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NMR Shielding Calculations across the Periodic Table: Diamagnetic Uranium Compounds. 1. Methods and Issues

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In this and a subsequent article, the range of application for relativistic density functional theory (DFT) is extended to the calculation of nuclear magnetic resonance (NMR) shieldings and chemical shifts in diamagnetic actinide compounds. In the given first paper, various issues are explored that are related to this goal. It is shown that both the relativistic DFT-ZORA (zeroth-order regular approximation, as developed for NMR properties by Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 7689) and the older quasi-relativistic (QR) DFT methods are applicable to these compounds. Another popular relativistic method, the use of relativistic effective core potentials (ECP) for the calculation of ligand NMR parameters, is tested as well. It is demonstrated that the ECP approach is beyond its limits for the very heavy actinide compounds. Comparing the ZORA and Pauli approaches, it is found that Pauli is more accurate for the ^{1}H NMR in $UF_{6-n}(OCH_3)_n$ compounds whereas ZORA is more accurate in other cases. This is in contrast to earlier studies that always showed ZORA to be superior. The neglect of spin−orbit effects, leading to scalar relativistic approximations, is possible in some cases. In other cases, however, spin−orbit cannot be neglected. For instance in $UF_5(OCH_3)$, a large spin−orbit chemical shift of about 7 ppm has been found for the ^{1}H nuclei but only small effects for the other ligand nuclei. The large influences of the reference geometry, the reference compound, and the exchange correlation (XC) functional are demonstrated and discussed. The ^{19}F chemical shift tensor in UF_6 is well reproduced by the ZORA and QR methods. However, for the ^{19}F chemical shifts in $UF_{6-n}Cl_n$ compounds, only some experimental trends could be reproduced by the calculations. Possible explanations are discussed for these shortcomings, including the choice of model XC functional.

1. Introduction

Nuclear magnetic resonance (NMR) shieldings and chemical shifts are known to be *sensitive to everything*.

On the experimental side, this appears to be the reason that NMR may be considered the single most important spectroscopic technique for chemistry and beyond.[1] Indeed, information regarding, e.g., the molecular structure (geometry), chemical environment, intra- and intermolecular bonding, composition, or dynamic processes is routinely extracted from experimental NMR spectra.[1]

This same *sensitivity to everything* poses considerable challenges for the theoretical researcher if s/he attempts to describe NMR parameters based on first principle quantum mechanics. Thus, it was only within the past decade or so that it has become possible to carry out accurate NMR shielding (chemical shift) calculations routinely for light, in particular first row compounds.[2−6] The computational challenges are even greater in heavy element compounds, and theoretical NMR methods have only very recently become available or are still being developed. Applications to, e.g., transition metal complexes are far from routine yet.[7−9]

In this paper and in a subsequent publication[10] (hereafter Paper II), we will explore the calculation of NMR chemical shifts in diamagnetic compounds of actinide elements, choosing uranium as a representative example. Our calculations are based on density functional theory (DFT);[11−15] relativistic effects have to be included.[8] In this way, we will extend the first principle calculation of NMR parameters to the heaviest part of the periodic table, i.e., to f-block compounds. Thus, the entire periodic table is now, for the very first time, accessible to the theoretical study of NMR parameters.[16,17]

In the given first paper, we will concentrate mostly on an evaluation of the methods[18−20] that we shall use for the calculation of NMR shieldings (chemical shifts) in heavy element compounds. In other words, we will discuss and test (many of) the issues that arise in the first principle calculation of NMR chemical shifts of actinide compounds. In the subsequent Paper II, we shall apply these methods to various uranium compounds and discuss the calculated ligand and metal (^{235}U) chemical shifts.

Mostly, we apply two relativistic methods for the calculation of NMR shieldings and chemical shifts, the older quasi-relativistic (QR) approach[21,22] and the more modern zeroth order regular approximation (ZORA) for relativistic effects.[23−26] The former had been developed by Schreckenbach and Ziegler for nonrelativistic[27−30] and scalar relativistic[18] NMR calculations and extended by Wolff and Ziegler[19] to include spin−orbit relativistic effects as well. The latter NMR method is the work of Wolff and co-workers.[20]

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2. Issues in the Calculation of NMR Chemical Shifts

As mentioned in the Introduction, and as any practitioner in the field will know, calculated chemical shifts are sensitive to *about everything imaginable*. In the following, we shall list and discuss some of the most important of these issues. This shall set the stage for the rest of the paper where we will investigate a number of such issues as they arise for the heavy actinide compounds. The items listed in the following are points that will be relevant in one form or another in most calculations of NMR chemical shifts. However, some of them might be more prominent and pressing for the very heavy actinide compounds than would be the case for the lower part of the periodic table.

