

Four-Component Relativistic DFT Calculations of NMR Shielding Tensors for Paramagnetic Systems

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Abstract

A four-component relativistic method for the calculation of NMR shielding constants of paramagnetic doublet systems has been developed and implemented in the RESPECT program package. The method uses a Kramer unrestricted non-collinear formulation of density functional theory (DFT), providing the best DFT framework for property calculations of open-shell species. The evaluation of paramagnetic NMR tensors (pNMR) reduces to the calculation of the electronic g tensors, hyperfine coupling tensors and NMR shielding tensors. For all properties, modern four-component formulations were adopted. The use of both restricted kinetically and magnetically balanced basis sets along with gauge-including atomic orbitals ensures rapid basis set convergence. These approaches are exact in the framework of the Dirac-Coulomb Hamiltonian, thus providing useful reference data for more approximate methods. Benchmark calculations on Ru(III) complexes demonstrate the good performance of the method in reproducing experimental data and also its applicability to chemically relevant medium-sized systems. A decomposition of the temperature-dependent part of the pNMR tensor into the traditional contact and pseudocontact terms is proposed.

1 Introduction

Nuclear magnetic resonance (NMR) spectroscopy is routinely used in many areas of chemical research.¹ Although the vast majority of studies deals with diamagnetic systems, the NMR of paramagnetic substances (pNMR) is becoming crucial in many areas of research, for example in the development of new magnetic materials^{2,3} or in studies of biological systems.^{4,5} Bertini *et al.*⁴ note that one third of all proteins are metalloproteins, and a significant number of these metalloproteins are paramagnetic. It is therefore reasonable to expect a growth in the importance of pNMR, especially in view of recent pNMR instrumental improvements.⁶ In turn, this requires new theoretical approaches for the analysis and interpretation of experimental data. It would also be very desirable to assess the accuracy of the approximations currently used in experimental studies and to propose better shift-structure relations.

It is customary to decompose the pNMR shift of nucleus M into three contributions (here we will restrict ourselves to the isotropic part of the pNMR tensor)⁷

$$\delta_M = \delta_M^{\text{orb}} + \delta_M^{\text{fc}} + \delta_M^{\text{pc}}, \quad (1)$$

where δ_M^{orb} , δ_M^{fc} and δ_M^{pc} denote the orbital, contact and pseudocontact shifts, respectively. In theoretical calculations, based on the Ramsey theory of NMR^{8,9} (see also ref 10 and references therein), the orbital shift δ_M^{orb} is evaluated as the difference between the chemical shielding of some reference compound and the orbital contribution to the shielding tensor of the investigated paramagnetic systems

$$\delta_M^{\text{orb}} = \sigma_M^{\text{ref}} - \sigma_M^{\text{orb}}. \quad (2)$$

The orbital contribution is approximately temperature independent (neglecting the vibrational motion of the nuclei) and in both theoretical as well as experimental studies it is usually approximated by the NMR shift of the diamagnetic analogue of the molecular system. To avoid this approximation in experimental studies, the temperature-(in)dependent parts of Eq. (1) can be separated by a least square fit ($1/T$ dependence) of NMR spectra measured at different temperatures. From this fit, it is also possible to assign the measured NMR signals to the shielding constants of individual nuclei. However this approach requires precise measurements of pNMR shifts over a wide temperature range, and its applicability is therefore somewhat limited.

The contact and pseudocontact terms^{7,11,12} in Eq. (1) are temperature dependent and they appear in addition to the usual Ramsey orbital term only if the populated states are degenerate. These terms are therefore unique for paramagnetic systems. In the simplest case, when the system obeys the Curie law [*i.e.* in the absence of Zero-Field Splitting (ZFS) and when the $(2S + 1)$ degenerate ground state is well separated from excited energy levels] the contact shift obeys¹¹

$$\delta_M^{\text{fc}} = \frac{\mu_e}{\gamma_M} \frac{S(S+1)}{3kT} g^{\text{iso}} A_M^{\text{iso}}, \quad (3)$$

where μ_e is the Bohr magneton, γ_M – the gyromagnetic ratio of nucleus M, kT – the thermal

energy, $(2S + 1)$ – the multiplicity of the ground state, g^{iso} – the isotropic part of the g tensor and $A_{\text{M}}^{\text{iso}}$ – the isotropic part of the hyperfine coupling tensor. In this particular case, the contact shift originates from the isotropic hyperfine interaction, which is represented in non-relativistic theory by the Fermi contact operator (hence the acronym contact shift), and the "averaged electron spin at the position of the nucleus".⁴ The contact shift in this approximate form can therefore be used to extract the spin density at nucleus M (see ref 3 and references therein).

If the electron spin on the paramagnetic center can be considered as a point dipole (with respect to the measured nucleus) and if the studied system obeys the Curie law, the pseudocontact shift can be evaluated as¹²

$$\delta_{\text{M}}^{\text{pc}} = \frac{\mu_{\text{e}}}{\gamma_{\text{M}}} \frac{S(S+1)}{9kT} \text{Tr} \left(\mathbf{g}^{\text{ani}} \mathbf{A}_{\text{M}}^{\text{dip}} \right), \quad (4)$$

where \mathbf{g}^{ani} denotes the g -tensor anisotropy and $\mathbf{A}_{\text{M}}^{\text{dip}}$ is the dipolar part of the hyperfine coupling tensor. Eq. (4) can be written in different forms.^{4,7,12} We have chosen the form which is consistent with the theory presented in Section 2. The pseudocontact shift can be rationalized as the dipolar interaction between an averaged electron magnetic moment (typically centered on the metal center) and the magnetic moment of the nucleus of interest. From the experimental point of view, the pseudocontact shift contains useful structural information and can help *e.g.* to determine the structure of metalloproteins (see refs 4,5 and references therein).

Although these simple models for pNMR have been applied successfully for more than 50 years, modern quantum-chemical methods have during the last decade gradually been abandoning many of the assumptions and approximations invoked in the derivation of the pNMR shielding constant. This started in 2003 when Rinkevicius *et al.*¹³ calculated the orbital term directly for paramagnetic systems. They calculated the corresponding quantities only to the lowest order in the fine-structure constant c^{-2} (often referred to as the "non-relativistic" limit), thus neglecting the spin-orbit (SO) as well as scalar relativistic (SR) corrections to the shielding constant. Due to these approximations, they were not able to obtain the isotropic pseudocontact shift. Therefore the method could only be applied to systems containing light elements¹⁴ with large HOMO-LUMO gaps because the SO effect otherwise can be big even for a relatively light system.¹⁵

A new chapter in the development of computational approaches for pNMR came with the work of Moon and Patchkovskii,¹⁶ where the authors presented a modern theory of the pNMR shift (recently an alternative theory was proposed by Van Den Heuvel and Soncini^{17,18}). Inspired by the work of Moon and Patchkovskii, Pennanen and Vaara,^{19–21} and Hrobárik *et al.*²² formulated a theory which also includes relativistic spin-orbit corrections to the calculated pNMR shifts. These effects were formulated consistently to order c^{-4} , using a perturbation theory based on the Breit–Pauli Hamiltonian.²³ However, in the actual calculations some of the SO terms were calculated approximately using an atomic mean-field approach (AMFI).²⁴ Moreover, all SO operators contributing to the orbital shift in Eq. (2) were neglected, except for the calculation of the diamagnetic reference value in the work of Hrobárik *et al.*²² who used a third-order perturbation theory to include these corrections.^{25–27}

