and 3s orbitals are also orthogonal. The fourth term is negligible with respect to the second and third terms, since \(\Delta 2s^u(r)\)
Figure 5. Orthogonality of 2s and 3s orbitals in Mn$^{2+}$(ROHF result). The function $f = 2s(r)3s(r)^2$ integrates to zero. For comparison, the functions $2s(r)^2$ and $3s(r)^2$ are also shown. For $2s$, the phase convention differs from that used elsewhere.\(^{36}\)

\[ \langle 2s | 3s \rangle < < 2s_{\text{rg}} \text{ and } \Delta 3s^2(r) < < 3s_{\text{rg}}(r). \]

Hence,

\[ \langle 2s_{\text{rg}}(r) | \Delta 3s^2(r) \rangle + \langle \Delta 2s^2(r) | 3s_{\text{rg}}(r) \rangle \approx 0 \quad (12) \]

Analogously, it may be shown that

\[ \langle 2s_{\text{rg}}(r) | \Delta 3s^2(r) \rangle + \langle \Delta 2s^2(r) | 3s_{\text{rg}}(r) \rangle \approx 0 \quad (13) \]

Figure 6 illustrates eq 12 for Mn$^{2+}$. The function $\Delta 3s^2(r)2s_{\text{rg}}(r)^2$ is positive at most $r$ values, as $2s_{\text{rg}}(r)$ and $\Delta 3s^2(r)$ have equal sign where they overlap significantly. The function $\Delta 3s^2(r)2s_{\text{rg}}(r)^2$ integrates to zero; see text.

Figure 6. Consequences of the orthogonality between 2s and 3s orbitals in Mn$^{2+}$. The function $\Delta 3s^2(r)2s_{\text{rg}}(r)^2 + \Delta 3s^2(r)2s_{\text{rg}}(r)^2$ integrates to zero; see text.

have equal sign where they overlap significantly. The function $\Delta 3s^2(r)2s_{\text{rg}}(r)^2$ is negative everywhere, as regions of negative $\Delta 3s^2(r)$ always match those of positive $3s_{\text{rg}}(r)$, and vice versa.\(^{36}\)

The total area under $\Delta 3s^2(r)3s_{\text{rg}}(r)^2$ and under $\Delta 3s^2(r)2s_{\text{rg}}(r)^2$ is calculated to be $0.000238$ and $-0.000238$, respectively. The approximation in deriving eq 12 from eq 11 appears thus to be well-justified. The spin polarization contributions

\[ \langle \psi | \alpha \rangle = \int \psi(r)^* \psi(r) r^2 \, dr \]

where $\psi(r)$ and $\chi(r)$ are radial parts of the orbitals $\psi(r)$ and $\chi(r)$, respectively.

\(^{36}\) Molecular or atomic orbitals are unique except for a phase factor. Unless noted otherwise, in this work all s-type orbitals are defined as to be positive at the nucleus. The choice of phase does not alter the physical mechanism.
Figure 7. Effect of nuclear charge on the 2s and 3s orbitals. Comparison of \([2s(r)]^2\) and \([3s(r)]^4\) for \(\text{Cr}^2+\) and \(\text{Fe}^{3+}\) (ROHF results).

Figure 8. Core-shell spin polarization in \(\text{Cr}^2+\) and \(\text{Fe}^{3+}\): \(\Delta 2s^\alpha(r)\), \(\Delta 3s^\alpha(r)\).

\(\Delta 3s^\alpha(r)\) and \(\Delta 2s^\alpha(r)\) have to match the restricted orbital distributions \(2s_{\text{g}}(r)^2\) and \(3s_{\text{g}}(r)^2\), to fulfill eq 12.

Figure 7 examines the changes in the ROHF 2s and 3s radial distributions upon increasing the nuclear charge by two (the \(d^5\) ions \(\text{Cr}^2+\) and \(\text{Fe}^{3+}\) are compared). Both 2s and 3s contract and increase their overlap with \(\Delta 3s^\alpha\) and \(\Delta 2s^\alpha\), respectively. The redistribution of the electron density is more pronounced for the more polarizable 3s orbital. This is seen most clearly when comparing the area confined between the curves \(3s(\text{Fe}^{3+})\) and \(3s(\text{Cr}^2+)\) with the area confined between the curves \(2s(\text{Fe}^{3+})\) and \(2s(\text{Cr}^2+)\). The contraction of 3s and 2s will thus enhance \(\langle \Delta 3s^\alpha(r)\rangle_{\text{Fe}^{3+}} - \langle \Delta 3s^\alpha(r)\rangle_{\text{Cr}^2+}\) and \(\langle \Delta 2s^\alpha(r)\rangle_{\text{Fe}^{3+}} - \langle \Delta 2s^\alpha(r)\rangle_{\text{Cr}^2+}\). The contribution of \(\Delta 3s^\alpha(r)\) and \(\Delta 2s^\alpha(r)\) to the total spin contribution is identical as for the 2s orbital: the \(\alpha\) component expands, whereas the \(\beta\) component contracts. Both processes produce a negative contribution to \(\rho_\text{N}\) (cf. Tables 1 and 3).

Spin Polarization and Energy Gain. The gain in exchange energy, due to spin polarization, between the five SOMOs and the doubly occupied orbitals in \(\text{Mn}^{2+}\) (−0.005 345 a.u.; see Table 4) corresponds to 104% of the difference between the total UHF and ROHF potential energies (Table 5). For the \(\text{N}^4\) atom, the corresponding gain in exchange energy represents 105% of the total reduction in potential energy \(E_{\text{pot}}\) (Table 5). This is consistent with the usual interpretation of spin polarization as being due to improved exchange interactions between the SOMO(s) and the doubly occupied orbital(s) in the UHF wave function.

Additionally, the spin polarization creates a new equilibrium between electron-electron repulsion and electron-nuclear attraction. The crucial role of electron-nuclear attraction energy \(E_{\text{NC}}\) is demonstrated in Table 5. It provides the main energy gain upon going from ROHF to UHF wave functions. This may be rationalized as follows: As the ROHF wave function is not relaxed with respect to exchange interactions between the SOMO and the other spin-orbitals, the density is too diffuse. Spin polarization helps to contract the metal 3d\(^8\), 3p\(^5\), and 3s\(^5\) orbitals and thus enhances electron-nuclear attraction. Part of this energy gain is compensated by the decontraction of the

![Table 5. Analysis of ROHF and UHF Total Energies of \(\text{Mn}^{2+}\) and \(\text{N}^4\) (au)](image)

- Total kinetic + potential energy of the system. * Total potential energy \(E_{\text{pot}} = E_{\text{NC}} + E_{\text{E}}\). † Total energy of the electrons due to nuclear attraction. \(E_{\text{NC}} = E_{\text{C}} + E_{\text{X}}\). / The sum of all Coulomb integrals, including self-interactions. & The sum of all exchange integrals, including self-interactions.

(37) The strongly localized 1s shell experiences ~2 orders of magnitude less exchange interactions with 3d than 2s does.
charge density in 1s\(^a\), 2s\(^a\), 2p\(^a\), as well as in 3s\(^b\), 2s\(^b\), 2p\(^b\) contract and thus lower \(E_{\text{soc}}\). Tables 4 and 5 show that the spin polarization improves exchange \((E_X)\) but increases the total \(E_{\text{soc}}\). This is also a consequence of an overall more contracted charge density. Nevertheless, \(E_{\text{pot}}\) decreases, due to the large contribution from \(E_{\text{NC}}\). The total kinetic energy \((E_{\text{kin}})\) increases, in agreement with the virial theorem.\(^{38}\)

Table 4 also shows that, due to formal similarity, the exchange integrals and their changes upon spin polarization are closely connected with the radial overlap of the corresponding orbitals. (a) The exchange interaction increases in the series \((3d,1s), (3d,2s)\) and \((3d,3s)\) and so does the radial overlap; (b) the spin polarization increases the exchange integral with the SOMO when the radial overlap with the SOMO increases and vice versa.\(^{32}\) In contrast, the Coulomb interaction increases along the series \((3d,3s), (3d,2s),\) and \((3d,1s)\), even though the 2s and particularly the 1s maximums are far from the 3d maximum. This implies that \((1/r_1)\) may actually increase with increasing distance between the radial maximums and vice versa. Compared to the 1s wave function, the 3s wave function occupies a larger angular space. Thus, the electrons in 3s and 3d orbitals are on average further apart (despite the large overlap of the corresponding radial wave functions).

Coming back to the historical interpretations of spin polarization in transition metal systems (section 21.15), we conclude that the expansion of the 2s\(^a\) orbital reduces its electrostatic repulsion with the SOMO, both by reduced Coulomb interaction (angular correlation) and by improved exchange (radial correlation). This would correspond to the usual “effective attraction” of like-spin electrons on a radial scale. On the other hand, the boundary condition of orthogonality to 2s forces the 3s spin polarization (expansion of 3s\(^a\), contraction of 3s\(^b\), irrespective of the resulting partial energy loss.

Comparison to the Main-Group Case (\(^4\)N). The quartet ground state of the nitrogen atom is a good main-group example to be compared with, as it exhibits a spherical distribution of the three unpaired electrons in the 2p orbitals. The positive 2s contribution to \(\rho_N\) (0.91 au, UHF result) overcompensates the negative 1s contribution (−0.74 au), giving an overall positive \(\rho_N\) (cf. ref 19e). The spin polarization of the nitrogen 1s and 2s orbitals (Figure 2a,b) may be compared to the polarization of the 2s and 3s orbitals in \(^{16}\)Mn\(^2\) (Figure 4a,c). For nitrogen, the 1s\(^b\) and 2s\(^b\) orbitals expand, whereas the 1s\(^a\) and 2s\(^a\) orbitals contract. Note that, in contrast to the situation for the 3s and 3d orbitals in \(^{24}\)Mn\(^2\) (see above), the second maximum of the 2s distribution is located at slightly larger radius than the 2p maximum.

The opposite direction of the polarization of the 1s\(^b\) and 2s\(^b\) orbitals is again required by their mutual orthogonality. However, in contrast to the \(^{24}\)Mn\(^2\) case, in this case, the spin polarization enhances the exchange interaction with the 2p SOMO for both s orbitals, despite the slight decrease of radial overlap between 2s\(^a\) and 2p\(^a\) (Table 6). This appears to be due to the dominant role of the second maximum of 2a\(^b\). Spin polarization brings the latter closer to the 2p\(^a\) maximum and thus enhances 2s\(^a\)/2p\(^a\) exchange. The accompanying increase in 2s\(^a\)/2p\(^a\)

\(^{38}\) Levin, I. N. Quantum Chemistry; Allyn and Bacon: Boston, 1975; p 363.

\(^{39}\) Exchange interactions are more short-ranged than Coulomb repulsion and thus parallel more closely the radial overlap (see, e.g., Bethe, H. A.; Jackiw, R. Intermediate Quantum Mechanics; W. A. Benjamin, Inc.: Reading, MA, 1974). In contrast, Coulomb repulsion may also be large for two nonoverlapping pointlike charge distributions, provided their distance is not too large. Of course, even the exchange interactions may deviate from the behavior of the radial overlap integrals, due to the influence of the \(r_1^{-3}\) factor in the integrand of eq 4 (cf. also discussion for \(^4\)N).

### Table 6. Exchange, Coulomb, and Radial Overlap Integrals between the SOMO and the Doubly Occupied Orbitals for \(^4\)N (au)

<table>
<thead>
<tr>
<th>Exchange integrals</th>
<th>1s</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
</tbody>
</table>

\[3 \sum_{\alpha^b} - \langle \psi_1 | \alpha^b | \psi_1 \rangle + \langle \psi_1 | \alpha^b | \psi_1 \rangle - \langle \psi_1 | \alpha^b | \psi_1 \rangle = -0.008 106\]

<table>
<thead>
<tr>
<th>Coulomb integrals</th>
<th>1s</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radial overlap integrals</th>
<th>1s</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>\alpha^b</td>
<td>\psi_1 \rangle)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nuclear attraction integrals</th>
<th>1s</th>
<th>2s</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \psi_1</td>
<td>Z/r^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>Z/r^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>Z/r^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>Z/r^b</td>
<td>\psi_1 \rangle)</td>
</tr>
<tr>
<td>(\langle \psi_1</td>
<td>Z/r^b</td>
<td>\psi_1 \rangle)</td>
</tr>
</tbody>
</table>

\(^\text{a ROHF and UHF results. \text{b See also corresponding footnote to Table 4.}}\)

Coulomb repulsion is compensated by reduced 2s\(^a\)/2p\(^a\) repulsion and increased nuclear-electron attraction (Table 6).