(A) Relativity. It is, by now, well-known that scalar and often also spin−orbit relativistic effects have to be included for even a qualitative understanding of the chemistry of heavy elements.[31] This is true for NMR properties also.[8] Here, we use two relativistic methods, the older QR approach[21,22] that employs a Pauli Hamiltonian[32] and the more modern ZORA method.[23−26] The accuracy of such approximate relativistic methods is an issue. More generally, these are very new methods for the calculation of the NMR shielding, and further evaluation is required. In addition, for the Pauli operator, one has to be concerned about stability problems[33−35] that are not present for some of the more modern approaches including ZORA. Furthermore, either relativistic method can be used at different levels of approximation that should be investigated. For instance, spin−orbit effects can be neglected or included.

Other methods of including relativistic effects into NMR shielding calculations have been proposed in the literature. In particular, Kaupp et al.[36,37] employed effective core potentials (ECP) at the heavy nuclei. The use of an ECP on a certain nucleus leads, by construction, to the wrong asymptotic behavior of the valence molecular orbitals (MO) near that nucleus, and NMR shielding calculations are obviously not possible for the heavy element proper. However, DFT-ECP calculations have been performed successfully for the NMR shielding of neighboring light ligand nuclei in transition metal complexes.[7,9,37] In the context of the given study, the question arises whether the ECP approach to relativity is still useful for the NMR properties of the very heavy actinide systems.

(B) Quantum Mechanical Approximation, Electron Correlation. The (nonrelativistic) level of theory is an issue, not just for chemical shift calculations. This concerns, in particular, the effects of electron−electron correlation. Here, we choose density functional theory (DFT).[11−15] DFT includes electron correlation implicitly and effectively. Moreover, the relativistic calculation of NMR chemical shifts has so far only been achieved for DFT-based methods.[38−42]

Having chosen DFT, there are still different approximations possible to the (unknown) exact exchange-correlation (XC) functional. Hence, it remains to evaluate whether the chosen approximate XC functional, the *flavor of DFT*, is appropriate.[8]

(C) Gauge Problem. The so-called gauge problem of magnetic properties is well-known in the theoretical literature.[2,3] In brief, it is the—unphysical—dependence of approximate calculations (employing finite basis sets) on the choice of gauge for the magnetic vector potential. In particular, results that were obtained with finite basis sets may depend on the— arbitrary— position of the coordinate origin.

Here, we will use the gauge including atomic orbitals (GIAO) method.[43−45] Hence, we can consider the gauge problem as being completely solved. In addition, it has been shown in the literature that the GIAO method converges better with the size of the basis set than any alternative.[45−49] Thus, it appears to be the most accurate method for a given basis set level.

(D) Basis Sets. Calculated NMR shieldings and chemical shifts are very sensitive to the size of the basis set, even if an accurate method like GIAO has been chosen. Thus, the choice of basis set is an issue, and there is a considerable literature on the basis set requirements for NMR calculations.[6] For the given heavy element compounds, there is an additional twist if the older Pauli operator is used. This is the case in the QR method. Then, certain limitations for the basis sets are necessary to avoid a variational collapse, see below.[35] These limitations originate from the mentioned stability problems of the Pauli operator. No such limitations are known for the ZORA method.

(E) Geometries. Calculated as well as experimental NMR chemical shifts are well-known to be extremely sensitive to subtle geometry changes.[6] (see, e.g., refs. 20 and 50 for some examples.) Hence, one should base any calculation on accurate experimental geometries or employ geometry optimizations. We prefer to use high quality experimental geometries, in cases where such data is accessible. However, experimental structures (e.g., X-ray, neutron diffraction) are often unavailable. In these instances, one has to use theoretical geometries. This, then, raises the question whether these optimized geometries are good enough for the given purpose.