A popular way to include relativistic effects in calculations is to use the Zero-Order Regular Approximation (ZORA).²⁸ In contrast to Breit–Pauli perturbation theory described in the previous paragraph, the wave function obtained when using the ZORA Hamiltonian contains scalar and spin-orbit effects from the outset. However, since all efficient ZORA implementations use an atomic approximation to the potential in the ZORA kinetic energy term,^{29,30} all two-electron scalar and SO interactions originating from the Coulomb interaction are approximate (such as the spin-same-orbit²³ contribution) and all two-electron terms arising from the Gaunt interaction (such as the spin-other-orbit²³ contribution) are neglected. These approximations can lead to significant errors in the g tensor calculations (up to 25–30 % for light-element compounds and about 10 % for compounds containing heavy elements).³¹ The first calculations of pNMR shifts based on the ZORA Hamiltonian were performed by Rastrelli and Bagno.³² They used Eq. (3) and an analogue of Eq. (4) (based on the susceptibility tensor) to calculate the contact and pseudocontact isotropic shift, respectively. Autschbach *et al.*³³ revised some of the isotropic pNMR shifts from ref 32, noticing in particular the importance of a spin-unrestricted formalism for the calculation of the g tensors and hyperfine coupling tensors and the unsatisfactory quality of the pseudocontact shifts estimates from the susceptibility tensor. Recently, Autschbach and coworkers^{34,35} used the theory

of Moon and Patchkovskii¹⁶ to calculate pNMR shifts. In their implementation, one-electron scalar relativistic effects were included variationally in the unperturbed wave function, whereas the SO effects were added as a perturbation in the calculations of the hyperfine coupling and the g tensors. However the SO corrections were omitted in the calculation of the orbital contribution to the pNMR shift (Eq. 1).

From this brief review of the developments made in the calculation of pNMR shifts during the last decade, we note that all available methods involve (sometimes significant) approximations to the fully relativistic approach for calculating pNMR, restricting the applicability of these methods only to the upper rows of the periodic table. Even in the case of light elements one must be very careful when omitting relativistic SO effects. Since pNMR spectroscopy by default treats systems with higher spin multiplicity, special care must be taken to properly incorporate SO effects even for systems containing relatively light elements. To illustrate this, let us note that in a system without any SO interaction, the anisotropy of the g tensor will vanish, making the pseudocontact isotropic shift zero [Eq. (4)], and therefore no structural information will be obtained. This is in clear contradiction with experimental observations where the pseudocontact shift is used to obtain structural information of metalloproteins.^{4,5}

Here we present an efficient DFT approach to the calculation of pNMR shifts based on the full Dirac-Coulomb Hamiltonian, thus lifting most of the approximations described above, and relying on our long-standing experience with four-component calculations of EPR and NMR parameters.³⁶⁻⁴³ Our aim is not only to provide useful data against which other more approximate methods can be benchmarked, but also to demonstrate the applicability of the current implementation to systems of chemical interest. For this purpose we have chosen two Ru(III) complexes previously studied in the work of Rastrelli and Bagno.³² Both complexes have been studied experimentally (*mer*-Ru(ma)₃⁴⁴ and NAMI⁴⁵) and they are also interesting because of their potential medical applications. Note that our goal here is to compare our approach with previous relativistic calculations rather than a detailed analysis of the experimental data.

In this work, we will apply our method to the study of effective doublet systems, consequently

avoiding systems with ZFS effects (in contrast to refs 17,18,20–22,35 where such effects were included). In a forthcoming publication, we will extend the approach presented here to systems with non-zero ZFS.

The remainder of the paper is organized as follows. In Section 2 we present the theory of our relativistic four-component DFT approach to the calculation of pNMR shifts. In Section 3 we describe the computational details and the results of our calculations are reported in Section 4. Concluding remarks and an outlook are given in Section 5.

2 Theory

Let us consider a paramagnetic system in an external magnetic field \vec{B} . Because of the electrons, nucleus M in this system experiences a local magnetic field different from \vec{B} . In NMR spectroscopy, the interaction of this electron-induced magnetic field and the magnetic moment $\vec{\mu}^M$ of nucleus M is measured and quantified in terms of the shielding constant. In diamagnetic systems, the NMR shielding tensor is the bilinear derivative of the energy of the non-degenerate ground state with respect to the perturbations \vec{B} and $\vec{\mu}^M$. An important feature of paramagnetic systems is that, under experimental conditions (in the presence of an external magnetic field), there is more than one thermally accessible state, including both the Zeeman-split ground state and other low-lying excited states. The energy of the system in thermal equilibrium must then be averaged over the ensemble of these states. The pNMR shielding tensor can then be expressed as follows^{7,16–18}

$$\sigma_{uv}^M = \frac{\partial^2 \langle E(\vec{B}, \vec{\mu}^M) \rangle}{\partial B_u \partial \mu_v^M} \Bigg|_{\vec{B}=\vec{\mu}^M=0}, \quad (5)$$

where $\langle E(\vec{B}, \vec{\mu}^M) \rangle$ denotes the thermal average of the energy and B_u and μ_v^M are Cartesian components of vectors \vec{B} and $\vec{\mu}^M$, respectively. In this work, we will only consider the simplest case where in the absence of an external magnetic field, all excited states are well separated from the doubly degenerate ground state. Although there exist two different ways of expressing the pNMR

shielding tensor within these assumptions,^{16–18} here we follow the work of Soncini and Van den Heuvel^{17,18} as this approach does not require the symmetrization of the g tensor $\mathbf{G} = \mathbf{g}\mathbf{g}^T$ and it is thus more general. The paramagnetic NMR shielding tensor then reads

$$\boldsymbol{\sigma}^M = \boldsymbol{\sigma}_M^{\text{orb}} - \frac{\mu_e}{4\gamma_M kT} \mathbf{g}\mathbf{A}_M^T, \quad (6)$$

where $(\boldsymbol{\sigma}_M^{\text{orb}})_{uv}$, g_{ut} and $(A_M)_{vt}$ are the NMR shielding tensor, g tensor and hyperfine coupling (HFC) tensor of the M 'th nucleus, respectively, and t is a Cartesian component of an effective spin operator \vec{S}_{eff} . We note that all assumptions needed for deriving Eq. (6) also holds for the Dirac–Coulomb Hamiltonian that we are going to use in this work, and in particular the time-reversal symmetry of the relativistic operators.

$\boldsymbol{\sigma}_M^{\text{orb}}$ in Eq. (6) is the usual NMR shielding tensor known from Ramsey's theory^{8,9} with the difference that the reference wave function is one of the Kramer states. We will refer to $\boldsymbol{\sigma}_M^{\text{orb}}$ as the orbital contribution to the pNMR shielding tensor and we will use it to obtain the orbital part of the pNMR shift in Eq. (2).

In the relativistic theory there is ambiguity in the separation of the second term on the right-hand side of Eq. (6) into the contact and pseudocontact contribution [Eq. (1)]. This ambiguity is already observed when using perturbation theory.^{19,22} In the four-component relativistic theory, the separation will become even more difficult since relativistic effects are included variationally into the four-component wave function. Therefore one can only ensure the correct non-relativistic limit for this separation. To achieve such a separation, we follow the work of Bertini *et al.*,⁴ where the contact pNMR tensor depends on the isotropic Fermi contact contribution to the HFC tensor and the orientation-dependent induced electron magnetic moment,^{7,46} and the pseudocontact pNMR tensor involves the traceless dipole interaction operator [see the definitions in Eqs. (10) and (11)].