Valence-Shell Spin Polarization in \(^{16}\)Mn\(^2\). As a first step toward a better understanding of valence-shell spin polarization in transition metal systems, we examine the spin polarization of the 4s orbital in the \(^{16}\)Mn\(^2\) atom, comparing ROHF and UHF wave functions and energies. The spin polarization is qualitatively the same as discussed above for the 2s orbital in nitrogen: the \(\alpha\)-component contracts, whereas the \(\beta\) component expands (Figure 9). The exchange interaction between 3d and 4s (0.006 581 au at the ROHF level) is overall less pronounced than between 2s and 3d in \(^{24}\)Mn\(^2\) (0.026 949 au; cf. Table 4), but the energy gain upon spin polarization is still significant (+0.000 872 au). This is due to the large polarizability of the 4s shell, which also leads to a significant redistribution of spin density (Figure 9) and to a larger spin polarization contribution to \(\rho_N\) from 4s compared to 3s (Table 1). We may also view this, within a configuration–interaction framework, as a consequence of the lower excitation energies of the 4s valence compared to the 3s core orbital (for the same reason, spin contamination is largely connected to valence-shell spin polarization; see below). The same argument holds of course for the comparison between valence-shell 2s vs core-shell 1s spin polarization in nitrogen (see above).

6. Valence-Shell Spin Polarization in Molecules

As discussed above, the spin polarization of the core shells does not depend much on the particular bonding situation. It is similar for molecules and for atomic systems (cf. Tables 1 and

by an interaction of the metal 3d$_c$ and 3d$_b$ orbitals with the appropriate linear combination of ligand 2p$_x$ orbitals (1e"). The third linear combination of ligand 2p$_x$ orbitals is nonbonding (3a$_u^{''}$). [Mn(CO)$_5$] and [Mn(CN)$_5$N]$^-$ adopt square-pyramidal structures (C$_4v$ symmetry). [Mn(CO)$_5$] is a low-spin d$_{5}$ complex. Its SOMO is composed of metal 3d$_z^2$ and 4p$_y$ orbitals (17$a_1$). The 4p$_y$ admixture reduces the $\sigma$-antibonding interaction with the axial ligand by polarizing the SOMO toward the opposite side. The metal 4s contribution to the SOMO is small, giving a small, positive direct SOMO contribution to $\rho_N$. [Mn(CN)$_5$N]$^-$ is a d$_5$ complex with a single metal 3d$_{xy}$-type SOMO (2b). In both square-pyramidal complexes, two $\sigma$ bonds in the equatorial plane are formed by an interaction between a metal 4s/3d$_z$ hybrid, the metal 3d$_z^2$-$_y^2$ orbital, and the corresponding ligand $\sigma$-bonding hybrids (a$_1$ and b$_2$ MOs). The $\sigma$ bond to the axial ligand involves mainly the metal 3d$_z$ orbital. The metal 3d$_y$ orbital (b$_1$) is partially $\pi$ bonding to the equatorial ligands, the 3d$_{xy}$, 3d$_{yz}$, and 3d$_{z^2}$ electrons (e) interact also with the axial ligand. The antibonding counterparts of the latter three orbitals (which may be derived from the well-known t$_{2g}$ set in octahedral symmetry) correspond to the six nonbonding d electrons of [Mn(CO)$_5$].

The valence-shell spin polarization concentrates $\alpha$ spin density at the metal (cf. discussion above for the Mn$^6$ atom and ref 18). An excess of $\beta$ spin density is left at the ligands. In [Mn(CN)$_5$N]$^-$, the spin polarization increases the atomic spin population of Mn from 0.51 (SOMO contribution) to 1.18 (total spin population$^{41}$). The $\alpha$ spin density is withdrawn mainly from the axial ligand and added mainly to d-type orbitals of Mn (0.25, 0.10, 0.10, 0.07, and 0.06 electrons to d$_{xy}$, d$_{yz}$, d$_{z^2}$, d$_x^2$-$y^2$, and d$_z^2$, respectively). This likely enhances the overall negative core-shell spin polarization contributions to $\rho_N$ (cf. section 5). The spin population of the 4s orbital increases also slightly (several metal $\sigma$-bonding orbitals are involved), resulting in a small contribution to $\rho_N$ of +0.04 au (Table 1). This is much less than the valence-shell contribution in Mn (+0.93 au), where the spin polarization of the fully occupied 4s orbital contributes (note also that [Mn(CN)$_5$N]$^-$ has only one unpaired electron whereas Mn has five).

Similarly, spin polarization increases the spin population at the metal in Mn(CO)$_5$ from 0.58 (SOMO contribution) to 0.82. The increase concentrates mostly in orbitals of e symmetry (the metal 3d$_z$, 3d$_z$, 4p$_x$, and 4p$_y$ orbitals, total gain ~0.13). The spin population in orbitals of a$_1$ symmetry increases only slightly, by 0.04 for d$_z^2$ and by 0.03 for 4s. The increase is only 0.03 and 0.01 for 3d$_{xy}$ and 3d$_{z^2}$-$y^2$, respectively (with significant consequences for $A_{dip}$, cf. below).

Negative valence-shell contributions to $\rho_N$ are found for the isoelectronic TiF$_3$ and MnO$_3$, due to an interesting rehybridization mechanism: The spin polarization, mainly of the metal $\sigma$-bonding 6a$_1^{''}$ MO, shifts $\alpha$ density from the ligands toward the metal. Therefore, the spin population at the metal is enhanced from 0.93 (SOMO contribution) to 1.04 in TiF$_3$, and from 0.64 to 1.19 in MnO$_3$ (the larger effect for the manganese complex is a consequence of the larger covalence of the $\sigma$ bonds). However, at the same time, the metal contribution to this bonding MO loses 4s character and gains 3d character. Therefore, the overall valence-shell spin polarization contribution to $\rho_N$ and thus to $A_{dip}$ is negative (and that to $A_{dip}$ positive, cf. below), in particular for the very covalent MnO$_3$. We also note that, in TiF$_3$, the excess $\alpha$ spin density is distributed almost equally over all five metal d orbitals. In contrast, the excess spin population in MnO$_3$ pertains mostly to the d$_z^2$, d$_{xy}$, and d$_z$ orbitals (+0.17, +0.13, and +0.13, respectively) and less to the d$_{xy}$ and d$_{z^2}$-$y^2$ orbitals (each +0.05).

Table 7. Orbital Contributions to $A_{dip}$ for TiF$_3$ and MnO$_3$ (au)$^a$

<table>
<thead>
<tr>
<th>MO</th>
<th>Character</th>
<th>TiF$_3$</th>
<th>MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a$^{''}$</td>
<td>(metal 3d$_z^2$ + 3d$_y$, singly occupied MO)</td>
<td>0.441</td>
<td>0.640</td>
</tr>
<tr>
<td>3a$^{''}$</td>
<td>(ligand 2p$_x$)</td>
<td>0.012</td>
<td>0.052</td>
</tr>
<tr>
<td>1c$^{''}$</td>
<td>(metal 3d$_z$, 3d$_y$, ligand 2p$_x$)</td>
<td>0.005</td>
<td>0.147</td>
</tr>
<tr>
<td>6a$'$</td>
<td>(metal 4s, 3d$<em>z^2$, 3d$</em>{xy}$, 2p$_y$, 2p$_x$)</td>
<td>0.013</td>
<td>0.206</td>
</tr>
<tr>
<td>5e$'$</td>
<td>(metal 3d$<em>z$, 3d$</em>{xy}$, 2p$_y$, 2p$_x$)</td>
<td>-0.014</td>
<td>-0.113</td>
</tr>
<tr>
<td>4c$'$</td>
<td>(ligand 2s)</td>
<td>0.051</td>
<td>0.008</td>
</tr>
<tr>
<td>2a$'$</td>
<td>(metal 3p$_x$)</td>
<td>-0.086</td>
<td>-0.018</td>
</tr>
<tr>
<td>3e$'$</td>
<td>(metal 3p$_y$, 3p$_z$)</td>
<td>-0.108</td>
<td>-0.152</td>
</tr>
<tr>
<td>1a$^{''}$</td>
<td>(metal 2p$_z$)</td>
<td>-0.067</td>
<td>-0.143</td>
</tr>
<tr>
<td>2e$'$/1e$'$</td>
<td>(metal 2p$_x$, 2p$_y$)</td>
<td>0.048</td>
<td>0.108</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>0.305</td>
<td>0.746</td>
</tr>
<tr>
<td>$\exp&lt;\mathbf{s}$&gt;</td>
<td></td>
<td>0.221(1)...0.027(1)$^b$</td>
<td>0.622(2)$^b$</td>
</tr>
<tr>
<td>$\exp&lt;\mathbf{s}^2&gt;$</td>
<td></td>
<td>0.7526</td>
<td>0.7875</td>
</tr>
</tbody>
</table>

$^a$ DFT(BP86) results. All values have been divided by the nuclear g value. Contributions, which were for both molecules smaller than 0.01 au, have been omitted. $^b$ Reference 11.

2). In contrast, the spin polarization of the valence shells is characteristic of the specific chemical environment and bonding. We have selected the four examples, TiF$_3$, MnO$_3$, [Mn(CO)$_5$], and [Mn(CN)$_5$N]$^-$, to discuss valence-shell spin polarization contributions to $\rho_N$. DFT results obtained with the BP86 functional will be examined (Tables 1 and 2).

These complexes represent a variety of different bonding situations (cf. Tables 7 and 8 for a characterization of the MOs). TiF$_3^{22}$ and MnO$_3$ are isoelectronic, trigonal planar (D$_3h$) d$^1$ complexes. Their SOMO (7a$^{''}$) is metal $\sigma$ antibonding and is dominated by the metal 3d$_z^2$ orbital, with some 4s character mixed in. While the SOMO in TiF$_3$ is localized to 94% at the metal (with 76% 3d$_z^2$, and 18% 4s character$^{41}$), in MnO$_3$, it is more delocalized (with 49% 3d$_z^2$, 15% 4s, and 36% ligand character). Three $\sigma$-bonding orbitals (5e$'$, 6a$'$) are formed by the interaction of metal 3d$_z$, 3d$_{xy}$, and 3d$_{z^2}$-$y^2$ orbitals (e$'$), a metal 3d$_z$ orbital with 4s admixture (a$'$), and the appropriate ligand orbital combinations. In addition, two partial π bonds are formed

$^{41}$ The orbital compositions and spin populations reported here have been obtained using a Mulliken population analysis of the BP86 Kohn–Sham wave function.
and the equatorial ligands. In MnO$_3$ it is the orbital, the (again, DFT results with the BP86 functional are compared).

<table>
<thead>
<tr>
<th>MO in [Mn(CN)$_3$N]$^-$/[Mn(CO)$_5$]</th>
<th>character</th>
<th>[Mn(CN)$_3$N]$^-$</th>
<th>[Mn(CO)$_5$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-1/17a_1$</td>
<td>(Mn 3d$_x^2$, 4p$_y$, 4s, SOMO in [Mn(CO)$_5$])</td>
<td>0.763</td>
<td>0.302</td>
</tr>
<tr>
<td>$-1/1e$</td>
<td>(Mn 3d$_x^2$, 3d$_z^2$; eq ligands 2p$_y$)</td>
<td>0.030</td>
<td>0.002</td>
</tr>
<tr>
<td>2b/2b</td>
<td>(Mn 3d$_x^2$, eq lig 2p$_y$, 2p$_z$, SOMO in [Mn(CN)$_3$N]$^-$)</td>
<td>0.015</td>
<td>0.000</td>
</tr>
<tr>
<td>13a/14a$_1$</td>
<td>(eq ligands sp$_x$, sp$_y$, hybrids; Mn 4s)</td>
<td>0.015</td>
<td>0.000</td>
</tr>
<tr>
<td>5b/5b$_2$</td>
<td>(eq ligands sp$_x$, sp$_y$, hybrids; Mn 3d$_x^2$)</td>
<td>0.010</td>
<td>0.021</td>
</tr>
<tr>
<td>1b/1b$_2$</td>
<td>(Mn 3d$_x^2$, eq ligands 2p$_y$, 2p$_z$)</td>
<td>0.010</td>
<td>0.021</td>
</tr>
<tr>
<td>6e/10e</td>
<td>(Mn 3d$_x^2$, 3d$_z^2$; eq ligands 2p$_y$, 2p$_z$)</td>
<td>0.009</td>
<td>0.013</td>
</tr>
<tr>
<td>11a$_1$/12a$_1$</td>
<td>(Mn 4s+3d$_x^2$, eq ligands 2s+2p$_x+2p_y+2p_z$)</td>
<td>0.018</td>
<td>0.002</td>
</tr>
<tr>
<td>8a$_1$/9a$_1$</td>
<td>(Mn 3p$_x$)</td>
<td>0.076</td>
<td>0.057</td>
</tr>
<tr>
<td>4e/4e</td>
<td>(Mn 3p$_x$, 3p$_y$)</td>
<td>0.121</td>
<td>0.044</td>
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<td>3a$_1$/2a$_1$</td>
<td>(Mn 2p$_x$)</td>
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<td>0.094</td>
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<tr>
<td>1e/1e</td>
<td>(Mn 2p$_x$, 2p$_y$)</td>
<td>0.163</td>
<td>0.048</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>0.882</td>
<td>0.727</td>
</tr>
<tr>
<td>exp</td>
<td></td>
<td>0.929$^b$</td>
<td>0.68$^b$(6,$^h$) 0.70(5)$^h$</td>
</tr>
<tr>
<td>$&lt;S^2&gt;$</td>
<td></td>
<td>0.7729$^b$</td>
<td>0.7544</td>
</tr>
</tbody>
</table>

$^a$ DFT(BP86) results. See also footnote to Table 7. $^b$ Reference 11.