(F) Reference Compound. The direct result of a theoretical NMR calculation is the absolute shielding. While there are experimental absolute shielding scales for a number of light nuclei,[51,52] one often wants to convert the calculated absolute shieldings (or shielding tensors) into chemical shifts (or chemical shift tensors). In this way, a direct comparison to experiment becomes possible, even for cases where an accurate experimental absolute shielding scale has not yet been determined. The transformation between absolute shieldings and chemical shifts involves the absolute shielding of the reference compound for the given nucleus (e.g., tetramethylsilane, TMS, for ^{1}H, ^{13}C, and ^{29}Si), cf. eq 1 below. Hence, any error made in the calculation for the reference compound will carry through to the chemical shifts. This may hide systematic errors in the absolute shieldings if the same error is made in the reference molecule and the actual compound. Alternatively, it may introduce systematic errors into the calculated chemical shift itself. This would be the case if, for some reason, a particularly large error was associated with the reference compound.

(G) Condensed Phases, Temperature, and Pressure. Most experimental NMR measurements have been performed in solution or the solid state. Furthermore, experiments have to be carried out at finite temperatures and pressures. Calculations, however, typically consider an isolated, rigid molecule. The zero-pressure, zero-temperature limit of a gas-phase experiment comes closest to this ansatz.

The effects can be rather large for both temperature and the physical and chemical environment (arising, for instance from finite pressure and solvation). Solvation effects have been determined by comparing gas phase and solution measurements, or also by comparing chemical shifts in different solvents. (See, e.g., Paper II where we cite an example of considerable experimental solvent shifts.) Temperature effects can be measured in the gas phase.[51] So far, they have only been modeled for very small compounds, using ro-vibrational averaging.[6]

3. Methods

In this section, we will outline some of the methods that have been used for the NMR calculations in this study and in Paper II. We will present the formulas only as far as they are required in the context of the subsequent discussions, and no attempt will be made for completeness. Instead, we refer the reader to the original literature[18−20,27−30] or the reviews.[8,9,17,29] Atomic units are employed for the following equations.

(A) NMR Shielding and Chemical Shift. The NMR shielding tensor $\vec{\vec{\sigma}}$ is calculated in the usual way as an energy derivative[6] using the energy expression of relativistic DFT. The shielding tensor is related to the experimentally determined chemical shift tensor $\vec{\vec{\delta}}$ by the following relation

$$\delta = \sigma_{\mathrm{ref}} - \sigma \tag{1}$$

where σ and δ are the isotropic averages (traces) of the respective second rank tensors and σ_{ref} is the absolute shielding of the reference compound. We will cite results in either form, as chemical shifts or as absolute shieldings. Note that changes in the shielding and chemical shift, respectively, will have the opposite sign, according to eq 1.

(B) Density Functional Theory (DFT). As mentioned in the Introduction, we have based our calculations on relativistic DFT.[11−15]

(Nonrelativistic) DFT is based on an exact expression for the total energy E of an n-electron system[11]

$$E = \sum_i^n \int \mathrm{d}\vec{r}\ \Psi_i{}^*\left(\frac{p^2}{2} + V_{\mathrm{N}}\right)\Psi_i + \frac{1}{2}\int \mathrm{d}\vec{r}_1\,\mathrm{d}\vec{r}_2 \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} + E_{\mathrm{XC}} \tag{2}$$

In this equation, $\rho = \sum_i^n \Psi_i^*\,\Psi_i$ is the electronic density of the n-electron system. Further, $\vec{p}$ is the electronic momentum operator, the $\{\Psi_i\}$ form a set of n orthonormal one-electron functions that are also known as the Kohn−Sham (KS) orbitals, and V_{N} is the external (nuclear) potential. Hence, the first integral in eq 2 represents the kinetic and potential energy of a hypothetical model system with exactly the same density but without electron−electron interaction. The second term is the average (Coulomb) interaction of the electronic density with itself. The last term is the exchange−correlation (XC) energy E_{XC}. E_{XC} and hence E proper are functionals of the electronic density. From eq 2, the KS equations are usually derived[12,13]

$$h_{\mathrm{KS}}\Psi_i = \epsilon_i\Psi_i \tag{3}$$

where

$$h_{\mathrm{KS}} = \frac{p^2}{2} + V_{\mathrm{KS}} = \frac{p^2}{2} + V_{\mathrm{N}} + \int \mathrm{d}\vec{r}_2 \frac{\rho(\vec{r}_2)}{|\mathrm{r}_1 - \vec{r}_2|} + V_{\mathrm{XC}} \tag{4}$$

The XC potential V_{XC} is the functional derivative of the XC energy E_{XC} with respect to the density ρ.[13] The exact functional form for the XC functional E_{XC} is unknown, and some suitable approximation has to be chosen in practical applications of DFT. Relativistic extensions of eqs 2 to 4 are possible,[53] see also below.