Let us first decompose the HFC tensor and g tensor into isotropic and anisotropic parts

$$\mathbf{X} = X^{\text{iso}}\mathbf{1} + \mathbf{X}^{\text{ani}}, \quad (7)$$

$$X^{\text{iso}} \equiv \frac{1}{3}\text{Tr}[\mathbf{X}], \quad (8)$$

$$\mathbf{X}^{\text{ani}} \equiv \mathbf{X} - X^{\text{iso}}\mathbf{1}. \quad (9)$$

In the spirit of the above discussion, we use this decomposition of the hyperfine coupling tensor into the isotropic and anisotropic parts as a guideline for the separation of the contact and pseudo-contact contributions to the pNMR shift tensor

$$\delta_{\text{M}}^{\text{fc}} = \frac{\mu_{\text{e}}}{4\gamma_{\text{M}}kT} \mathbf{g}\mathbf{A}_{\text{M}}^{\text{iso}}, \quad (10)$$

$$\delta_{\text{M}}^{\text{pc}} = \frac{\mu_{\text{e}}}{4\gamma_{\text{M}}kT} \mathbf{g}\mathbf{A}_{\text{M}}^{\text{ani},T}, \quad (11)$$

with the isotropic part

$$\delta_{\text{M}}^{\text{fc}} = \frac{\mu_{\text{e}}}{4\gamma_{\text{M}}kT} g^{\text{iso}} A_{\text{M}}^{\text{iso}}, \quad (12)$$

$$\delta_{\text{M}}^{\text{pc}} = \frac{\mu_{\text{e}}}{12\gamma_{\text{M}}kT} \text{Tr} \left(\mathbf{g}^{\text{ani}} \mathbf{A}_{\text{M}}^{\text{ani},T} \right). \quad (13)$$

Note that the conventional equations for the isotropic part of the pNMR shift [Eqs. (3) and (4)] are consistent with the definitions in Eqs. (12) and (13). This separation is also consistent with the definitions in refs 19,22, but it should be kept in mind that the contact and pseudocontact terms in Eqs. (10) and (11) keep their traditional meaning only approximately.¹⁹ For example, the contact shift in Eq. (12) is not defined exclusively by the spin density at the nucleus because in the relativistic theory the spin-dipolar and paramagnetic spin-orbit operators also give isotropic contributions to the HFC tensor. Similarly, the pseudocontact shift does not contain structural information in the form as anticipated in ref 4, because for example the Fermi contact operator have an anisotropic contribution to the HFC tensor.

In the following, we summarize the important aspects of the four-component relativistic calculations of all ingredients in Eq. (6). For more details about the evaluation of the g tensor, HFC tensor and chemical shielding tensor at the four-component DFT level, we refer the interested reader to refs 36–38,40,41. First we will discuss the orbital part of the pNMR tensor, followed by a brief summary of the four-component calculations of the g tensor and the HFC tensor.

We begin with the expression for the Dirac-Kohn-Sham energy in the presence of the external magnetic field and the magnetic field due to the magnetic moment of a nucleus. In the framework of the Born–Oppenheimer approximation (using the Hartree system of atomic units throughout this paper) we can write

$$E^{(\vec{B}, \vec{\mu}^M)} = E_{\text{kin}}^{(\vec{B}, \vec{\mu}^M)} + E_{\text{nuc}}^{(\vec{B}, \vec{\mu}^M)} + E_{\text{ce}}^{(\vec{B}, \vec{\mu}^M)} + E_{\text{xc}}^{(\vec{B}, \vec{\mu}^M)}. \quad (14)$$

The right-hand side of this equation consists of the relativistic kinetic energy, the electron-nucleus Coulomb energy, the electron-electron Coulomb energy and the exchange–correlation energy functional, respectively. We write the relativistic kinetic energy, in the framework of DFT, as

$$E_{\text{kin}}^{(\vec{B}, \vec{\mu}^M)} = \left\langle \varphi_i^{(\vec{B}, \vec{\mu}^M)} \left| (\beta - \mathbf{1})c^2 + c\vec{\alpha} \cdot \vec{p} + \vec{\alpha} \cdot \vec{A}_{\vec{B}0} + \vec{\alpha} \cdot \vec{A}_{\vec{\mu}^M} \right| \varphi_i^{(\vec{B}, \vec{\mu}^M)} \right\rangle. \quad (15)$$

We have here and in the following assumed implicit summation over repeated indices. In this equation, c is the speed of light, \vec{p} is the momentum operator, φ_i represents the i 'th four-component molecular orbital (MO), $\vec{A}_{\vec{B}0}$ is the vector potential generated by the external magnetic field \vec{B} with gauge origin \vec{R}_0 , $\vec{A}_{\vec{\mu}^M}$ denotes the vector potential generated by the magnetic moment of nucleus $\vec{\mu}^M$ and the four-by-four matrices β and $\vec{\alpha}$ have the usual two-by-two representation

$$\beta \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \vec{\alpha} \equiv \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad (16)$$

where $\vec{\sigma}$ are the Pauli matrices. Superscripts $(\vec{B}, \vec{\mu}^M)$ denote the dependence of the quantities on

the applied perturbations. It is useful to decompose the four-component MOs in Eq. (15) into the large- and small-component parts

$$\varphi_i^{(\vec{B}, \vec{\mu}^M)} = \begin{pmatrix} \varphi_i^{L(\vec{B}, \vec{\mu}^M)} \\ \varphi_i^{S(\vec{B}, \vec{\mu}^M)} \end{pmatrix}. \quad (17)$$

We can furthermore express the large and small components of the four-component MOs as linear combinations of basis functions χ_λ^L and χ_λ^S

$$\varphi_i^{L(\vec{B}, \vec{\mu}^M)} = C_{\lambda i}^{L(\vec{B}, \vec{\mu}^M)} \chi_\lambda^{L(\vec{B}, \vec{\mu}^M)}, \quad (18)$$

$$\varphi_i^{S(\vec{B}, \vec{\mu}^M)} = C_{\lambda i}^{S(\vec{B}, \vec{\mu}^M)} \chi_\lambda^{S(\vec{B}, \vec{\mu}^M)}. \quad (19)$$

We will refer to \mathbf{C}^L and \mathbf{C}^S as MO coefficients for the large and the small component, respectively. For more details we refer to ref 40.

The coupling mediated by the operator $\vec{\alpha}$ in Eq. (15) is the source of serious numerical problems.⁴⁷ However, in the absence of magnetic fields it is possible to avoid them by using a restricted kinetically balanced basis set (RKB) for the small component.^{47,48}

$$\chi_\lambda^{L(0,0)} \equiv \chi_\lambda, \quad (20)$$

$$\chi_\lambda^{S(0,0)} \equiv \frac{1}{2c} \vec{\sigma} \cdot \vec{p} \chi_\lambda, \quad (21)$$

where χ_λ denotes the λ 'th atomic orbital (AO) centered on an nucleus at \vec{R}_λ .

Although the RKB basis in the absence of magnetic fields has been shown to be an excellent solution to the numerical problems, in the presence of magnetic fields it leads to very poor basis set convergence even for rare-gas chemical shieldings.⁴⁹ A very efficient solution to this problem is to use restricted magnetically balanced (RMB) basis sets^{40,41,43} (for alternative methods, see refs 50,51). To get even faster basis set convergence in the presence of the external magnetic field, one

should combine the RMB basis with the well-known London atomic orbitals^{41,52,53}

$$\chi_{\lambda}^{\text{L}(\vec{B}, \vec{\mu}^{\text{M}})} \equiv \omega_{\lambda}^{(\vec{B})} \chi_{\lambda}, \quad (22)$$

$$\chi_{\lambda}^{\text{S}(\vec{B}, \vec{\mu}^{\text{M}})} \equiv \frac{1}{2c} \omega_{\lambda}^{(\vec{B})} \left(\vec{\sigma} \cdot \vec{p} + \frac{1}{c} \vec{\sigma} \cdot \vec{A}_{\vec{B}\lambda} + \frac{1}{c} \vec{\sigma} \cdot \vec{A}_{\vec{\mu}^{\text{M}}} \right) \chi_{\lambda}, \quad (23)$$

where the gauge of the vector potential $\vec{A}_{\vec{B}\lambda}$ is at the center of the atomic orbital χ_{λ} and the London phase factor $\omega_{\lambda}^{(\vec{B})}$ is given by

$$\omega_{\lambda}^{(\vec{B})} \equiv \exp \left\{ -\frac{i}{2c} [\vec{B} \times (\vec{R}_{\lambda} - \vec{R}_0)] \cdot \vec{r} \right\}. \quad (24)$$

The phase factor $\omega_{\lambda}^{(\vec{B})}$ shifts the global gauge origin \vec{R}_0 to the natural gauge of the λ 'th atomic orbital \vec{R}_{λ} ,⁵⁴ chosen to be the position of the nucleus to which the orbital is attached.