In both [Mn(CN)$_3$N]$^-$ and MnO$_3$, the largest valence-shell spin polarization is experienced by doubly occupied orbitals which are the bonding counterparts of the partly antibonding SOMO (this holds at the BP86 level but is altered upon adding Hartree–Fock exchange; see section 8). In [Mn(CN)$_3$N]$^-$, this is the 1b$_1$ orbital which represents $\pi$ bonding between the metal and the equatorial ligands. In MnO$_3$, it is the $\sigma$-bonding 6a$_1$ orbital. This observation may again be rationalized by a tendency to maximize the exchange interaction with the SOMO; i.e., the $\alpha$ component of the doubly occupied MO is oriented toward the metal (where the SOMO is largely localized), the $\beta$ component toward the ligands. Due to the large overlap with the SOMO, the spin polarization is particularly effective in these MOs. The abovementioned rehybridization in the $\alpha$ and $\beta$ components of the $\sigma$-bonding 6a$_1$ MO of MnO$_3$ and TiF$_3$ may be understood analogously: The SOMO has more 3d$_x^2$ than 4s$_z$ character, and thus an increase of the relative $\alpha$ character in the $\alpha$ component of the bonding MO improves the exchange interaction with the SOMO. In TiF$_3$ and Mn(CO)$_5$, the bonding counterparts of the (antibonding) SOMO are not polarized significantly. In TiF$_3$, this is due to the ionic character of the bond. In Mn(CO)$_5$, the SOMO is polarized away from the ligands (by 4p$_y$: admixture) and thus has also little overlap with the doubly occupied valence MOs.

### 7. Effect of Spin Polarization on Dipolar Coupling Constants

While spin polarization is usually considered for the dipolar hyperfine coupling (cf. Introduction), two recent computational studies have shown that in transition metal systems spin polarization may have a significant influence.$^{11,22}$ The most important MO contributions to the metal dipolar couplings of our four example systems are summarized in Tables 7 and 8 (again, DFT results with the BP86 functional are compared).

As expected, the largest contribution in all cases is the direct one from the SOMO. This is positive for TiF$_3$, MnO$_3$, and [Mn(CO)$_5$] but negative for [Mn(CN)$_3$N]$^-$. However, contributions due to the spin polarization of the doubly occupied orbitals are clearly nonnegligible. We may discriminate again between core- and valence-shell spin polarization.

#### Core-Shell Spin Polarization

A common feature of all four systems are the significant contributions to $A_{dip}$ from metal $p$-type core orbitals. The metal 2p$_x$ contributions are always negative; the 2p$_y$ and 2p$_z$ contributions are always positive. This is consistent with the discussion in section 5: Spin polarization expands the 2p$_x$ orbitals and contracts the 2p$_y$ orbitals. Thus, the positive contribution from 2p$_y$ to $A_{dip}$ becomes smaller than the negative one from 2p$_x$, and the negative contributions from 2p$_x$ and 2p$_y$ become smaller than the positive ones from 2p$_x$ and 2p$_y$. In a system of cubic or higher symmetry, these contributions would cancel exactly. In less symmetric systems, the anisotropy of the 2p spin polarization disturbs the balance between the two contributions. For our four systems, the effect is clearly nonnegligible, corresponding to $\sim 5\%$–10\% of the total $A_{dip}$. The 2p$_x$ orbital dominates the 2p$_x$ shell contributions in TiF$_3$, MnO$_3$, and [Mn(CO)$_5$] (the 3d$_z^2$-type SOMO affects particularly the 2p$_x$ component), whereas spin polarization contributions from 2p$_y$ and 2p$_z$ orbitals are larger in [Mn(CN)$_3$N]$^-$ (the 3d$_y^2$-type SOMO affects mostly 2p$_x$ and 2p$_y$).

The requirement of orthogonality between the 3p and 2p shells for atoms, as stated in section 5, does not hold strictly for molecules. Nevertheless, the 3p$_x$ and 3p$_y$ contributions to $A_{dip}$ generally have the opposite sign of the 2p$_x$ and 2p$_y$ contributions. The 2p$_x$ and 3p$_y$ contributions are also of opposite sign for [Mn(CO)$_5$] and [Mn(CN)$_3$N]$^-$. Therefore, the positive 3p$_x$ and the negative 3p$_y$ and 3p$_z$ contributions partially cancel, leading to a relatively low overall 3p contribution. In TiF$_3$ and MnO$_3$, the presence of the d$_z^2$-type SOMO forces both 2p$_x$ and 3p$_y$ orbitals to expand. Therefore, 3p$_x$ and 3p$_y$/3p$_z$ contributions do not compensate but enhance each other. Therefore, the spin polarization contributions from the 3p shell in TiF$_3$ and MnO$_3$ are particularly large and amount to $\sim 23\%$ of the total $A_{dip}$ in MnO$_3$ and even to $\sim 64\%$ in TiF$_3$.$^{11,22}$

#### Valence-Shell Spin Polarization

In the relatively ionic complex TiF$_3$, valence-shell spin polarization contributions to $A_{dip}$ are small, with the largest individual MO contribution arising from a nonbonding fluorine 2s orbital combination of 4e$^\sigma$ symmetry (this and other results of our analysis for TiF$_3$ are consistent with earlier results by Belanzoni et al.$^{22}$). We find larger valence-shell contributions for MnO$_3$ (Table 7). The covalency of the Mn–O $\sigma$ and $\pi$ bonds enables a significant

(42) The dipolar hyperfine interaction is a vector property and depends on the orientation of the orbitals involved. For a single $\alpha$ electron in a d$_z^2$ orbital, the $(A_x, A_y, A_z)$ vector is of the form $(-B_x, -B_y, +2B_z)$. For the other d orbitals, the signs are reversed. For d$_{x^2-y^2}$, $A_x$ is 0, $A_y$ is $(B_x - 2B_y)$, and so on. Analogous considerations hold for p orbitals. For $p_x$, $A_x$ is $(B_y - B_z)$, for $p_y$, $A_y$ is $(2B_x - B_z)$, and for $p_z$, $A_z$ is $(B_x - B_y)$. See, e.g., ref 2 for a detailed discussion.
shift of α spin density toward the metal (cf. above). Large positive contributions to $A_{dp}$ arise from the 6α and 1e" MOs (involving the metal d\textsubscript{2g} and d\textsubscript{x2-y2} orbitals, respectively), whereas the 5e" MO (involving the metal d\textsubscript{xy} and d\textsubscript{yz} orbitals) contributes negatively. Thus, while the overall negative spin polarization contributions to $A_{dp}$ in TiF\textsubscript{3} involve mainly the core shells (in particular 3p), additional significant, overall positive valence-shell contributions dominate for the more covalent MnO\textsubscript{3}. This has consequences for the sensitivity to spin contamination (see below).

Valence-shell spin polarization contributions to $A_{dp}$ in [Mn(CN)\textsubscript{4}N\textsuperscript{−}] are relatively small and partially compensate each other (Table 8). This appears to be a direct consequence of the character of the SOMO, which overlaps very little with the other valence MOs. In contrast, valence-shell contributions in [Mn(CN)\textsubscript{5}NO\textsuperscript{2−}] are significant. The largest contribution arises from the energetically high-lying, doubly occupied counterpart (1b\textsubscript{1g}) of the 2b\textsubscript{1g} SOMO. If it were not for its very large, negative contribution, the remaining valence-shell spin polarization contributions would almost cancel each other: A significant positive contribution from the π bonding 6e MO is compensated by negative contributions from equatorially σ-bonding MOs. The significant valence-shell spin polarization contribution to $A_{dp}$ (29% of the total value) in [Mn(CN)\textsubscript{4}N\textsuperscript{−}] is thus at least in part due to the presence of a doubly occupied MO that has particularly large overlap with the SOMO.

8. Spin Polarization and Spin Contamination

The above discussion shows clearly that the two complexes MnO\textsubscript{3} and [Mn(CN)\textsubscript{5}NO\textsuperscript{2−}] exhibit particularly pronounced valence-shell spin polarization, due to the presence of high-lying doubly occupied bonding MOs that overlap strongly with the SOMO. These two systems were also two of the most critical cases in our systematic validation of different density functionals for the calculation of hyperfine coupling constants.\textsuperscript{11} In particular, spin contamination turned out to be a problem when hybrid functionals were used. For [Mn(CN)\textsubscript{4}N\textsuperscript{−}], we found that the spin contamination was related to a mixing in of low-lying excited states that involve π-type orbitals. Upon going from a pure gradient-corrected (“GGA”) functional like BP\textsubscript{86} to hybrid functionals incorporating exact exchange, the population of each of the metal d\textsubscript{xy} and d\textsubscript{yz} orbitals increased dramatically, e.g., from 0.08 for BP\textsubscript{86} to 0.62 for the “half-and-half” BHP\textsubscript{86} functional. At the same time, the S\textsuperscript{2} expectation value of the Kohn–Sham wave function\textsuperscript{13} indicated a significant increase in spin contamination (BP\textsubscript{86}: <S\textsuperscript{2}> = 0.773; BHP\textsubscript{86}: <S\textsuperscript{2}> = 1.784). Similar effects were noted with MnO\textsubscript{3}.\textsuperscript{11} Obviously, the exact-exchange contribution to the hybrid functionals favors excited states of higher spin multiplicity to the extent that the UKS wave functions for the ground state of these types of systems become significantly spin-contaminated.

In both systems, the description of $A_{dp}$ deteriorated significantly with hybrid functionals, becoming too positive for MnO\textsubscript{3} and insufficiently negative for [Mn(CN)\textsubscript{4}N\textsuperscript{−}]. Our present analysis indicates that the spin contamination produces too large spin populations in d\textsubscript{xy} and d\textsubscript{yz}-type orbitals and thus too large positive contributions to $A_{dp}$ from these orbitals. For similar reasons, hybrid functionals underestimated $A_{dp}$ in the related complex [Mn(CN)\textsubscript{5}NO\textsuperscript{2−}].\textsuperscript{11} At the same time, the isotropic coupling constants, i.e., the spin density at the metal nucleus,

9. Conclusions

The present study has shed light from various directions on hyperfine coupling in 3d transition metal complexes. From the detailed analysis of the spin polarization of the metal core shells in atomic systems, we have learned that the opposite contributions from the metal 2s and 3s shells to the spin density at the metal nucleus, $\rho_N$, and of the 2p and 3p shells to the dipolar coupling constants, $A_{dp}$, is a consequence of the orthogonality requirement between orbitals of the same angular momentum. While the 2s and 2p orbitals maximize their exchange interaction with the SOMO, the 3s and 3p orbitals are forced to lose some of their exchange to stay orthogonal to their respective penultimate shell. Changes of the ratio between 2s and 3s (and between 2p and 3p) contributions to $\rho_N$ along the 3d series may be understood from the nodal structure of the orbitals. We expect that similar considerations apply to 4d and 5d systems.

Parts of this analysis are consistent with traditional views of spin polarization, e.g., in main-group compounds, as being due to enhanced exchange between the α component of the respective doubly occupied orbitals and the SOMO. A complete view, however, has to include the complementary polarization of the β spin–orbitals, as well as changes in Coulomb repulsion and nuclear–electron attraction.

While the core-shell spin polarization contributions to the isotropic hyperfine couplings have been found to be proportional to the spin population in the metal 3d orbitals, they are relatively independent of other details of the bonding. In contrast, the valence-shell spin polarization depends strongly on the electronic structure of the system. Particularly large valence-shell spin polarization contributions to both isotropic and dipolar coupling constants are found for systems in which the SOMO overlaps significantly with certain high-lying doubly occupied valence orbitals. These are the same cases in which our previous study\textsuperscript{11} found dramatic spin contamination effects to plague unrestricted Kohn–Sham calculations with hybrid functionals. In addition to providing some basic insight into the mechanisms of spin polarization in transition metal systems, the results of the present work may also be used to pinpoint the weaknesses of certain theoretical approaches for the calculation of hyperfine couplings and thus hopefully also to develop improved methods.

In contrast to the assumptions implicit in many qualitative\textsuperscript{2} and quantitative\textsuperscript{44,45} schemes in current use by experimentalists, both core- and valence-shell spin polarization may significantly contribute to transition metal dipolar coupling constants. Moreover, for TiF\textsubscript{3} and MnO\textsubscript{3}, we have identified an interesting 3d/4s rehybridization of the SOMO upon including spin
polarization. These features complicate the extraction of spin densities and orbital character from experimental $A_{dip}$ values. Explicit quantum chemical analyses are thus to be preferred instead.

Acknowledgment. This study has been supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie. Part of this work benefitted also from the graduate college “Moderne Methoden der magnetischen Resonanz in der Materialforschung” at Universität Stuttgart. We are grateful to Drs. Dominik Munzar (Brno), Bernd Schimmelpfennig (Stockholm), and Vladimir Malkin (Bratislava) for helpful discussions.
Concepts without factual content are empty; sense data without concepts are blind.... The understanding cannot see. The senses cannot think. By their union only can knowledge be produced.