Existing model functionals can be roughly divided into three types. The simplest and oldest model is the local density approximation[54] (LDA) where the XC energy functional is approximated by the free electron gas value, i.e., as a function of the density only

$$E_{\mathrm{XC}}[\rho] \approx E_{\mathrm{XC}}(\rho) \tag{5}$$

In generalized gradient approximations (GGA),[55−58] the nonuniformity of the density is taken into account by including the gradient of the density

$$E_{\mathrm{XC}}[\rho] \approx E_{\mathrm{XC}}(\rho)(\rho,\nabla\vec{\rho}) \tag{6}$$

Finally, in hybrid functionals (also known as adiabatic connection methods), the GGA expressions are augmented by including some part of the exact Hartree−Fock (HF) exchange.[59,60]

All of these types of functionals have been applied to NMR shielding calculations. Experience to date shows that the simple LDA is insufficient.[8] The situation is less clear-cut regarding the comparison of hybrid and GGA functionals; there are cases where the hybrid functionals are superior,[61] and others where just the opposite is true.[62] In this paper and in Paper II, we will mostly use GGAs but we will also present a limited comparison with hybrid functionals.

Besides having to choose a model for the nonrelativistic, field-free XC functionals as has been discussed so far, it is, in principle, necessary to use modified functionals for the relativistic case[53,63] and for the case of a magnetic field.[64−66] Here, we will neglect either contribution. At least for the relativistic corrections to the XC functional, it has been shown that this is a good approximation because the effects are small.[63]

(C) Relativistic Methods. As mentioned already, we employ two different relativistic DFT methods for the calculation of the shielding tensor, the quasi-relativistic (QR) method[21,22] that is based on a Pauli Hamiltonian,[32] and the zeroth-order relativistic approximation (ZORA) for relativistic effects.[23−26]

In the QR method, a Pauli Hamiltonian is included into the self-consistent solution of the Kohn−Sham equations of DFT, eqs 3 and 4. This Pauli operator is in a DFT framework given by

$$h^{\mathrm{Pauli}} = h^{\mathrm{MV}} + h^{\mathrm{Dar}} + h^{\mathrm{SO}} \tag{7}$$

Its contributions are, in this order, the mass−velocity, Darwin, and spin−orbit operators:

$$h^{\mathrm{MV}} = -\frac{1}{8c^2}p^4 \tag{8}$$

$$h^{\mathrm{Dar}} = \frac{1}{8c^2}\nabla^2 V_{\mathrm{KS}} \tag{9}$$

and

$$h^{\mathrm{SO}} = \frac{1}{4c^2}\vec{\sigma}_S\cdot[\nabla\vec{V}_{\mathrm{KS}} \times \vec{p}] \tag{10}$$

Here, c is the speed of light, $\vec{p}$ is again the electronic momentum operator, $\vec{\sigma}_{\mathrm{S}}$ is the three-component vector of the Pauli spin matrices (not to be confused with the shielding tensor, $\vec{\vec{\sigma}}$, of eq 1!), and V_{KS} is the total one-electron Kohn−Sham potential of eq 4.[67] The mass−velocity and Darwin operators of eqs 8 and 9 are known as scalar relativistic operators since they do not contain the electronic spin. Thus, neglecting or including the spin−orbit operator of eq 10 leads to scalar or spin−orbit relativistic approaches, respectively.

The ZORA Hamiltonian is given by

$$h^{\mathrm{ZORA}} = \vec{\sigma}_{\mathrm{S}}\cdot\vec{p}\frac{K}{2}\vec{\sigma}_S\cdot\vec{p} + V \tag{11}$$

with the operator K being defined as

$$K = (1 - V/2c^2)^{-1} \tag{12}$$

TABLE 1: Selected Orbital Energies for a U^{6+} Ion (au)

atomic level	calculated energy[a] unscaled	calculated energy[a] scaled	scale factor
$1s_{1/2}$	−4864.26	−4245.66	0.8728
$2s_{1/2}$	−802.47	−795.84	0.9700
$3s_{1/2}$	−205.23	−203.10	0.9896
$4s_{1/2}$	−54.037	−53.832	0.9962
$5s_{1/2}$	−14.113	−14.095	0.9988
$6s_{1/2}$	−4.1969	−4.1955	0.99966
$7s_{1/2}$	−1.8323	−1.8321	0.99989