By considering Eqs. (17), (22) and (23), we note that the magnetic response of the four-component MO can be decomposed into a regular, a magnetic and a London part

$$\varphi_i^{(1,0)_u} = \varphi_i^{r(1,0)_u} + \varphi_i^{m(1,0)_u} + \varphi_i^{\omega(1,0)_u}, \quad (25)$$

where $(1,0)_u$ and $(0,1)_v^{\text{M}}$ denote derivatives with respect to B_u and μ_v^{M} , respectively. The different contributions in Eq. (25) represent derivatives with respect to different parts of the MOs in Eq. (17). The regular contribution arises from the response of the MO coefficients, the magnetic part originates from the magnetic balance with respect to the external magnetic field [second term in the brackets in Eq. (23)] and the London contribution arises from the phase factor in Eq. (24).

As already discussed, the orbital part of the pNMR tensor for the doublet system Eq. (6) can be expressed as the usual NMR shielding tensor for a diamagnetic system

$$(\sigma_{\text{M}}^{\text{orb}})_{uv} = \left. \frac{\partial^2 E(\vec{B}, \vec{\mu}^{\text{M}})}{\partial B_u \partial \mu_v^{\text{M}}} \right|_{\vec{B}=\vec{\mu}^{\text{M}}=0}. \quad (26)$$

The bilinear derivative of the energy can be expressed as (see Appendix A in ref 40)

$$(\sigma_{\mathbf{M}}^{\text{orb}})_{uv} = \langle \varphi_i^{(1,0)u} | D^{(0,1)\mathbf{M}} | \varphi_i^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | D^{(0,1)\mathbf{M}} | \varphi_i^{(1,0)u} \rangle, \quad (27)$$

where

$$D^{(0,1)\mathbf{M}} \equiv \frac{\partial}{\partial \mu_{\mathbf{M}}} (\vec{\alpha} \cdot \vec{A}_{\mu^{\mathbf{M}}}). \quad (28)$$

We note that in the relativistic theory (in contrast to the non-relativistic theory) there is no term expressed as an expectation value of a bilinear operator over unperturbed MOs (the so-called diamagnetic term) in the MO representation. However, if we switch to the AO representation, the missing diamagnetic term will arise from the magnetic part of the MO $\varphi_i^{m(1,0)u}$

$$(\sigma_{\mathbf{M}}^{\text{orb}})_{uv}^{\text{D}} \equiv \langle \varphi_i^{m(1,0)u} | D^{(0,1)\mathbf{M}} | \varphi_i^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | D^{(0,1)\mathbf{M}} | \varphi_i^{m(1,0)u} \rangle \quad (29)$$

This is an intrinsic feature of an explicitly magnetically balanced basis such as the one defined in Eq. (23). Without the magnetic balance, the diamagnetic contribution is "hidden" in the formally paramagnetic term, in particular in its part that involves the summation over negative-energy states.⁵⁵ Consequently, for reproducing correctly the diamagnetic contribution, a very large basis set is required. Clearly, the use of a magnetically balanced basis is preferable since it allows one to significantly reduce the computational efforts.

The calculation of the orbital contribution at the 4-component level was performed according to the procedure for calculations of other properties of open-shell systems (such as the HFC tensor, g tensor and ZFS), *i.e.* using 3 SCF procedures - one for each of the principal axes of the g tensor.^{36–38,56}

The usual paramagnetic contributions can be obtained from the regular and London parts of the response MO Eq. (25). For a detailed derivation of the working equations, see refs 40,41.

We will employ the following definition of the g tensor and HFC tensor for an effective doublet

system

$$g_{ut} = 4c \left. \frac{\partial E(\vec{B}, J_t)}{\partial B_u} \right|_{\vec{B}=0}, \quad (30)$$

$$(A_M)_{vt} = 2 \left. \frac{\partial E(\vec{I}^M, J_t)}{\partial I_v^M} \right|_{\vec{I}^M=0}, \quad (31)$$

where \vec{I}^M is the nuclear spin and \vec{J} represents the total magnetization vector. From Eqs. (30) and (31) it is clear that in the relativistic domain, the g tensor and the HFC tensor are first-order properties. Using the Hellman-Feynman theorem in the x representation,^{57,58} we can write

$$g_{ut} = 4c \left\langle \varphi_i^{(0, J_t)} \left| \frac{\partial}{\partial \vec{B}_u} \left(\vec{\alpha} \cdot \vec{A}_{\vec{B}0} \right) \right| \varphi_i^{(0, J_t)} \right\rangle, \quad (32)$$

$$(A_M)_{vt} = 2 \left\langle \varphi_i^{(0, J_t)} \left| \frac{\partial}{\partial I_v^M} \left(\vec{\alpha} \cdot \vec{A}_{\vec{I}^M} \right) \right| \varphi_i^{(0, J_t)} \right\rangle. \quad (33)$$

Note that because the MOs in the above expressions do not depend on the magnetic fields, it is sufficient to use the RKB basis [Eqs. (20) and (21)]. For more details on the four-component calculation of the g tensor and the HFC tensor, see ref 36–38.

3 Computational Details

All calculations have been carried out at the four-component matrix Dirac–Kohn–Sham (mDKS) level of theory with the RESPECT program package (version 3.3.0).⁵⁹ A non-collinear Kramers-unrestricted formulation of the BP86 functional was used to account for exchange and correlation effects.^{60–62} We have chosen BP86 functional to remain consistent with previous work by Rastrelli and Bagno.³² Dyall’s all-electron uncontracted basis sets of valence double-zeta (21s14p10d2f), triple-zeta (28s20p13d4f2g), and quadruple-zeta (33s25p17d5f4g2h) quality were used for the ruthenium atom.⁶³ For the light elements, we employed the uncontracted pcJ- X ($X=1,2,3$) basis sets of Jensen.⁶⁴ Unless otherwise stated, we present the results obtained with the valence triple-zeta basis sets. The molecular structures have been taken from ref 32.

The integration of the exchange-correlation parts was done numerically on a molecular grid of ultra-fine quality with an adaptive size in the angular part combined with a fixed number of radial quadrature grid points: H (50), second-row elements (60), third-row elements (70), and Ru (90). The exchange-correlation potential was calculated analytically by means of an automatic differentiation technique, as implemented in the XCFun library.⁶⁵ First derivatives of the BP86 exchange-correlation potential (kernel) were evaluated for closed-shell systems analytically, whereas for open-shell systems a finite difference method (with a step length of 10^{-3}) was used⁶⁶ In order to improve the convergence of the coupled-perturbed equations, we evaluated the XC kernel using only a local SVWN5⁶⁷ potential (ALDA approach). The error that arises from the use of the ALDA approximation was estimated from closed-shell analogues of the Ru-complexes and did not exceed 0.5 ppm for NAMI and 1.1 ppm for *mer*-Ru(ma)₃.

All relativistic SCF calculations were done with a finite-size nucleus model employing a Gaussian charge distribution, whereas for the chemical shielding and hyperfine coupling tensors, the point model for the nuclear charge and magnetic moment distributions was assumed. The nuclear magnetic moment of ¹H was taken to be $2.79284734 \mu_N$.⁶⁸ The computed nuclear shieldings were converted to chemical shifts (δ , in ppm) relative to the shielding of tetramethylsilane (calculated four-component value for TMS: 30.87 ppm) and all temperature-dependent NMR signals were evaluated for experimental temperatures.