Immanuel Kant (1724-1804)

8 A Density Functional Study of EPR-Parameters for Vanadyl Complexes Containing Schiff Base Ligands

Introduction

The coordination chemistry of vanadium has recently received increased attention due to the reported biochemical activity of vanadyl complexes. The latter is being related to the interplay between four-coordinate, tetrahedral structures of vanadates(V) and five-coordinate, trigonal bipyramidal structures of vanadyl(IV) or vanadyl(V) complexes. Structural distortions have been found to be reflected characteristically in the EPR spectra of vanadyl(IV) complexes. The following paper reports density functional calculations of electronic $g$-tensors and metal hyperfine coupling tensors for a series of four of these vanadyl complexes with structures ranging from nearly trigonal bipyramidal (TBP-5) to nearly square pyramidal (SQP-5). The EPR spectroscopic parameters have been rationalized in terms of electronic and geometrical structures. The author of this thesis performed all of the calculations included in the study, most of the interpretational work, and contributed significantly to the preparation of the manuscript.

Results

The $\Delta g$-tensor components are underestimated systematically by ca. 40%. Good agreement with experiment is obtained for hyperfine tensor components calculated with hybrid functionals that account better for the spin polarization of the core orbitals than GGA functionals. The rhombicity of the hyperfine tensor is reproduced well at all levels of theory applied. It is mainly determined by the SOMO composition. The latter explains the increasing rhombicity of the $A$-tensor with increasing distortion of the
SQP-5 structures along the series of complexes studied. The orientational dependence of the principal tensor components on the local vanadium coordination is much more pronounced for the $g$-tensor than for the $A$-tensor.

Conclusions and outlook

The paper provides interpretations of the observed trends in the spin Hamiltonian parameters in terms of the SOMO compositions and of spin-orbit coupling. In addition to the magnitudes of the principal components of both tensors, the calculations provide also their orientations relative to each other, and relative to the molecular framework. Such information is more difficult to obtain experimentally. The orientation of $A$- and particularly $g$-tensors with respect to the molecular framework, or the experimentally more accessible relative orientations of $g$- and $A$- tensors appears to be very sensitive probes of the local symmetry and coordination of the oxovanadium group.

Apart from interpretational purposes, the present study has also served as a further validation of DFT approaches for the calculation of EPR-parameters in transition metal complexes. Hybrid functionals provide better agreement with experimental hyperfine tensors than gradient-corrected functionals. Preliminary tests suggest that hybrid functionals may provide better accuracy also for $\Delta g$-tensor components that are underestimated systematically within the LDA and GGA approaches.\textsuperscript{3}
References


A Density Functional Study of EPR-Parameters for Vanadyl Complexes Containing Schiff Base Ligands

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Abstract. Deviations of the coordination arrangement of vanadyl complexes from a regular square pyramid are thought to influence, among other things, their biological function. Such structural distortions have been found to be reflected characteristically in EPR spectra (Cornman et al. \textit{Inorg. Chem.} 1997, 36, 6401). In this work, density functional calculations of electronic $g$-tensors and metal hyperfine coupling tensors have been carried out for a series of four of these vanadyl complexes with structures ranging from nearly trigonal bipyramidal (TBP-5) to nearly square pyramidal (SQP-5). The EPR spectroscopic parameters have been rationalized in terms of electronic and geometrical structures. Using all relevant perturbation operators together with local or gradient-corrected density functionals, $\Delta g$-tensor components are underestimated systematically by ca. 40%. Good agreement with experiment is obtained for hyperfine tensor components calculated with hybrid functionals (B3PW91, BHPW91), which account better for the spin polarization of the core orbitals than GGA functionals like BP86. The rhombicity of the hyperfine tensor is reproduced well at all levels of theory applied. It is mainly determined by the SOMO composition. The latter explains the increasing rhombicity of the $A$-tensor with increasing distortion of the SQP-5 structures along the series of complexes studied. The orientational dependence of the principal tensor components on the local vanadium coordination is much more pronounced for the $g$-tensor than for the $A$-tensor. The principal axes of the $g$- and $A$- tensors are found to be rotated with respect to each other by as much as $41^\circ$.

Keywords. Bioinorganic chemistry, density functional theory, EPR hyperfine coupling tensors, $g$-tensors, vanadyl complexes.
1. Introduction

The coordination chemistry of vanadium has recently received increased attention, due to the discovery of enzymes requiring vanadium for activity,\(^1\) and due to the insulin-like effects elicited by vanadium complexes in diabetic animals.\(^2\) The biochemical activity of vanadium is often related to the interplay between four-coordinate, tetrahedral structures of vanadates(V) and five-coordinate, trigonal bipyramidal (TBP-5) structures of vanadyl(IV) or vanadyl(V) complexes.\(^3\) The TBP-5 coordination appears to be the consequence of significant steric constraints, as square pyramidal (SQP-5) or distorted SQP-5 complexes are formed in the absence of bulky ligands.\(^4\) To probe these constraints, Cornman et. al. have recently prepared a series of vanadyl complexes, in which the coordination arrangement varied from approximately SQP-5 to approximately TBP-5.\(^5\) An angular structural parameter \(\tau\) (ranging from \(\tau=0\) for purely SQP-5 coordination to \(\tau=1\) for purely TBP-5 coordination) has been introduced to quantitatively compare the coordination sphere of the metal. The value of \(\tau\) varied from 0.26 to 0.70 for the complexes studied in ref 5. EPR and pulsed ENDOR studies showed that both hyperfine coupling (HFC) tensor components and nuclear quadrupole coupling constant \(P\) provide a sensitive measure of changes in the arrangement of the ligands.\(^5,6,7\) In particular, it was noted\(^5\) that the EPR spectra of all complexes are rhombic, and that the rhombicity increases with \(\tau\).

Our previous systematic applications of density functional theory (DFT) to the calculation of hyperfine tensors in a series of 3d transition metal complexes have taught us, that explicit quantum chemical studies may provide considerably refined interpretations of the observed spectroscopic parameters.\(^8,9\) A recently developed DFT approach\(^10\) for the calculation of electronic \(g\)-tensors allows us furthermore to extend our computational investigations also to this property. Here we report a detailed DFT study of hyperfine coupling and \(g\)-tensors for some of the complexes studied by Cornman et al.,\(^5\) and for bis(2-methylquinoline-8-olate)oxovanadium(IV). For the latter complex, single-crystal EPR studies have provided magnitudes, as well as absolute and relative orientations, of the hyperfine and \(g\)-tensors.\(^11\) We will relate the experimental and computational findings to the distribution of spin density within the complexes studied and will provide an interpretation of the correlation between the rhombicity of the tensors and \(\tau\).
2. Theoretical Formalism and Computational Details

**$g$-Tensor calculations.** The theoretical background of EPR parameters is covered in detail in text books.\textsuperscript{12,13,14,15,16,17} Hence we summarize only the most relevant points and the expressions used in our calculations. The $g$-tensor is calculated as correction to the free electron value (given in ppm), i.e.

$$g = g_e I + \Delta g,$$

with $g_e = 2.002322$. Up to the level of second-order perturbation theory, the $g$-shift $\Delta g$ consists of the relevant Breit-Pauli terms

$$\Delta g = \Delta g_{SO/OZ} + \Delta g_{RMC} + \Delta g_{GC},$$

of which the „paramagnetic“ second-order spin-orbit/orbital Zeeman cross term, $\Delta g_{SO/OZ}$, dominates (except for extremely small $\Delta g$-values; we also include $\Delta g_{RMC}$ and the $\Delta g_{GC}$ (1el.) in the calculations\textsuperscript{10}). Within the present uncoupled DFT (UDFT) approach, its cartesian components $u,v,w$ are computed as\textsuperscript{10,18}

$$\Delta g_{SO/OZ,av} = \frac{\alpha^2}{2} g_e \left[ \sum \sum \sum \sum \right] \frac{\langle \psi^a_k | H_{SO,x} | \psi^a_k \rangle \langle \psi^a_k | H_{SO,y} | \psi^a_k \rangle - \langle \psi^a_k | H_{SO,z} | \psi^a_k \rangle \langle \psi^a_k | H_{SO,y} | \psi^a_k \rangle}{\varepsilon_k^a - \varepsilon_k^a}$$

We calculate the spin-orbit (SO) operator $H_{SO}$ in the atomic mean-field approximation (AMFI).\textsuperscript{19,20} This approach has been shown\textsuperscript{10} to give results to within better than a few percent of the exact Breit-Pauli one- and two-electron SO-Hamiltonian, at a small fraction of the computational effort required for the latter. For comparison, we also report results in which the two-electron spin-orbit contributions have been neglected, and only the one-electron part due to the nuclear charges has been retained. We employed a common gauge at the transition metal nucleus. Unrestricted Kohn-Sham calculations were performed within the local density approximation (VWN functional).\textsuperscript{21} Gradient corrected functionals do not improve the results in the case of $g$-tensors of transition metal complexes.\textsuperscript{10} The (15s11p6d)/[9s7p4d] metal basis set employed in our previous studies\textsuperscript{8,9,10} has been used. DZVP basis sets\textsuperscript{22} were used for the main group atoms. Polarization p-functions have been omitted for hydrogens of the methyl- and $t$-butyl substituents.

**Hyperfine Tensor Calculations.** The hyperfine coupling parameters describe the interactions of unpaired electrons with various magnetic nuclei. The $3 \times 3$ hyperfine
interaction tensor $A$ can be separated into its isotropic and anisotropic (dipolar) components. The isotropic part reflects the spin density at the point of the magnetic nucleus. The anisotropic part yields additional information about the local environment of a paramagnetic center. In the first-order approximation (neglecting spin-orbit effects; cf. below), isotropic hyperfine splittings $A_{iso}(N)$ correspond to the Fermi-contact term $A_{FC}$:

$$A_{iso}(N) = A_{FC} = \frac{4\pi}{3} \beta_e \beta_N g_e g_N \langle S_Z \rangle \sum_{\mu,\nu} P_{\mu,\nu}^{\alpha-\beta} \left( \phi_\mu | \delta(R_N) | \phi_\nu \right).$$

(4)

Here $\beta$ is the Bohr magneton, $\beta_N$ the nuclear magneton, $g_N$ is the g-value of the nucleus $N$, $\langle S_Z \rangle$ is the expectation value of the z-component of the total electronic spin, $P_{\mu,\nu}^{\alpha-\beta}$ is the spin density matrix, and the summation runs over all occupied molecular orbitals. In the first-order approximation, the components $T_{ij}$ of the anisotropic tensor are given by:

$$T_{ij}(N) = \frac{1}{2} \beta_e \beta_N g_e g_N \langle S_Z \rangle \sum_{\mu,\nu} P_{\mu,\nu}^{\alpha-\beta} \left( \phi_\mu | r_N^5 \delta_{ij} - 3r_{N,i}r_{N,j} \right) | \phi_\nu \rangle.$$  

(5)

where $r_N = r - R_N$ ($R_N$ is the position vector of nucleus $N$). In the following, we will generally refer to the metal hyperfine interaction and argument $N$ will be omitted.

All-electron unrestricted Kohn-Sham calculations of hyperfine structure were done with the Gaussian98 program. We have used three different combinations of exchange and correlation potentials ($\nu_x[\rho]$ and $\nu_c[\rho]$, respectively), abbreviated as BP86, B3PW91, and BHPW91. The BP86 functional combines Becke’s generalized-gradient-correction (GGA) functional for exchange (B) with Perdew’s 1986 GGA (P86) for correlation. B3PW91 contains Becke’s three-parameter hybrid functional for exchange (B3, including ca. 20% Hartree-Fock exchange), while the last combination employs the “half-and-half” hybrid exchange functional (BH), incorporating as much as 50% Hartree-Fock exchange. The latter two exchange functionals have been combined with the GGA for correlation of Perdew and Wang (PW91). Additional BP86 calculations of the dipolar hyperfine coupling constants have been carried out with a modified version of the deMon-EPR code, in which we have implemented a routine for the analysis of orbital contributions to $A_{dip}$.

The same vanadium orbital basis set has been used as in the $g$-tensor calculations (see above), in combination with the 6-31G(d) basis set for the ligands. The default
integration grids (int=finegrid option\textsuperscript{23}) of the Gaussian98 program and tight SCF convergence criteria (10\textsuperscript{-7} in RMS DM, 10\textsuperscript{-5} in MAX DM) have been applied.

**Relationship between Spin-Hamiltonian Parameters and Electronic Structure.** One of the aims of this study is to relate the spin Hamiltonian parameters obtained from theory/experiment to the electronic and molecular structure of a given paramagnetic center. This can be done along the lines of the classical second-order perturbation theory (PT) approach of Abragam and Pryce,\textsuperscript{31} as further discussed by McGarvey\textsuperscript{15}, Abragam and Bleaney\textsuperscript{12}, and by Mabbs and Collison.\textsuperscript{16} This approach also enables us to provide a rough semiempirical estimate of spin-orbit (SO) contributions to the hyperfine coupling which are not explicitly accounted for in our present DFT calculations of hyperfine tensors.