[a] ADF[69−75] based ZORA spin−orbit calculations;[23−26] basis "all-electron ZORA V", PW91 XC functional.[58]

Within the Kohn−Sham formalism of DFT (eqs 2 to 4), V is substituted by the Kohn−Sham potential V_{KS} of eq 4 or some suitable approximation thereof. Expanding eq 11 a little, we obtain

$$h^{ZORA} = \vec{p}\cdot\frac{K}{2}\vec{p} + V + \frac{\vec{\sigma}_S}{2}\cdot(\nabla\vec{K} \times \vec{p}) \qquad (13)$$

We note from eq 13 that scalar and spin−orbit relativistic calculations are possible also for the ZORA method. This is because only the last term in eq 13 contains the electronic spin operator.

The ZORA formalism can be extended by a simple scaling procedure for the one-electron energies.[25] This improves the agreement of the ZORA one-electron energies with the fully relativistic Dirac results, for the core orbitals in particular. Thus, let

$$h^{ZORA}\Psi_i = \epsilon_i\Psi_i \qquad (14)$$

(cf. eq 3). Then, the scaled ZORA MO energies are

$$\epsilon_i^{\text{scaled}} = \xi_i\epsilon_i \qquad (15)$$

where[20,25]

$$\xi_i = \left[1 + \left\langle\Psi_i\middle|\vec{\sigma}_S\cdot\vec{p}\frac{c^2}{(2c^2 - V)^2}\vec{\sigma}_S\cdot\vec{p}\middle|\Psi_i\right\rangle\right]^{-1} \qquad (16)$$

The total energy expression of the scaled ZORA approach has to be modified also.[20,25] We apply the scaled ZORA approach in this work and in Paper II, unless otherwise noted.[20]

To illustrate the effect of the scaling procedure of eqs 15 and 16, we have performed calculations for a U^{6+} ion.[68] We present selected MO energies from these calculations in Table 1. Results for the higher angular momentum shells are very similar. We notice that the scaling procedure of eqs 15 and 16 reduces the energy of the core $1s_{1/2}$ shell by a large amount, about 13%. The $6s_{1/2}$ and $7s_{1/2}$ valence shells are, on the other hand, practically not influenced, and the reduction in energy amounts to only 0.03% and 0.01%, respectively, Table 1. This illustrates that the ZORA scaling procedure is mostly only relevant for the core levels where the effects of relativity are largest.

(D) Stability of Relativistic Methods. The Pauli operator of eqs 7 to 10 has been derived from first-order perturbation theory. Consequently, the use of Pauli type Hamiltonians beyond first-order perturbation theory has been criticized in the literature.[34] In particular, it has been shown that the mass−velocity operator (eq 8) is valid for small electron velocities only. It is wrong for larger velocities that approach the speed of light.[33] This is the case for core electrons of heavy elements that have a high probability of being close to the nucleus. One consequence is that any Hamiltonian containing the mass−velocity operator is not bound from below.[33] In practical calculations, this will lead to a variational collapse, i.e., to arbitrarily large negative one-electron energies.[35]

The stability problems are circumvented in the QR method by using the frozen core approximation.[21,22,69] Here, only valence electrons are treated variationally. Such electrons are located far from the core. Hence, they have small average velocities, and the Pauli Hamiltonian should be applicable. Core shells are assumed to be the same in the atomic and molecular cases. They are obtained from atomic density functional calculations, and kept frozen in subsequent molecular calculations. Their potential is calculated from four-component, fully relativistic atomic density functional calculations. Valence molecular orbitals are orthogonalized against all cores in the molecule. This feature constitutes a principal difference to ECP methods. It is an essential condition for heavy element NMR calculations because it ensures the proper nodal structure and asymptotic behavior near the nuclei.

A further consequence of the mentioned stability problems is that only certain types of basis sets can be used. For instance, the core part of the basis set must not be larger than of single-ζ quality, see below. Clearly, this may limit the accuracy of NMR shielding calculations. Basis set requirements for the QR method have been discussed in more detail by van Lenthe et al.[35] who have also given an illustration of the variational collapse.

The more modern ZORA method is variationally stable. Indeed, it has originally been derived with the fundamental problems of the QR method in mind. Hence, all electron or frozen core calculations are possible, and no restrictions are known for the choice of basis sets.