Finally, we highlight two important points; first, all calculations of the NMR shielding tensors were performed without any accelerating techniques, such as the density fitting approach used in our previous studies,⁴² and all results are therefore free of errors that arise from using auxiliary basis sets. Second, the present implementation of the *g* tensor does not include London atomic orbitals (LAO) and the results are therefore not fully gauge invariant. We performed several test calculations on the NAMI molecule in order to estimate the error introduced by using a common gauge origin (CGO) approximation in the calculation of *g* tensors. The components of the *g* tensor varied by less than 0.1% when moving the gauge origin from the center of mass to different atomic centers.

4 Results and Discussion

We will here discuss the results obtained with our new approach for two Ru(III) complexes (see schemes in Figure 1). These systems were chosen because the results of relativistic ZORA calculations (by Rastrelli and Bagno³²) and reliable experimental data [*mer*-Ru(ma)₃⁴⁴ and NAMI⁴⁵] are available for both complexes.

NAMI: Our results together with the results of Rastrelli and Bagno³² and available experimental data are collected in Table 1. For the theoretical results, the individual contributions to the isotropic pNMR shielding constants are also reported. From these data (graphically presented in Figure 2), we note that all theoretical methods systematically overestimate the experimental results, although the four-component method performs best. To analyze the effect of the basis set quality on the results, additional calculations with different basis sets were performed. These results are collected in Table 2. Table 2 reveals fast basis set convergence for our approach. Even the double-zeta basis set gives reliable results considering the scale of the proton shieldings. To be on the safe side, we have chosen to use the triple-zeta quality basis set for the rest of our calculations. One of the possible reasons for the discrepancy of the theoretical and experimental results may be the neglect of vibrational corrections and/or effects of the solvent in our theoretical calculations. To shed some light on this topic, we have performed calculations with modified geometries for NAMI. In one series of calculations, we investigated the effect of stretching the Ru-N bond (see Figure 3). The overall agreement with experiment as well as the trend in the calculated results was improved when enlarging the Ru-N distance. More importantly, all calculations displayed a larger effect of geometry changes on the H-2 proton shielding than on the rest of the protons in the system. Since the shift on this proton has the poorest agreement with experiment, this confirms our hypothesis that vibrational and solvent effects need to be taken into account in order to fully reproduce the experimental data. Rotating the imidazole group around the Ru-N bond confirmed this trend, although the overall changes in the pNMR shifts were smaller than in the case of the stretching of the Ru-N bond (the H-2 pNMR shielding varied between 7.5 and 10.9 ppm).

An analysis of the different contributions to the pNMR shift calculated at the four-component

level (see Table 1) suggests that the pseudocontact term should not be neglected, in particular for protons closer to the metal center (H-2 and H-4). Autschbach *et al.*³³ calculated the pseudocontact shift using the ZORA Hamiltonian (with the PBE functional and a slightly different definition of δ_M^{PC}), obtaining qualitatively similar results as us using the full relativistic Hamiltonian (CH₃: 1.41 ppm, H-2: 2.09 ppm, H-4: 2.30 ppm, H-5: 0.98 ppm, NH: 0.99 ppm).

There are surprisingly large differences between the ZORA and mDKS results for the orbital and contact terms. The orbital contributions obtained with ZORA are systematically underestimated compared to their four-component counterparts. Figure 4 reveals that even the non-relativistic data better agree with the four-component results for the orbital term than those obtained with ZORA. This suggests that for the complexes considered, the relativistic effects for the orbital term are negligible. This was independently confirmed by a comparison of the mDKS results with data obtained using third-order perturbation theory²⁵ for the Ru(II) complex (the closed-shell analogue of NAMI), where the biggest SO correction was only 0.5 ppm for the H-2 proton. The largest difference in the contact term between the two relativistic approaches (ZORA and mDKS) is for proton H-2. A closer analysis of the four-component results for the HFC constants shows that the PSO operator contributes 3.1 ppm to the total value of -6.42 ppm (thus partially cancelling the rest of the contributions). Because the PSO contribution for protons arises to a great extent from SO effects, it is clear that in order to obtain the correct values, a proper treatment of both relativistic and spin-polarization effects is mandatory.

***mer*-Ru(**ma**)₃**: In Table 3 we have collected the theoretical and experimental data. Also here the different contributions to the calculated values of the pNMR shieldings are shown. The data presented in Table 3 exhibit very small differences [except for the CH₃(a) and CH₃(b) groups] between the results of the two relativistic methods (mDKS and ZORA). This outcome could be expected as all protons are rather far away from the metal center and thus SO relativistic effects can be expected to be small. Since the H-5 and H-6 protons are positioned in the plane of the rings, they are less affected by spin polarization going very effectively via the extended π -electron system. This requires additional spin-polarization of the σ orbitals by the π -orbitals in order to contribute

significantly to the contact shift on those protons. However, spin-polarization of the π -electron system has a non-zero effect on the protons of the CH₃ groups giving rise to the larger values observed for CH₃(a) and CH₃(b) [according to Rastrelli and Bagno,³² the very small values for the contact contribution to the CH₃(c) proton are caused by "the distorted coordination geometry of the maltolato moieties"]. This can be nicely seen from the analysis of the hyperfine coupling constants (HFCC) for the individual protons in the CH₃ groups. The HFCC are much smaller for the (approximately) in-plane hydrogens (0.26 MHz for in-plane versus 2.29 MHz and 3.69 MHz for out-of-plane hydrogens in the CH₃(a) group and 0.15 MHz for in-plane versus 3.59 MHz and 4.42 MHz for out-of-plane hydrogens in the CH₃(b) group). When the CH₃(c) group was rotated to have one hydrogen in-plane, the corresponding HFCC show the same trend (0.06 MHz for the in-plane hydrogen versus 0.50 MHz and -0.43 MHz for the out-of-plane hydrogens) as in the groups *a* and *b* but on a smaller scale. The only noticeable difference between the mDKS and ZORA results is in the contact term for the CH₃(a) and CH₃(b) groups. Most likely this is a consequence of using less flexible basis sets in the ZORA calculations. Autschbach *et al.*³³ observed similar relative differences for HFC constants when the JCPL basis set instead of TZ2P was used. This confirms the well-known sensitivity of HFC constants to basis set quality, exchange-correlation functionals employed as well as the general numerical stability of the code. Thus one must take special care in choosing a basis set that would ensure practical convergence of the results with respect to basis set quality. The values obtained for the pseudocontact term are small and have negligible effect on the results. This can also be due to the large distance between the metal center and the protons.

In Table 4 the calculated *g* tensors for NAMI and *mer*-Ru(ma)₃ compounds are presented. For NAMI, the non-relativistic calculations⁶⁹ significantly overestimate the *g* tensor in comparison with our four-component calculations, whereas for the *mer*-Ru(ma)₃ compound both approaches give similar results. The ZORA results differ significantly from the fully relativistic mDKS data for both compounds. Since we intentionally used the same functional and geometry for the compounds as in the ZORA calculations, this discrepancy indicates shortcomings in the ZORA two-component approach in comparison to four-component method, already for 4d element compounds.

Whereas there are several aspects of the accuracy of the calculations presented here that might be improved in future studies (such as taking a better DFT functional or by modeling solvent effects) we still believe we can address an important point affecting the comparison between theoretical results and experimental data. How reliable are the experimental assignments? Can a better agreement with the theoretical data be achieved by reassigning some of the experimental shielding constants? In the experimental pNMR study of Kennedy *et al.*,⁴⁴ a coupling between protons H-5 and H-6 was observed and therefore their relative assignment is fixed. However the assignment of pairs of protons to the different ligands is more problematic. Assuming that we can reassign some of the experimental data (switching protons 5 and 6 between groups a and c in contrast to the assignment of Rastrelli and Bagno;³² see Table 3). A comparison of the left (original assignment) and right plots (our assignment) in Figure 5 suggests that a reassignment may be in order. However, in order to make a definite conclusion, a wider variety of DFT functionals must be tested.