Within the approach of Mabbs and Collison, the components of the $\Delta g$-tensor and of the metal hyperfine tensor are given by\textsuperscript{16}

$$
\Delta g_{ij} = -2\xi_{n,i} \Lambda_{ij} ,
$$

(6)

$$
A_{ij} = P \left[ -\kappa \delta_{ij} - 3c l_y - 2\xi_{n,i} \Lambda_{ij} + 3c \xi_{n,i} \Lambda_{ij} \right] .
$$

(7)

Here $P = g_n g_s \beta_c \beta_s \langle \psi_o | p^{-1} | \psi_o \rangle$ (\(\psi_o\) is the singly occupied molecular orbital - SOMO),\textsuperscript{32} \(c = 2/[((2l-1)(2l+3)]\) (2/21 for a \(d\) electron), and

$$
I_y = \langle \psi_o | \hat{l}_y \hat{l}_y + \hat{l}_y \hat{l}_y | \psi_o \rangle - \frac{1}{3} l(l+1)\delta_{ij} .
$$

The $-\kappa \delta_{ij}$ term accounts for the Fermi contact contribution to the isotropic part of the tensor, whereas the $-3c Pl_{ij}$ term represents the first-order (SOMO) contribution to the anisotropic part of the tensor. $\xi_{n,i}$ is the spin-orbit coupling constant. The terms $\Lambda_{ij}$ and $\Lambda_{ij}'$ are defined as

$$
\Lambda_{ij} = \sum_m \frac{\langle \psi_o | \hat{l}_y | \varphi_m \rangle \langle \varphi_m | \hat{l}_y | \psi_o \rangle}{\varepsilon_m - \varepsilon_o} ,
$$

(8)
\[
\Lambda_{ij} = -\frac{i}{2} \sum_{m} \varepsilon_{m} \sum_{r} \langle \phi_{o} | \hat{l}_{r} | \phi_{m} \rangle \langle \phi_{m} | \hat{l}_{r} + \hat{l}_{r} \rangle | \phi_{o} \rangle / (\varepsilon_{m} - \varepsilon_{o}) .
\]

(9)

In the latter expression, \( \varepsilon_{m} \) is 1 (-1) if \((i,t,r)\) is an even (odd) permutation of \((x,y,z)\) and 0 otherwise. The summation over \( m \) runs over all virtual \( d \)-type orbitals (cf. below). In the expression (11) for the \( \Delta g \)-tensor, \( \Lambda_{ij} \) approximates the paramagnetic part of \( \Delta g \), given by eq. 5. In the \( \Lambda \)-tensor expression (12), the \( \Lambda_{ij} \) elements account for the cross-terms between orbital Zeeman and spin dipolar operator,\(^{33}\) the elements \( \Lambda'_{ij} \) represent second-order spin-dipolar contributions. One third of the trace of \( T_{ij} \) gives the second-order “pseudocontact” contribution \( (A_{PC}) \) to the isotropic coupling.\(^{34}\)

Equations 6 and 7 are often used either to determine MO compositions from the known spin Hamiltonian parameters or vice versa. The elements \( l_{ij} \), \( \Lambda_{ij} \), and \( \Lambda'_{ij} \) are expressed in terms of compositions and relative energies of the SOMO, \( \phi_{o} \), and of those virtual MOs, \( \phi_{m} \), which are dominated by metal \( d \)-orbital contributions (cf. ref 16, Chapter 9). The values of \( \varepsilon_{m} - \varepsilon_{o} \) and of \( \xi_{m,j} \) are usually estimated experimentally. Beyond interpretation purposes, this approach will in the following be used to estimate SO effects on the hyperfine tensor for the \( \text{VO(L}^{2}\text{)}_2 \) complex. The latter system is a \( d^1 \) complex possessing \( C_2 \) symmetry. The detailed expressions for the spin Hamiltonian parameters in this point group can be found on pages 384-386 of ref 16 (the reference appears to contain two typing errors\(^ {35} \)). The coefficients of the metal \( d \)-orbitals in MOs \( \phi_{o}, \phi_{1}, \ldots, \phi_{5} \) \(^{36} \) have been determined from a restricted open-shell BP86 calculation. Each coefficient has been taken as the square root of the Mulliken gross orbital population summed over all basis functions of a given symmetry.\(^ {37} \) The value of the parameter \( P \) has been determined from the same calculation, using the fact that, within the first-order approximation, \( T_{zz} = -3c P l_{zz} \). The relative energies, as well the \( g \)-tensor components - cf. equations (9.248)-(9.252) in ref 16 - have been taken from experiment (ref 5). The value of the SO coupling constant \( 148.4 \text{ cm}^{-1} \) has been taken from ref 11.

**Structures.** Figure 1 shows the complexes studied: [N,N’-ethylenebis(o-tert-butyl-p-methylsalicylaldiminato)oxovanadium(IV) = VO\(^{1}\) \((\tau=0.26)\), bis(N-methylsalicylaldiminato)oxovanadium(IV) = VO(L\(^2\))\(_2 \) \((\tau=0.55)\), bis(N-methyl-o-(tert-butyl-p-methylsalicylaldiminato)oxovanadium(IV) = VO(L\(^3\))\(_2 \) \((\tau=0.70)\), and bis(2-methylquinoline-8-olate)oxovanadium(IV) = VO(L\(^4\))\(_2 \).
For VOL\textsuperscript{1}, VO(L\textsuperscript{2})\textsubscript{2}, and VO(L\textsuperscript{3})\textsubscript{2}, structural data from X-ray diffraction have been used.\textsuperscript{5} Of these complexes, only VO(L\textsuperscript{2})\textsubscript{2} has crystallographically imposed symmetry (C\textsubscript{2}). No experimental structural data have been available for VO(L\textsuperscript{4})\textsubscript{2}. We have therefore optimized the structure in unrestricted Kohn-Sham calculations with the B3LYP functional (using the Gaussian98 program\textsuperscript{23}). The optimization employed a small-core effective-core potential (ECPs) and (8s7p6d)/[6s5p3d] GTO valence basis set for the metal,\textsuperscript{38} ECPs with (4s4p1d)/[2s2p1d] basis sets\textsuperscript{39} for the ligand atoms, and a (4s1p)/[2s1p] hydrogen basis.\textsuperscript{40} The optimization has been performed within the C\textsubscript{2} symmetry indicated by experiment.\textsuperscript{11} The resulting structure parameters are reported as supporting information. The optimized |VO\textsubscript{axial}| bond length for VO(L\textsuperscript{4})\textsubscript{2} (1.59 Å) is (within 0.01 Å) the same as found experimentally for VOL\textsuperscript{1}, VO(L\textsuperscript{2})\textsubscript{2}, VO(L\textsuperscript{3})\textsubscript{2}. The optimized |VO\textsubscript{ph}| bond length for VO(L\textsuperscript{4})\textsubscript{2} (1.94 Å) lies also within the range of bond lengths found for the other complexes (1.89-1.94 Å). The optimized |VN| bond length for VO(L\textsuperscript{4})\textsubscript{2} (2.16 Å) is somewhat longer than in the other complexes (2.06-2.10 Å). The distortion parameter \(\tau\) for optimized VO(L\textsuperscript{4})\textsubscript{2} structure, 0.55, is the same as for VO(L\textsuperscript{2})\textsubscript{2}.

**Orientation.** All g- and \(A\)-tensor calculations have been performed for the following standard cartesian coordinate system: The \(\vec{VO}_{\text{axial}}\) vector defines the positive \(z\) direction. For VOL\textsuperscript{1}, the \(y\) axis lies in the \(\vec{VO}_{\text{ph,1}}\leftrightarrow\vec{O}_{\text{ph,2}}\) plane, perpendicular to the \(z\)-axis.\textsuperscript{41} For VO(L\textsuperscript{2})\textsubscript{2}, VO(L\textsuperscript{3})\textsubscript{2}, and VO(L\textsuperscript{4})\textsubscript{2}, the \(y\) axis is defined in the same way but is additionally rotated by +45° around the \(\vec{VO}_{\text{axial}}\) vector. This choice of the coordinate system, shown in Figures 2 and 3, is the same as used by Mabbs and Collison\textsuperscript{16} for \(d\textsuperscript{1}\) complexes possessing genuine or approximate \(C\textsubscript{2}\) or \(C\textsubscript{s}\) symmetries.

**3. Results and Discussion**

Each of the complexes studied here contains one unpaired electron and may be regarded as a \(d\textsuperscript{1}\) system. The SOMO is generally dominated by a metal \(d\textsubscript{x,y}^2\text{-type orbital (ca. 80%)}, and the largest ligand contribution corresponds to phenolate oxygen \(\rho\) orbitals (ca. 10%). The total spin population at vanadium reaches 1.10 due to the spin polarization of the V=O\textsubscript{axial} bond; a negative spin population of ca. –0.10 is left at the axial oxygen (all numbers refer to Mulliken population analyses of UBP86 results for the four complexes).
3.1. g-Tensor Calculations. Computed $\Delta g$ components with respect to standard and principal axes are given in Tables 1 and 2, respectively. Both tables refer to the accurate atomic mean-field treatment of the $\Delta g_{SO/OZ(1e)}$ and $\Delta g_{SO/OZ(2e)}$ terms. In Table 2 we have also included results obtained if the $\Delta g_{SO/OZ(2e)}$ contributions are neglected. As found previously for a series of 3d complexes, the latter results are in apparently better agreement with experiment than the former, obviously due to a compensation of errors due to the neglect of the $\Delta g_{SO/OZ(2e)}$ terms and errors in the DFT treatment. The proper inclusion of both one- and two-electron SO terms leads to a systematical underestimate of all components by ca. 40%. Gradient-corrected functionals also underestimate paramagnetic contributions to $^{57}$Fe or $^{59}$Co NMR chemical shifts by roughly the same relative amount, whereas hybrid functionals perform significantly better. We are therefore presently implementing the calculation of g-tensors with hybrid functionals. Preliminary tests suggest that this approach may indeed provide improved accuracy.

After completion of this work, Carl et al. reported on their DFT calculations of A- and g-tensors of some vanadyl(IV) model complexes, with the aim of interpreting EPR spectra of VO$^{2+}$ exchanged zeolites. For their g-tensor calculations, they used the two-component ZORA approach of van Lenthe et al., with the BP86 GGA functional. Carl et al. report significantly larger g-shifts than in the present study and conclude that the DFT approach used provides excellent agreement with experiment. Unfortunately, this good performance is fortuitous and is probably due to cancellation of DFT errors with errors resulting from the neglect of spin polarization (and partly from the incomplete treatment of the $\Delta g_{SO/OZ(2e)}$ terms) in the two-component ZORA approach used.

The orientations of the g-tensors are displayed in Figures 2-5. Table 3 includes the angles between the principal axes of the g-tensor and the standard axes. The full specification of principal relative to the standard axes is provided as supporting information. Table 3 shows that for complexes with a trans-arrangement of the phenolate oxygen atoms, the $g_1$ principal axis is either parallel or almost parallel to the $z$ axis, whereas $g_2$ and $g_3$ are rotated with respect to $y$ and $x$, on average by $30^\circ$. For VOL$^1$, $g_2$ is almost parallel to the $y$ axis whereas $g_1$ and $g_3$ are rotated with respect to $z$ and $x$ by $12^\circ$ and $10^\circ$, respectively (note that neglect of the $\Delta g_{SO/OZ(2e)}$ terms affects the tensor orientation negligibly). For these three systems, there is no experimental information to be compared with regarding the orientation of the g-tensor with respect to the molecular framework. We focus therefore on the interpretation of the computational results. We will base our discussion on the perturbational approach discussed in section 2.

We are dealing here with d$^1$ complexes possessing genuine $C_2$ symmetry (VO(L$^2$)$_2$, VO(L$^4$)$_2$), approximate $C_2$ symmetry (VO(L$^3$)$_2$), or approximate $C_s$ symmetry
(VOL\textsuperscript{1}). As a consequence, for VO(L\textsuperscript{2})\textsubscript{2} and VO(L\textsuperscript{4})\textsubscript{2} one of the principal axes (g\textsubscript{1}) must coincide with the two-fold axis (z) for symmetry reasons.\textsuperscript{14} In a hypothetical VOL\textsuperscript{1} molecule possessing genuine C\textsubscript{s} symmetry, one of the principal axes would have to be perpendicular to the xz symmetry plane and thus coincident with the y axis. The actual deviation of g\textsubscript{2} from y (6°, cf. Table 3) may thus be considered to be a measure of the distortion from C\textsubscript{s} symmetry. For VO(L\textsuperscript{3})\textsubscript{2}, by analogy, the deviation of g\textsubscript{1} from z (7°) corresponds to the distortion from C\textsubscript{2} symmetry.

The extent of the rotation of the principal axes relative to the standard axes depends upon the values of the off-diagonal tensor elements,\textsuperscript{16} but also on the relative sizes of the principal components. For genuinely C\textsubscript{2} symmetrical complexes, it can be shown that the angle \( \phi \) between g\textsubscript{2} and y and between g\textsubscript{3} and x is related to the off-diagonal matrix g\textsubscript{xy} element and the principal g\textsubscript{22} and g\textsubscript{33} components via

\[
2g_{xy} = (g_{22} - g_{33}) \sin 2\phi .
\]

The g\textsubscript{xy} component is of the same size (cf. Table 1) for VO(L\textsuperscript{2})\textsubscript{2} and VO(L\textsuperscript{4})\textsubscript{2}, but the value of \( |g_{22}-g_{33}| \) is smaller for the former complex (cf. Table 2). Consequently, g\textsubscript{2} and g\textsubscript{3} deviate more from the y and x directions, respectively, for VO(L\textsuperscript{2})\textsubscript{2} than for VO(L\textsuperscript{4})\textsubscript{2} (cf. Table 3).

According to Mabbs and Collison,\textsuperscript{16} the rotation of g\textsubscript{2} and g\textsubscript{3} relative to y and x is dominated by the magnitude of the \( d_{x^2-y^2} \rightarrow d_{xz}, d_{x^2-y^2} \rightarrow d_{yz} \) contributions (cf. eqs 9.233 - 9.237 in ref 16), which determine the magnitudes of the g\textsubscript{xx}, g\textsubscript{yy}, and g\textsubscript{xy} elements. By analogy, the rotation of g\textsubscript{1} and g\textsubscript{3} with respect to z and x for VOL\textsuperscript{1} is determined mainly by the \( d_{x^2-y^2} \rightarrow d_{xy}, d_{x^2-y^2} \rightarrow d_{yz} \) contributions (cf. eqs 9.243 and 9.247 in ref 16).\textsuperscript{46} An analysis of different contributions to the calculated g-shifts shows that the paramagnetic (1-electron and 2-electron SO) contributions represent 99% of the g-tensor components given in Tables 1 and 2. An analysis of the orbital contributions to g-tensor elements further reveals that the SO terms corresponding to the excitations from the SOMO greatly dominate the g-tensor elements. Thus, our results show that the approach of Mabbs and Collison, which emphasizes the SOMO contributions, provides a reasonable insight into the origin of the g-tensor.

3.2. A-Tensor Calculations. Our density-functional results for the hyperfine tensor of vanadium with respect to standard and principal axes are given in Tables 4 and 5, respectively. Part of the information in Table 5 is graphically displayed in Figures 6-8.\textsuperscript{47} The SOMO provides a small direct contribution to the isotropic hyperfine coupling
constants (HFCCs), due to a slight mixing-in of the metal 4s orbital. Nevertheless, overall $A_{\text{iso}}$ is dominated by spin polarization and is thus negative. The anisotropic tensor reflects the composition of the SOMO, having one negative component along the $z$ axis and two positive components within the $xy$ plane, pointing between the V-N and V-O phenolate bonds. Like the $g$-tensor, the $A$-tensor deviates from axial symmetry. The smaller of the positive components points into the direction of the chelate ligands, and the larger one points out of the complex.

At the nonrelativistic (first-order) level of theory, the BHPW91 functional provides the best agreement with experiment for both the isotropic and the anisotropic parts of the hyperfine tensor. As has been stressed in our recent study, GGA functionals typically underestimate the spin polarization of $s$-type metal core orbitals. The latter is enhanced by exact-exchange mixing into $v_x$, frequently leading to improved agreement with experimental $A_{\text{iso}}$ data with hybrid functionals (provided that spin contamination remains low). Figure 6 illustrates the enhancement of spin polarization by inclusion of exact exchange for three of the vanadyl complexes. It also shows that, for systems with related electronic structures, the deficiencies of the state-of-the-art density functionals are systematic. An underestimate of core-shell spin polarization with the BP86 GGA functional is also apparent from the results of the very recent $A$-tensor calculations of Carl et al. for a series of vanadyl model complexes.

Similarly, adequate spin polarization of metal $p$-type core orbitals is required to reproduce the hyperfine tensor anisotropy. The absolute values of the dipolar tensor components are quantitatively reproduced only with the BHPW91 functional (cf. Table 5 and Figure 7). B3PW91, and particularly BP86, underestimate all anisotropic components. On the other hand, all unrestricted DFT approaches applied describe the rhombicity of the hyperfine tensor well. The ($T_{33} - T_{22}$) difference does not suffer from the systematic underestimate of spin polarization, as it is determined mainly by the composition of the singly occupied molecular orbital. The relative magnitudes of spin polarization of the metal $2p_x$, $3p_x$ and $2p_y$, $3p_y$ orbitals correspond to the rhombicity of the SOMO contribution to the anisotropic HFC tensor. Thus, while the absolute values of the $T_{22}$, $T_{33}$ components are significantly affected by the spin-polarization contributions, the asymmetry of the tensor ($T_{33} - T_{22}$) is reduced only slightly by core-shell spin polarization.

The present DFT calculations do not include relativistic corrections, which may be quite important for systems with significant $g$-tensor anisotropy. To obtain a simple semiempirical estimate of SO corrections, as well as an improved interpretation of the HFC anisotropy, we have used the PT approach described in section 2 to express the $A$-tensor of VO($L^2$)$_2$. The first-order (SOMO) contributions to the anisotropic part of the $A$-tensor have been estimated as $-192.8$ ($T_{zz}$), $80.3$ ($T_{xx}$), $112.5$ ($T_{yy}$), and $1.4$ ($T_{xy}=T_{yx}$).
MHz. The second-order $\Lambda_{ij}$ elements provide additional $-17.9$ ($T_{zz}$), $-6.7$ ($T_{xx}$), and $-7.4$ ($T_{yy}$) MHz. Finally, the $\Lambda'_{ij}$ elements have been estimated as $-3.4$ ($T_{zz}$), $-0.6$ ($T_{xx}$), $-1.0$ ($T_{yy}$), $-0.1$ ($T_{yx}$), and $0.2$ ($T_{xy}$) MHz. After summing these contributions and transforming the resulting tensor to its principal axes, we obtain the following components: $-214.1$ ($T_{11}$), $75.1$ ($T_{22}$), and $102.1$ ($T_{33}$) MHz. This tensor has a nonzero trace that, multiplied by a factor of $1/3$, gives the pseudocontact contribution to the isotropic HFCC ($-12.3$ MHz). Subtracting the pseudocontact term from the $T_{ii}$ components, we obtain a traceless anisotropic HFC tensor in the 2nd-order approximation. The components of this tensor are $-201.8$ MHz, $87.4$ MHz, and $114.4$ MHz, respectively. After subtraction of these contributions from the experimental HFC tensor, the B3PW91 and BHPW91 functionals would appear to describe the 1st-order hyperfine coupling about equally well. The former underestimates and the latter overestimates $A_{iso}$ and all $T_{ii}$ components.

Besides an estimate of the SO contributions, the perturbation theoretical approach qualitatively reproduces and rationalizes the rhombicity of the $A$-tensor. As discussed above, the difference $T_{22} - T_{33}$ arises mainly from the 1st-order (SOMO) contribution. The only 1st-order term which can account for this is a very small (0.2%) symmetry-allowed mixing of the metal $d_{z^2}$ orbital into the SOMO, cf. eqs (9.239)-(9.242) in ref 16. This mixing hybridizes the unpaired electron density outside of the chelate rings (i.e. in the $x$ direction, cf. Figures 2, 3), so that $T_{22} < T_{33}$. This approximate treatment cannot aim at quantitative agreement with experiment. The rhombicity of the tensor ($T_{22} - T_{33}$) is overestimated. This is understandable, as explicit restricted (ROBP86) Kohn-Sham calculations, using formula (3), also overestimate $T_{ii}$ ($T_{11} = -192.8$ MHz, $T_{22} = 80.3$ MHz, and $T_{33} = 112.5$ MHz). The influence of the second-order contributions on the asymmetry of the hyperfine tensor is only minor ($T_{33} - T_{22}$ is decreased by 0.2 MHz), as both $\Lambda_{ij}$ and the $\Lambda'_{ij}$ contributions to $T_{33}$ and $T_{22}$ have identical sign and similar magnitudes. The rhombicity of the HFC tensor in VO(L$^4$)$_2$ can be understood along the same lines as for VO(L$^3$)$_2$. The situation is more complicated for VO(L$^3$)$_2$ and VO(L$^1$)$_2$, due to the lack of symmetry.

An interesting observation has been made by Cornman et al. on the correlation of $A_{33} - A_{22}$ (in their notation $A_{xx} - A_{yy}$) and the distortion parameter $\tau$ for VO(L$^1$)$_2$, VO(L$^2$)$_2$, and VO(L$^3$)$_2$. While one of the components was found to be relatively stable with respect to the distortion, the other experienced significant enhancement (cf. Figure 8). Our calculations allow an unambiguous breakdown of the experimental tensor into its isotropic and dipolar parts. While $T_{33}$ and $A_{iso}$ increase with increasing $\tau$ ($A_{iso}$ becomes less negative; cf. Figure 6), $T_{22}$ decreases by approximately the same magnitude (cf.
Figure 7). Due to the combination of these effects, $A_{22}$ remains constant, whereas $A_{33}$ changes significantly along the SQP-5 → TBP-5 distortion coordinate (Figure 8). Thus, in contrast to the interpretation in ref 5, increasing $\tau$ affects both in-plane dipolar contributions to a similar extent. The increased difference between $T_{22}$ and $T_{33}$ from VO(L$^2$)$_2$ to VO(L$^3$)$_2$ may be understood in terms of SOMO composition: i) The metal $d_{xz}$ and $d_{yz}$ orbitals mix into the SOMO with different coefficients for VO(L$^3$)$_2$ but not for VO(L$^2$)$_2$, where this is prohibited by symmetry. ii) The vanadium $d_{z^2}$ orbital mixes into the SOMO more for VO(L$^3$)$_2$ than for VO(L$^2$)$_2$. Both contributions hybridise the spin density further out of the chelate rings in VO(L$^3$)$_2$. In VO(L$^1$)$_2$, the metal $d_{xz}$ and $d_{yz}$ orbitals mix less into the SOMO than in VO(L$^3$)$_2$ and their contribution to the anisotropy in $T_{22}$ and $T_{33}$ is compensated by reduced $d_{z^2}$ mixing, resulting in a total anisotropy that is similar as in VO(L$^1$)$_2$.

A comparison of the A-tensor results for VO(L$^2$)$_2$ and VO(L$^4$)$_2$ (cf. Table 5) reveals that the anisotropic HFC tensor components of both complexes are very close, in agreement with identical distortion parameters $\tau$ (0.55) and similar $d_{xy}$, $d_{x^2-y^2}$, $d_{z^2}$ contributions to the SOMO. Due to a higher 4s orbital contribution to the SOMO for VO(L$^4$)$_2$, the isotropic HFCC is less negative than for VO(L$^2$)$_2$.

The orientations of the $A$-tensors are shown in Figures 2-5, together with those of the $g$-tensors. Table 3 includes the angles between the principal axes of the $A$- and $g$-tensors, and the standard axes. The full specification of the principal axes of the $A$-tensor with respect to the standard axes is given as supporting information. Table 3 shows that $a_1$ is oriented either parallel or close to parallel to the $z$ axis (rotated from $z$ by maximally 6°). The axes of $a_2$ and $a_3$ are rotated with respect to $y$ and $x$ by maximally 12°. This is much less than for the $g$-tensor axes, due to the fact that the off-diagonal elements of the $A$-tensor are much smaller with respect to the asymmetry in the principal components than for the $g$-tensor (cf. eq. 13; Tables 4 and 1). Generally, the hyperfine tensor is controlled by the nature of the ground state wave function. In contrast, the $g$-tensor reflects also energies and character of the excited states. These appear to be particularly sensitive to the local metal coordination. For the same reason, the SQP-5 → TBP-5 distortion influences the $A$-tensor orientation relatively little, whereas the $g$-tensor is reoriented significantly.

Only for VO(L$^4$)$_2$, experimental information is available on the relative orientation of $g$- and $A$-tensors. Single-crystal data indicate that the $g$-tensor component with the smallest g-shift (in our notation $g_{33}$) is rotated by 27.5° relative to the $A$-tensor component with the smallest magnitude of the dipolar interaction (in our notation $A_{22}$): $\angle(a_{22}, g_{33}) = 27.5°$. Our computational results suggest that the $A_{22}$ orientation is closer to the $g_{22}$ orientation than to the $g_{33}$ orientation: $\angle(a_{22}, g_{22}) = 35.7°$, $\angle(a_{22}, g_{33}) = 27.5°$. 


∠(a_2, g_3) = 54.3° (cf. Table 3). It is possible that deficiencies in our DFT treatment are responsible for the different rotation angles. However, the angle is neither affected significantly by the inclusion or neglect of the Δg_{SO/OZ(2e)} operators nor by the use of local or gradient-corrected density functionals. At the moment we can only state that theory agrees with experiment on a ca. 30° relative rotation of the “perpendicular” principal components of g- and A-tensors. Further theoretical and/or experimental work is needed to decide which g- and A-tensor components (a_2, a_3, g_2, g_3) have the most similar orientations.