There are apparent discrepancies between the experimental and the calculated pNMR shifts of the CH₃ groups. Rastrelli and Bagno attributed this to inaccuracies in the optimized geometry.³² Because we have employed the same geometries in our calculations, it is interesting to see to what extent a possible inaccuracy in the geometries might affect the resulting shifts. To check the geometry dependence of the results, we have performed calculations with rotated CH₃ groups and modified distances of the Ru-O bonds compared to the X-ray structure available in ref 44. These changes in the geometry have only a negligible effect on the proton shifts studied. We believe that the most probable reason for the discrepancy between our results and experiment is the limitation of DFT itself. The use of a better functional might improve the situation. Also, since the measurements were done in solution (CD₂Cl₂), solvent effects should be taken into account for a more reliable model.

It is worth noting that the calculated peaks of the CH₃(a) and CH₃(b) groups lies outside of the experimental range. That indicates that the reported experimental shifts of CH₃(a) and CH₃(b) groups might be misassigned and have a different origin (*i.e.* the peaks might arise from contaminants and not from the *mer*-Ru(ma)₃ compound). Confirming these speculations would however

require a more detailed analysis of the experimental procedures and additional calculations. We have not pursued this issue any further since it is beyond the scope of this work.

5 Conclusions

A four-component relativistic DFT theory for the calculation of NMR shielding tensors of paramagnetic doublet substances has been presented. The new method automatically includes all relativistic effects described by the Dirac–Coulomb Hamiltonian. The method has been implemented in the RESPECT program package,⁵⁹ taking advantage of the existing efficient implementations of EPR and NMR parameters. This allows us to apply the method to chemically interesting systems while at the same time retaining the high accuracy of the four-component relativistic theory, thus avoiding most of the approximations employed in earlier theoretical studies.

Separation to the contact and pseudocontact terms within relativistic theory for pNMR shieldings was proposed (Eqs. 10 and 11). The relativistic insight into the pseudocontact and contact terms revealed that their nature is more complicated than it is assumed by commonly used simplified models (see also ref 19). The extraction of the value of spin-density at the position of an investigated nucleus is even more problematic: at the two- or four-component relativistic level of theory, the Fermi contact contribution to the hyperfine-coupling constant is not defined solely by the spin density. This means that the development of more accurate relativistic methods for the calculation of pNMR shieldings must be accompanied by a development of new interpretation tools for the analysis of the results obtained and more advanced models for the interpretation of experimental results.

All calculated pNMR shifts are in good qualitative agreement with experimental data and the observed deviation from experiment for the NAMI complex can be attributed to the sensitivity of the pNMR results to the changes in geometry. Therefore, the inclusion of vibrational and/or solvent effects is necessary. The results for the *mer*-Ru(ma)₃ compound demonstrate the usefulness of quantum-chemical methods in helping to assign experimentally measured data.

We disagree with Rastrelli and Bagno in their conclusion that relativistic calculations for Ru(III) complexes are not required.³² Although only the ¹H pNMR shifts were investigated here, we found noticeable differences between the four-component results and those obtained with more approximate schemes. In the case of the NAMI compound, the orbital contribution to the shielding obtained with the ZORA Hamiltonian systematically undershoot our four-component data. Sizeable differences were observed for some of the calculated hyperfine-coupling constants, which is not surprising considering that the HFC tensor is a very sensitive property requiring an accurate treatment of relativistic and spin-polarization effects even for as light nuclei as hydrogen.

We finally note that an important limitation of the method presented here is the restriction that it can only be used for systems without ZFS. The extension of the approach to systems with higher degeneracies and non-negligible ZFS is currently being developed in our group.

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- (69) Strictly speaking, the non-relativistic g tensor shift (in the absence of SO effects) is zero. However, we will keep this notation in order to stay consistent with the work of Rastrelli and Bagno³² from where the data were taken. The NR results in Table 4 thus refer to methods in which SO effects are taken into account perturbationally.

Table 1: Calculated (BP86 functional) and experimental ^1H pNMR isotropic shieldings (in ppm)^a of NAMI compound.

Proton label	method ^b	A_{iso}	$\sigma_{\text{iso}}^{\text{orb}}$	$\sigma_{\text{iso}}^{\text{fc}}$	$\sigma_{\text{iso}}^{\text{pc}}$	σ_{iso}	δ_{iso}
CH ₃	NR	-0.17	33.41	5.39		38.80	-7.4
	ZORA	-0.32	27.78	9.41		37.18	-5.8
	mDKS	-0.28	32.83	7.98	2.15	42.96	-12.1
	Exp.						-14.5
H-2	NR	0.23	25.87	-7.28		18.59	12.9
	ZORA	0.09	22.66	-2.73		19.93	11.4
	mDKS	0.23	25.80	-6.42	3.45	22.82	8.0
	Exp.						-5.6
H-4	NR	-0.06	26.22	1.91		28.13	3.3
	ZORA	-0.11	22.53	3.21		25.73	5.6
	mDKS	-0.15	26.03	4.31	3.19	33.53	-2.7
	Exp.						-7.8
H-5	NR	-0.10	27.61	3.11		30.72	0.7
	ZORA	-0.15	25.09	4.29		29.38	2.0
	mDKS	-0.17	27.51	4.72	1.34	33.57	-2.7
	Exp.						-3.5
NH	NR	-0.00	24.55	0.00		24.56	6.9
	ZORA	-0.07	23.44	2.11		25.54	5.8
	mDKS	-0.04	24.80	1.25	1.28	27.33	3.5
	Exp.						-

^a HFC constants A_{iso} are in MHz. ^b NR, ZORA: Data taken from ref 32. mDKS: This work. Exp.: Experimental data taken from ref 45 ($T = 25^\circ\text{C}$).

Table 2: Basis set convergence of ^1H pNMR isotropic shifts (in ppm) calculated with mDKS method in NAMI compound.

basis set quality	CH ₃	H-2	H-4	H-5	NH
double-zeta	-12.0	7.3	-3.6	-3.0	3.1
triple-zeta	-12.1	8.0	-2.7	-2.7	3.5
quadruple-zeta	-12.0	7.8	-2.7	-2.5	4.4

Table 3: Calculated (BP86 functional) and experimental ^1H pNMR isotropic shieldings (in ppm)^a of *mer*-Ru(ma)₃ compound.

Proton label	method ^b	A_{iso}	$\sigma_{\text{iso}}^{\text{orb}}$	$\sigma_{\text{iso}}^{\text{fc}}$	$\sigma_{\text{iso}}^{\text{pc}}$	σ_{iso}	δ_{iso}
CH ₃ (a)	NR	2.38	28.59	-69.03		-40.44	71.89
	ZORA	2.53	29.64	-69.59		-39.95	71.3
	mDKS	2.08	28.78	-56.39	-1.27	-28.87	59.74
	Exp.						41.03
CH ₃ (b)	NR	3.08	28.71	-89.47		-60.76	92.21
	ZORA	3.27	29.65	-90.20		-60.55	91.9
	mDKS	2.72	29.42	-73.80	-0.32	-44.70	75.57
	Exp.						43.17
CH ₃ (c)	NR	-0.25	28.76	7.14		35.90	-4.45
	ZORA	-0.29	29.28	8.05		37.34	-6.0
	mDKS	-0.31	28.67	8.46	-1.11	36.01	-5.15
	Exp.						21.11
H-5a	NR	-0.16	24.94	4.70		29.63	1.82
	ZORA	-0.27	25.71	7.46		33.18	-1.8
	mDKS	-0.28	25.04	7.53	1.33	33.90	-3.03
	Exp.						-0.87
H-6a	NR	-0.41	23.85	11.81		35.66	-4.21
	ZORA	-0.35	25.18	9.53		34.71	-3.4
	mDKS	-0.29	24.13	7.94	0.36	32.44	-1.57
	Exp.						0.92
H-5b	NR	-0.41	24.84	11.97		36.81	-5.36
	ZORA	-0.58	25.74	16.04		41.78	-10.4
	mDKS	-0.54	24.78	14.70	1.35	40.83	-9.96
	Exp.						-4.61
H-6b	NR	0.03	23.83	-0.94		22.89	8.56
	ZORA	0.24	25.38	-6.71		18.67	12.7
	mDKS	0.26	24.36	-7.03	0.44	17.77	13.10
	Exp.						3.43
H-5c	NR	0.37	24.74	-10.88		13.86	17.59
	ZORA	0.38	25.30	-10.38		14.92	16.4
	mDKS	0.38	23.72	-10.21	-0.48	13.03	17.84
	Exp.						11.84
H-6c	NR	0.01	23.92	-0.30		23.62	7.83
	ZORA	0.07	24.74	-1.99		22.75	8.6
	mDKS	0.10	23.32	-2.63	-0.36	20.33	10.54
	Exp.						9.20

^a HFC constants A_{iso} are in MHz. ^b NR, ZORA: Data taken from ref 32. mDKS: This work. Exp.: Experimental data taken from ref 44 ($T = 22^\circ\text{C}$).

Table 4: Isotropic g tensor for NAMI and mer -Ru(ma)₃ compounds.

method ^a	NAMI	mer -Ru(ma) ₃
NR	2.345	2.172
ZORA	2.194	2.081
mDKS	2.035	2.160

^a NR, ZORA: Data taken from ref 32. mDKS: This work.

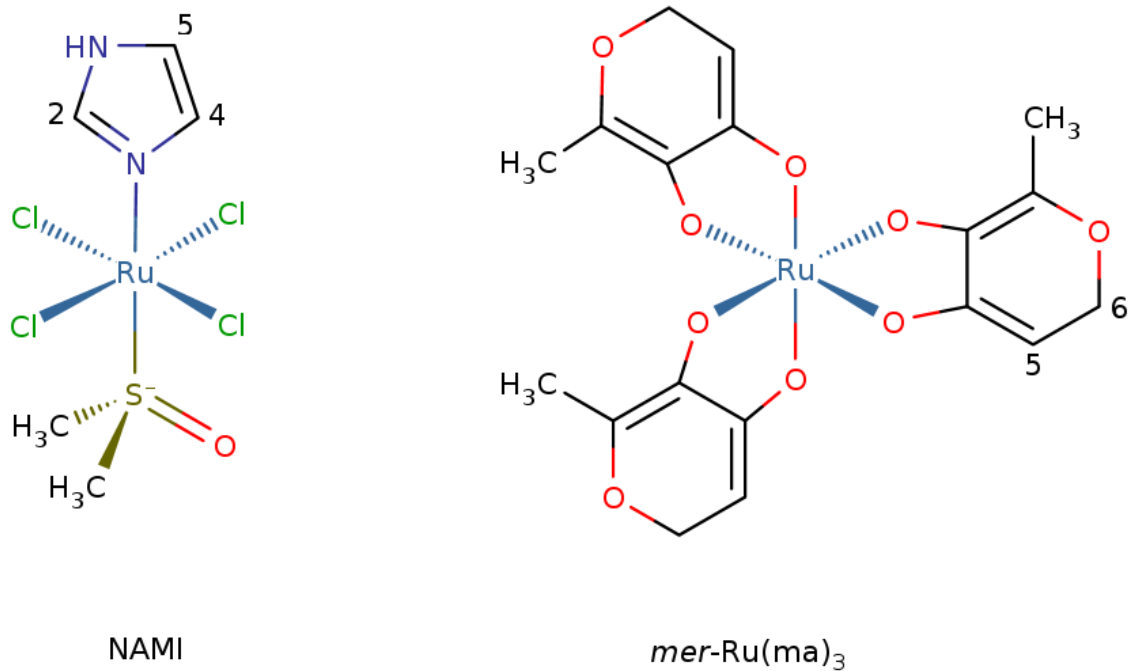


Figure 1: Structures and numbering of investigated Ru(III) systems.

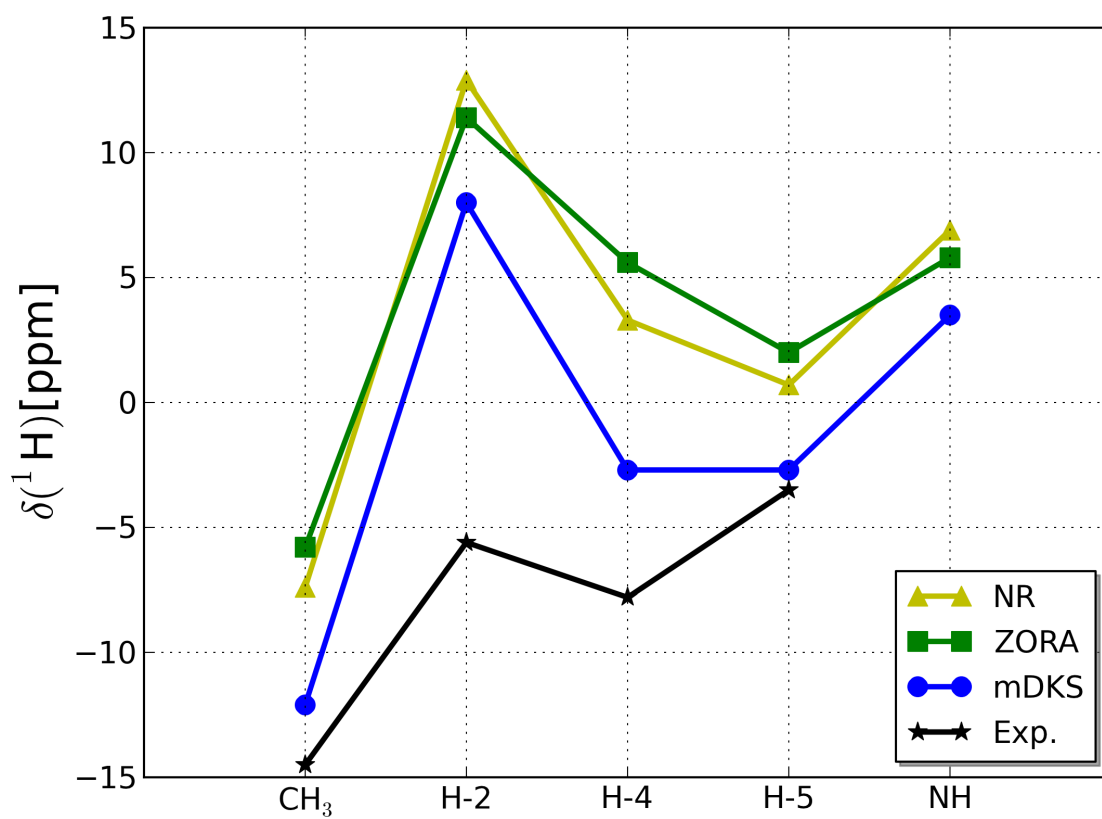


Figure 2: Calculated and experimental ^1H pNMR isotropic shifts of NAMI compound (for explanation of the legend see Table 1).