4. Conclusions

The increasing rhombicity of both A- and g-tensors with increasing deviations of the structures of vanadyl(IV) complexes from a regular square-pyramidal (SQP-5) coordination arrangement is reproduced by our density functional calculations. We could therefore provide improved interpretations of the observed trends in terms of the SOMO compositions and of spin-orbit coupling. In addition to the magnitudes of the principal components of both tensors, the calculations provide also their orientations relative to each other, and relative to the molecular framework. Such information is more difficult to obtain experimentally. In the present series of system, the necessary single-crystal experiments were only available for one of the systems, VO(L_4)_2. While some discrepancies remain in the designation of the components in this case, all calculations indicate clearly that the g-tensor is affected more by the structural distortions of the SQP-5 arrangement than the metal A-tensor. This may be rationalized by the fact that the hyperfine tensor depends only on the spin-density distribution of the ground state, whereas the g-tensor is a response property and thus also reflects the compositions of excited states. As a consequence, the A- and g-tensors are non-coaxial in all of the systems studied here. The orientation of A- and particularly g-tensors with respect to the molecular framework, or the experimentally more accessible relative orientations of g- and A-tensors, may be very sensitive probes of the local symmetry and coordination of the oxovanadium group. In the case of the A-tensor, the increasing rhombicity with increasing SQP-5 → TBP-5 distortion arises due to the mixing of metal d_{x^2} orbitals (made possible by the transformation from SQP-5 towards TBP-5 coordination), but also of metal d_{xz}, d_{yz} orbitals (allowed by the deviation from C_2 symmetry), into the d_{x^2-y^2} -type SOMO.

Apart from interpretational purposes, the present study has also served as a further validation of DFT approaches for the calculation of EPR-parameters in transition metal complexes. The vanadyl complexes studied here exhibit a SOMO with relatively little
overlap to doubly occupied metal valence orbitals. In agreement with our previous considerations, spin contamination with increasing exact-exchange mixing is therefore not a serious problem. Hybrid functionals (B3PW91, BHPW91) provide better agreement with experimental isotropic HFCCs than a GGA functional (BP86), due to an improved description of the spin polarization of metal s-type core shells. All functionals, including the BP86 GGA, reproduce well the experimentally observed trends in the anisotropy of the $A$-tensor with increasing structural distortion (which is dominated by the SOMO composition; cf. above).

As found already in the previous, extensive validation of our DFT approach for the calculation of electronic $g$-tensors, LDA or GGA functionals underestimate the paramagnetic ($\Delta g_{SO/OZ}$) contributions systematically by ca. 40% for 3d transition metal complexes (whereas a slight overestimate by ca. 10% is typical for main group radicals). In agreement with the suggestions of Patchkowskii and Ziegler, we attribute this to deficiencies of the GGA/LDA functionals in describing both energy denominators and matrix elements in the second-order perturbation theory expressions (cf. eq 3). While a partial or complete neglect of the $\Delta g_{SO/OZ}(2e)$ terms improves the agreement with experiment in the 3d complexes, this is certainly no satisfactory approach from a theoretical point of view. Preliminary tests suggest that hybrid functionals may provide better accuracy (cf. section 3.1).

Acknowledgments. We thank Drs. Pavel Kubaček, Dominik Munzar (Brno) and Juha Vaara (Helsinki) for helpful discussions. Drs. Olga L. Malkina (Bratislava) and Reinaldo Pis-Diez (UNLP, Argentine) kindly provided us with codes that simplified the analyses carried out. This work has been supported by Deutsche Forschungsgemeinschaft (Schwerpunktprogramm „Hochfeld-EPR“, SPP1051) and by Fonds der chemischen Industrie. Further support came from the graduate college “Moderne Methoden der Magnetischen Resonanz“ at Universität Stuttgart.
References

*Correspondence author, e-mail: kaupp@mail.uni-wuerzburg.de


20 The code used is due to: Schimmelpfennig, B. AMFI, Atomic Spin-Orbit Mean-Field Integral Program; Stockholms Universitet, Sweden 1996.


32 The parameter P depends on the radial wave function of the metal atom in the field of ligands and is usually treated as an adjustable parameter.

33 At this level of theory, the elements of $-2\xi_{n,l}\Lambda_{ij}$ correspond to the $\Delta g_{ij}$ elements.

34 While the first-order contribution to $T_{ij}$ is symmetrical and traceless, the $\Lambda_{ij}$ contribution is symmetrical but not traceless. In general, $\Lambda_{ij}$ is neither symmetrical nor traceless. See ref. 12 for a lucid discussion.

35 According to our calculation, the correct formulas for coefficients $C_7$ and $C_9$ should read: $C_7 = -3e_3a_1 - 3f_3b_1 - \sqrt{3}e_3c_1; \quad C_9 = 3f_3a_1 - 3e_3b_1 - \sqrt{3}f_3c_1$.

36 Formulas (9.248)-(9.252) of ref. 16 have been derived from (3)-(5), restricting the summation over $m$ to the four MOs with the largest d-orbital contributions. In our calculations, we have therefore chosen the four unoccupied MOs with largest computed metal d-character.

37 For the standard orientation of the molecule, we obtained the following d-orbital mixings: $\phi_0$(MO 45a) = 0.977 $d_{xz} + 0.098 d_{x^2-y^2} - 0.040 d_{z^2}^2; \quad \phi_1$(47a) = 0.095 $d_{xy} - 0.420 d_{x^2-y^2} + 0.387 d_{z^2}^2; \quad \phi_2$(44b) = 0.000 $d_{xz} + 0.764 d_{yz}, \quad \phi_3$(45b) = 0.721 $d_{xz} - 0.108 d_{yz}, \quad \phi_4$(49a) = $-0.082 d_{xy} + 0.516 d_{x^2-y^2} + 0.274 d_{z^2}^2$.

This definition is unique, unless the $\text{VO}^{\leftrightarrow}_{\text{ph},1}\text{O}_{\text{ph},2}$ plane is perpendicular to the $\text{VO}^{\rightarrow}_{\text{axial}}$ vector. This is not the case for any of the complexes studied here.

As Figures 6-9 serve the interpretation of the experimental findings in ref 5, we have not included the data for VO(L$^4_4$)$_2$.

This is rigorously true only for the two complexes possessing $C_2$ symmetry. For the two other complexes, we observe small deviations from the indicated directions, cf. below.

For the definition of the asymmetry (rhombicity) parameter, cf. ref 14, p. 116.

The corresponding contributions to $T_{x'y'}$ and $T_{y'x'}$ are zero, due to zero non-diagonal elements of the g-tensor (cf. Section 2).
We note that the asymmetry of the HFC tensor can be influenced also by mixing of the metal 4s orbital into the SOMO, which is symmetry-allowed. This mixing is not considered in the usual interpretations, cf. refs 12, 15, 16.

Table 1. $\Delta g$-Tensors in Standard Axes System (in ppt). $^a,b$

<table>
<thead>
<tr>
<th></th>
<th>$\Delta g_{xx}$</th>
<th>$\Delta g_{yy}$</th>
<th>$\Delta g_{zz}$</th>
<th>$\Delta g_{xy} = \Delta g_{yx}$</th>
<th>$\Delta g_{xz} = \Delta g_{zx}$</th>
<th>$\Delta g_{yz} = \Delta g_{zy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL$^1$</td>
<td>-10.3</td>
<td>-12.4</td>
<td>-27.9</td>
<td>0.3</td>
<td>-3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>VO(L$^2_1$)</td>
<td>-11.9</td>
<td>-13.0</td>
<td>-24.6</td>
<td>2.1</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>VO(L$^3_1$)</td>
<td>-10.1</td>
<td>-14.2</td>
<td>-25.6</td>
<td>2.7</td>
<td>0.7</td>
<td>-1.0</td>
</tr>
<tr>
<td>VO(L$^4_1$)</td>
<td>-10.0</td>
<td>-13.2</td>
<td>-29.8</td>
<td>2.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ UDFT-VWN results with AMFI approximation for $\Delta g_{SO/OZ(2e)}$. $^b$ The actually computed $g$-matrices are slightly asymmetric. This information is not obtainable from the experiment. It means that the principal-axes system is not strictly an orthogonal one. $^{14}$ The values reported here and the principal values reported in Table 2 have been determined using the symmetrization procedure described in ref 14, p. 91 (see also ref 17).

Table 2. Principal $\Delta g$-Tensor Components (in ppt). $^a$

<table>
<thead>
<tr>
<th></th>
<th>with $\Delta g_{SO/OZ(1e)}$ only</th>
<th>with $\Delta g_{SO/OZ(1e)} + \Delta g_{SO/OZ(2e)}$</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta g_{iso}$</td>
<td>$\Delta g_{11}$</td>
<td>$\Delta g_{22}$</td>
</tr>
<tr>
<td>VO(L$^2_1$)</td>
<td>-32.7</td>
<td>-48.8</td>
<td>-29.1</td>
</tr>
<tr>
<td>VO(L$^3_1$)</td>
<td>-34.8</td>
<td>-55.6</td>
<td>-31.5</td>
</tr>
<tr>
<td>VO(L$^4_1$)</td>
<td>-35.2</td>
<td>-59.7</td>
<td>-28.3</td>
</tr>
</tbody>
</table>

$^a$ UDFT-VWN results. See also footnote b to Table 1. $^b$ Ref 5, estimated error of $\Delta g$: $\pm$ 1 ppt, EPR on polycrystalline substance. $^c$ EPR on [VO(mquin)$_2$] in a dilute crystal of [GaCl(mquin)$_2$] (cf. ref 11). $^d$ Values obtained in pure crystal (cf. ref 11).
Table 3. Rotation Angles (in deg) between Principal Axes of $g$- and $A$- Tensors and the Standard Axes$^a$

<table>
<thead>
<tr>
<th>complex</th>
<th>$\angle(g_1,z)$</th>
<th>$\angle(a_1,z)$</th>
<th>$\angle(g_1,a_1)$</th>
<th>$\angle(g_2,y)$</th>
<th>$\angle(a_2,y)$</th>
<th>$\angle(g_2,a_2)$</th>
<th>$\angle(g_3,x)$</th>
<th>$\angle(a_3,x)$</th>
<th>$\angle(g_3,a_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL$^1$</td>
<td>11.6</td>
<td>4.7</td>
<td>6.9</td>
<td>6.1</td>
<td>11.5</td>
<td>11.1</td>
<td>10.0</td>
<td>12.4</td>
<td>12.0</td>
</tr>
<tr>
<td>VO(L$^2$)$_2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>37.7</td>
<td>11.3</td>
<td>49.0</td>
<td>37.7</td>
<td>11.3</td>
<td>49.0</td>
</tr>
<tr>
<td>VO(L$^3$)$_2$</td>
<td>6.6</td>
<td>0.8</td>
<td>6.2</td>
<td>26.9</td>
<td>5.1</td>
<td>31.9</td>
<td>26.2</td>
<td>5.2</td>
<td>31.4</td>
</tr>
<tr>
<td>VO(L$^4$)$_2$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>25.8</td>
<td>10.0</td>
<td>35.7</td>
<td>25.8</td>
<td>10.0</td>
<td>35.7</td>
</tr>
</tbody>
</table>

$^a$ UDFT-VWN results with AMFI approximation for $\Delta g_{SO/OZ(2e)}$ (g-tensor) and UBHPW91 results (A-tensor). See also footnotes to Table 1.

Table 4. $A$-Tensors in the Standard Axes (in MHz).$^a$

<table>
<thead>
<tr>
<th></th>
<th>$A_{xx}$</th>
<th>$A_{yy}$</th>
<th>$A_{zz}$</th>
<th>$A_{xx}=A_{yy}$</th>
<th>$A_{xz}=A_{yz}$</th>
<th>$A_{xy}=A_{yx}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL$^1$</td>
<td>107.6</td>
<td>98.0</td>
<td>-205.6</td>
<td>-1.7</td>
<td>-24.8</td>
<td>-1.7</td>
</tr>
<tr>
<td>VO(L$^2$)$_2$</td>
<td>112.4</td>
<td>93.5</td>
<td>-205.9</td>
<td>-3.9</td>
<td>0.0</td>
<td>-3.9</td>
</tr>
<tr>
<td>VO(L$^3$)$_2$</td>
<td>119.3</td>
<td>83.7</td>
<td>-202.9</td>
<td>-3.2</td>
<td>1.8</td>
<td>-3.2</td>
</tr>
<tr>
<td>VO(L$^4$)$_2$</td>
<td>114.7</td>
<td>90.9</td>
<td>-205.6</td>
<td>-4.3</td>
<td>0.0</td>
<td>-4.3</td>
</tr>
</tbody>
</table>

$^a$ UBHPW91 results.
Table 5. Principal \( A \)-Tensor Components (in MHz)

<table>
<thead>
<tr>
<th></th>
<th>BP86</th>
<th>B3PW91</th>
<th>BHPW91</th>
<th>Exp./nominal ( &lt;S^2&gt; )</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL(^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{iso} )</td>
<td>-183.0</td>
<td>-231.7</td>
<td>-299.6</td>
<td>-274.3</td>
</tr>
<tr>
<td>( T_{11}, T_{22}, T_{33} )</td>
<td>-177.9, 79.0, 98.9</td>
<td>-193.9, 89.5, 104.4</td>
<td>-207.8, 97.8, 110.0</td>
<td>-209.3, 96.8, 112.4</td>
</tr>
<tr>
<td>( &lt;S^2&gt;^b )</td>
<td>0.7566</td>
<td>0.7618</td>
<td>0.7754</td>
<td>0.7500</td>
</tr>
<tr>
<td>VO(L(^2))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{iso} )</td>
<td>-179.0</td>
<td>-230.1</td>
<td>-297.8</td>
<td>-273.9</td>
</tr>
<tr>
<td>( T_{11}, T_{22}, T_{33} )</td>
<td>-182.2, 79.6, 102.7</td>
<td>-194.3, 86.5, 107.8</td>
<td>-205.9, 92.7, 113.2</td>
<td>-208.8, 94.0, 114.7</td>
</tr>
<tr>
<td>( &lt;S^2&gt;^b )</td>
<td>0.7578</td>
<td>0.7661</td>
<td>0.7856</td>
<td>0.7500</td>
</tr>
<tr>
<td>VO(L(^2))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{iso} )</td>
<td>-157.6</td>
<td>-217.0</td>
<td>-290.4</td>
<td>-264.3</td>
</tr>
<tr>
<td>( T_{11}, T_{22}, T_{33} )</td>
<td>-172.9, 63.8, 109.1</td>
<td>-189.5, 74.1, 115.4</td>
<td>-203.0, 83.4, 119.6</td>
<td>-207.3, 86.2, 121.0</td>
</tr>
<tr>
<td>( &lt;S^2&gt;^b )</td>
<td>0.7586</td>
<td>0.7655</td>
<td>0.7838</td>
<td>0.7500</td>
</tr>
<tr>
<td>VO(L(^4))(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( A_{iso} )</td>
<td>-164.3</td>
<td>-216.8</td>
<td>-295.8</td>
<td>-262.9</td>
</tr>
<tr>
<td>( T_{11}, T_{22}, T_{33} )</td>
<td>-183.0, 76.7, 106.3</td>
<td>-194.3, 82.7, 111.7</td>
<td>-205.6, 90.2, 115.5</td>
<td>-208.7, 93.2, 115.4</td>
</tr>
<tr>
<td>( &lt;S^2&gt;^b )</td>
<td>0.7580</td>
<td>0.7645</td>
<td>0.7834</td>
<td>0.7500</td>
</tr>
</tbody>
</table>

\(^a\) Unrestricted Kohn-Sham calculations with specified exchange-correlation functionals.

\(^b\) These \( <S^2> \) values pertain to the Kohn-Sham wavefunction, i.e. to the non-interacting reference system rather than to the real system. Such data are nevertheless expected to give a reasonable and useful representation for the real system as well (see, e.g.: Baker, J.; Scheiner, A.; Andzelm, J. *Chem. Phys. Lett.* **1993**, *216*, 380).
Figure Captions.

Figure 1. The vanadyl complexes studied. (a) VOL\(^1\). (b) VO(L\(^2\))\(_2\) (R=H, R’=H) and VO(L\(^3\))\(_2\) (R=t-Bu, R’=Me). (c) VO(L\(^4\))\(_2\).

Figure 2. The standard orientation of the coordinate system, and the calculated \(g\)- and \(A\)-tensor for VOL\(^1\).

Figure 3. The standard orientation of the coordinate system, and the calculated \(g\)- and \(A\)-tensor for VO(L\(^2\))\(_2\).

Figure 4. Orientation of the calculated \(g\)- and \(A\)-tensor for VO(L\(^3\))\(_2\).

Figure 5. Orientation of the calculated \(g\)- and \(A\)-tensor for VO(L\(^4\))\(_2\).

Figure 6. Dependence of the isotropic hyperfine coupling constants on the distortion parameter \(\tau\). BP86, B3PW91, BHPW91, and experimental results are compared for VOL\(^1\), VO(L\(^2\))\(_2\), and VO(L\(^3\))\(_2\).

Figure 7. Dependence of the anisotropic hyperfine tensor components on the distortion parameter \(\tau\). BP86, B3PW91, BHPW91, and experimental results are compared.

Figure 8. Dependence of the total (isotropic+anisotropic) hyperfine tensor components on the distortion parameter \(\tau\). BHPW91 and experimental results are compared.
complex VO_L$^1$
complex \quad R \quad R' \\
\text{VO}_2(L^2)_2 \quad H \quad H \\
\text{VO}_2(L^3)_2 \quad t-\text{Bu} \quad \text{Me}
complex $\text{VO}_2(L^4)$
Figure 2
Figure 3
Figure 6

The figure shows a graph with the following elements:

- The x-axis represents \( \tau \) with values ranging from 0.2 to 0.8.
- The y-axis represents \( A_{\text{rot}} \) (MHz) ranging from -320 to -150.
- The graph plots data for different complexes labeled as \( \text{VOL}^1 \), \( \text{VO(L}^2\text{)}_2 \), and \( \text{VO(L}^3\text{)}_2 \) with \( \tau \) values of 0.26, 0.55, and 0.70, respectively.
- The lines and markers indicate different theoretical and experimental results:
  - BP86
  - B3PW91
  - exp
  - BHPW91
Figure 7
Figure 8

The figure shows a graph plotting various parameters against a parameter \( \tau \). The graph includes data for different systems such as \( \text{VOL}^1 \), \( \text{VO}(L^2) \), and \( \text{VO}(L^3) \), each with different values of \( \tau \) (0.26, 0.55, 0.70). The y-axis represents \( A_z \) in MHz, ranging from -140 to -210. The x-axis represents \( \tau \) ranging from 0.2 to 0.8.

Key points:
- \( A_{33}, \text{exp} \)
- \( A_{22}, \text{exp} \)
- \( A_{33}, \text{BHPW91} \)
- \( A_{22}, \text{BHPW91} \)
Supporting Information

S1. Optimized Structure of Bis(2-methylquinoline-8-olate)oxovanadium(IV)\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>O</td>
<td>0.000000</td>
<td>0.000000</td>
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</tr>
<tr>
<td>O</td>
<td>1.713629</td>
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<td>-0.897952</td>
</tr>
<tr>
<td>N</td>
<td>0.225038</td>
<td>-2.104342</td>
<td>-0.413117</td>
</tr>
<tr>
<td>C</td>
<td>2.207334</td>
<td>-1.166282</td>
<td>-1.292552</td>
</tr>
<tr>
<td>C</td>
<td>1.416075</td>
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<tr>
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<td>-0.115497</td>
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<td>H</td>
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<td>H</td>
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<tr>
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</tr>
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<tr>
<td>H</td>
<td>-1.646410</td>
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<td>1.603172</td>
</tr>
</tbody>
</table>

\textsuperscript{a}B3LYP/ECP optimized structure. \textsuperscript{b}Cartesian coordinates in Å. The first two atoms lie on the C\textsubscript{2} symmetry axis (z) which for each of the following atoms defines a symmetry-related counterpart. The latter atoms are omitted from this table.
### S2. Principal Axes of the $g$-Tensor Relative to the Standard Orientation

<table>
<thead>
<tr>
<th>complex</th>
<th>$g_{1x}$</th>
<th>$g_{1y}$</th>
<th>$g_{1z}$</th>
<th>$g_{2x}$</th>
<th>$g_{2y}$</th>
<th>$g_{2z}$</th>
<th>$g_{3x}$</th>
<th>$g_{3y}$</th>
<th>$g_{3z}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL$^1$</td>
<td>0.1708</td>
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<td>0.9797</td>
<td>0.0284</td>
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<td>0.1018</td>
<td>0.9849</td>
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</tr>
<tr>
<td>VO(L$^2$)$_2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
<td>-0.6112</td>
<td>0.7915</td>
<td>0.0000</td>
<td>0.7915</td>
<td>0.6112</td>
<td>0.0000</td>
</tr>
<tr>
<td>VO(L$^3$)$_2$</td>
<td>-0.0599</td>
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<td>0.4419</td>
<td>0.0110</td>
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<tr>
<td>VO(L$^4$)$_2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
<td>-0.4347</td>
<td>0.9006</td>
<td>0.0000</td>
<td>0.9006</td>
<td>0.4347</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

$^a$Both $\Delta g_{SO/OZ(1e)}$ and $\Delta g_{SO/OZ(2e)}$ operators have been included. $^b$ $g_1$, $g_2$ and $g_3$ are the axes corresponding to the $g_{11}$, $g_{22}$ and $g_{33}$ principal values.

### S3. Principal Axes of the Hyperfine Tensor Relative to the Standard Orientation

<table>
<thead>
<tr>
<th>complex</th>
<th>$a_{1x}$</th>
<th>$a_{1y}$</th>
<th>$a_{1z}$</th>
<th>$a_{2x}$</th>
<th>$a_{2y}$</th>
<th>$a_{2z}$</th>
<th>$a_{3x}$</th>
<th>$a_{3y}$</th>
<th>$a_{3z}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOL$^1$</td>
<td>0.0781</td>
<td>-0.0285</td>
<td>0.9967</td>
<td>0.1998</td>
<td>0.9798</td>
<td>0.0123</td>
<td>0.9767</td>
<td>-0.1981</td>
<td>-0.0822</td>
</tr>
<tr>
<td>VO(L$^2$)$_2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
<td>0.1965</td>
<td>0.9805</td>
<td>0.0000</td>
<td>0.9805</td>
<td>-0.1965</td>
<td>0.0000</td>
</tr>
<tr>
<td>VO(L$^3$)$_2$</td>
<td>-0.0016</td>
<td>0.0016</td>
<td>0.9999</td>
<td>0.0903</td>
<td>0.9960</td>
<td>-0.0006</td>
<td>0.9959</td>
<td>-0.0902</td>
<td>0.0127</td>
</tr>
<tr>
<td>VO(L$^4$)$_2$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.0000</td>
<td>0.1735</td>
<td>0.9849</td>
<td>0.0000</td>
<td>0.9849</td>
<td>-0.1735</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

$^a$ $a_1$, $a_2$ and $a_3$ are the axes corresponding to the $A_{11}$, $A_{22}$ and $A_{33}$ principal values.
9 Conclusions

The field of applied quantum chemistry has undergone a major development during the last four decades. The first applications of quantum mechanical methods in inorganic chemistry, introduced in the 1960s mainly by the school of Roald Hoffmann, were based on very simple semi-empirical models. The concepts that arose from these approaches have significantly shaped the ways of understanding the electronic structure and reactivity throughout the whole of chemistry. Over the years, a number of \textit{ab initio} quantum chemistry methods have been developed that enable much higher accuracy than the more qualitative semi-empirical approaches. Nowadays, applications of sophisticated \textit{ab initio} computational methods certainly dominate applied quantum chemistry. Unfortunately, the better agreement with experiment given by these methods is very often being obtained at the cost of reduced understanding of the results. Quantitative calculations easily move one’s attention away from the chemical and physical understanding to applied mathematics. However, questions posed at chemical level of complexity should be answered at the same level of complexity.\textsuperscript{1} Thus there is a great need for an interplay between the computational and interpretational aspects of applied quantum chemistry. One way of combining these aspects is to derive the general frameworks of understanding on a qualitative level and study the quantitative aspects at a higher level of theory. Two joint works of the author and Roald Hoffmann are an example of this type of approach.\textsuperscript{2}

In the author’s opinion, the most general outcome of the work reported in this thesis is the illustration of the importance of the opposite approach that starts with performing quantitative calculations and looking for the interpretation of the observed trends. The first step has been undertaken in a critical validation study of density functional approaches for the quantitative calculation of hyperfine tensors for transition
metal complexes (Chapter 5). The second step, the qualitative understanding of the observed trends, is given in the study of mechanisms of EPR hyperfine coupling in transition metal complexes (Chapter 7). The approach adopted in the latter paper is very closely connected to the concept of orbital interactions. It has proven to be particularly fruitful for understanding the physical mechanisms of transfer of spin density within the molecule.

A further important aspect of the studies reported in Chapters 5 and 7 is the identification of density functionals that are appropriate for reproducing and understanding EPR spectra in particular bonding situations. This has been illustrated in the application study reported in Chapter 8. It provides both the reproduction of experimental $A$-tensors for systems of chemical (and biological) interest but also interprets the observed trends in terms of spin Hamiltonian parameters.

Finally, the results of the validation studies for both $A$- and $g$-tensor calculations (Chapters 5 and 7), as well as the interpretational study are important from the point of view of development of density functional approaches. The studies have shown that the desirable, improved functionals should provide sufficiently large spin polarization for core and valence shells without exaggerating it for the latter, and thus introducing spin contamination. Generally, hyperfine coupling constants, in particular for transition metal systems, may turn out to be a particularly fruitful testing ground for new DFT (or alternative) approaches. Another important issue is the account of relativistic effects on the spin Hamiltonian parameters. In the present thesis, this aspect has been touched in some detail for the electronic $g$-tensors but only at the semi-empirical level for the hyperfine tensors. The theoretical results for electronic $g$-tensors suggest the direction in that further development of density functionals is needed. Furthermore, they illustrate once again the particularly fruitful interaction between experiment and theory that is so characteristic for the field of electron paramagnetic resonance.
References


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