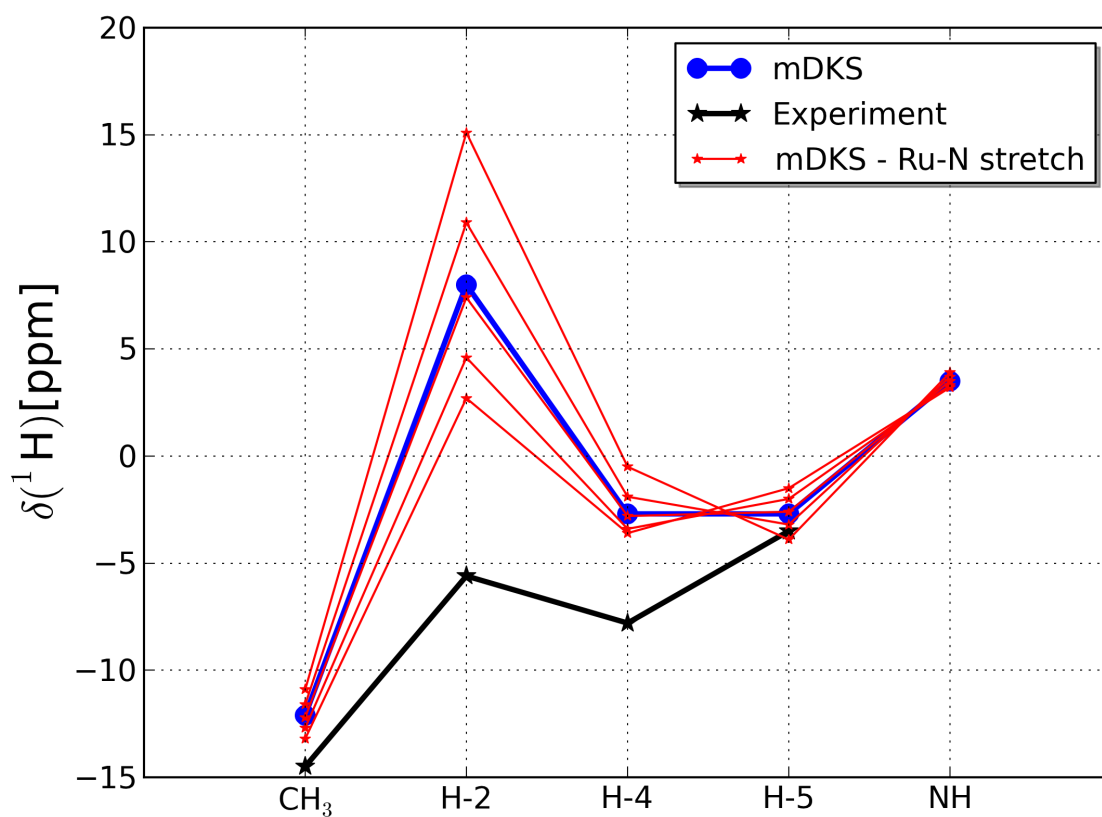


Figure 3: Effect of stretching of Ru-N bond [in the interval (1.9 Å, 2.3 Å)] on the ¹H pNMR isotropic shifts of NAMI compound. Closer to the experimental data are results with longer bonds. mDKS: Results with unchanged geometry (Ru-N 2.0813 Å). Experiment: ref 45.

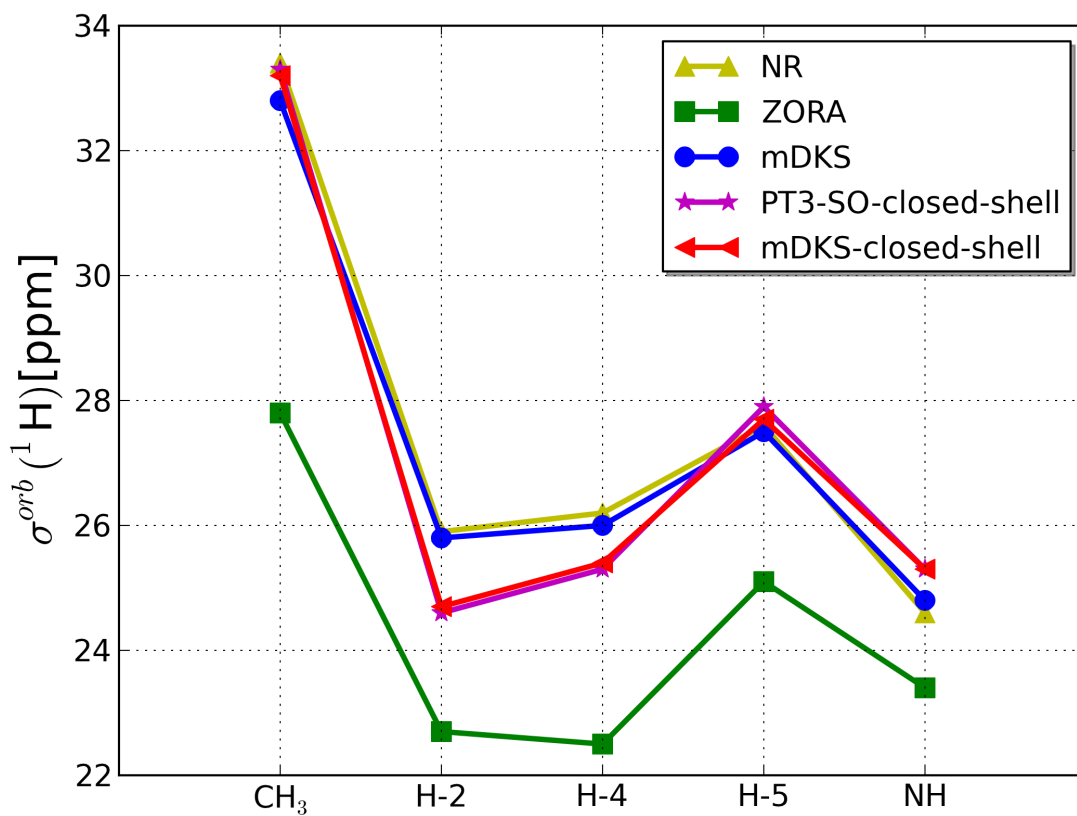


Figure 4: Orbital contribution to the ^1H pNMR isotropic shifts of NAMI compound. NR, ZORA: Data taken from ref 32. mDKS: Four-component open-shell calculations. PT3-SO-closed-shell: Third-order perturbation theory²⁵ calculations of closed-shell analogue of NAMI compound. mDKS-closed-shell: Four-component calculations of closed-shell analogue of NAMI compound using BP86 potential and kernel to match PT3-SO calculations.

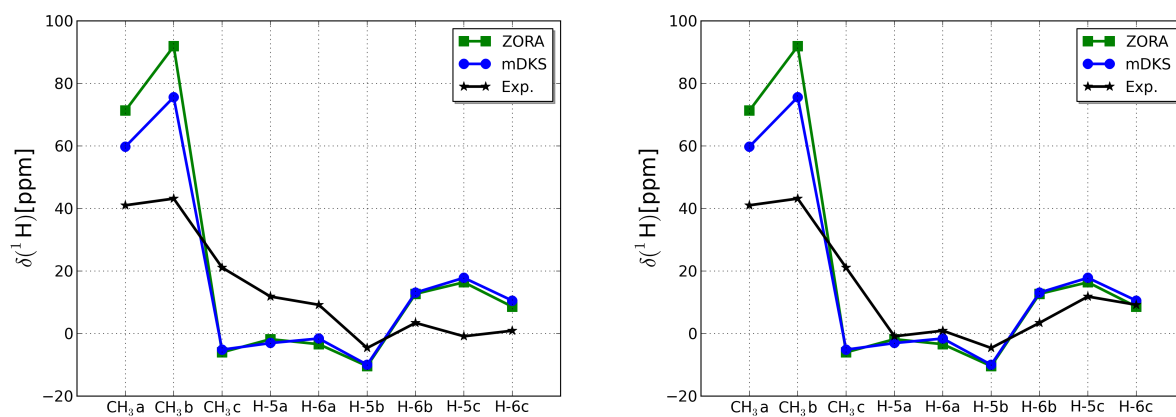


Figure 5: Calculated and experimental ^1H pNMR isotropic shifts of *mer*-Ru(ma)₃ compound. Left: Original assignment taken from ref 32. Right: Experimental data are assigned to better match the mDKS calculation (within experimental constrains). For explanation of the legend see Table 3.

Graphical TOC Entry