4. Computational Details

We calculate the NMR shielding tensor using DFT. The nonrelativistic and scalar QR (Pauli) approaches have been formulated and implemented by Schreckenbach and Ziegler.[18,27−30] This work has been extended by Wolff and co-workers to include the Pauli spin−orbit[19] and ZORA cases.[20] We use gauge-including atomic orbitals (GIAO) as field dependent basis functions[43−45] to deal with the gauge problem of magnetic properties,[2,3] Ssction 2.

Our NMR calculations are based on the Amsterdam density functional code ADF.[69−75] All relevant NMR integrals are evaluated with the accurate numerical integration schemes that are part of the ADF package.[72,76] We chose a dense integration grid to ensure numerical accuracy. (The ADF input parameter ACCINT was always set to 6 or higher.)

Unless otherwise noted, standard ADF basis sets are employed as follows. We use Slater type basis sets that are of triple-ζ quality in the valence region. These basis sets are augmented by two (all elements in ZORA calculations; elements H−Kr in QR calculations; ADF standard basis V) or one (all other elements in QR calculations; ADF standard basis IV) sets of polarization functions.[77] Further, for Pauli (QR) calculations, we use the frozen core approach[69] as described above. In our frozen core QR calculations, all shells up to and including the 1s (C, O, F), 2p (Cl), and 5d shells (U), respectively, are considered as core and kept frozen in molecular calculations. The (frozen) core orbitals are described by a double-ζ Slater type basis whereas the basis for the valence orbitals is of single-ζ quality in the core region. The ZORA calculations were performed with all-electron basis sets that are of double-ζ quality in the core region. (All-electron and/or double-ζ core basis sets cannot be used with the Pauli operator, cf. sections 2 and 3.[18] This restriction is necessary to avoid a variational collapse,[35] and of course, it limits the accuracy of the method.) A set of auxiliary s, p, d, f, and g STO functions, centered on all nuclei, is part of any ADF standard basis set. These auxiliary sets were employed to fit the electron density and to present the density dependent Coulomb and XC potentials accurately in each SCF cycle.[78]

We use the GGA XC functional due to Perdew and Wang[58] for all ADF NMR calculations, unless otherwise noted. This functional is known under the acronym PW91. Test calculations with another GGA (the BP86 functional[55,56]) gave very similar results. As noted in section 3, all current dependent terms[64−66] in the XC functional are neglected as are relativistic corrections to the XC functional.[53,63]

A few test calculations have been performed also with an ECP as developed by Hay and Martin[79] on the uranium atom. Spin−orbit effects have been neglected in these cases. The ECP calculations were based on the GAUSSIAN program system[80] where we employed the 6-311+G(2df) all electron Gaussian basis sets for the ligand atoms,[81] and a general ECP basis set in its totally uncontracted form for uranium.[79] Only ligand NMR shieldings have been calculated in this manner.

ECP calculations were done with the B3LYP hybrid functional[57,59,82] or the BPW91 GGA.[55,58] The latter combines Becke's GGA exchange[55] with the correlation part of the PW91 functional;[58] the exchange part of PW91 was not available with the Gaussian program.

Geometries. As mentioned above in section 2, we prefer to use high quality experimental geometries, in cases where this is possible. However, no experimental structural information is available for most of the compounds that were chosen for this study. Hence, we decided to use optimized geometries throughout, unless otherwise noted. For this purpose, we employed the same approach as in previous structural studies:[17,83−85] All structures were optimized with the Gaussian program system[80] where we employed an ECP as developed by Hay and Martin on uranium,[79] and the respective general ECP basis set in its totally uncontracted form. The 6-31+G* all-electron Gaussian basis set[81] was applied for all light ligand atoms. With this choice of basis set, we performed full geometry optimizations using DFT and the B3LYP hybrid XC functional.[57,59,60] Previous studies have shown that this combination gave good agreement between theory and experiment for a number of test cases.[83−85] Generally, experimental bond lengths were typically still overestimated to some degree.

5. Results and Discussion

(A) Chemical Shift Tensor: The Example of UF_6. The chemical shift (shielding) tensor is often thought to be a more stringent test of theoretical approaches than the isotropic average alone. This is because systematic errors may potentially cancel out in taking the average.

We have calculated the ^{19}F chemical shift tensor of uranium hexafluoride, UF_6. To the best of our knowledge, this is the only case where experimental tensor information is available for an actinide molecule.[86,87] Due to symmetry, the ^{19}F chemical shift tensor in UF_6 has two equivalent principal components orthogonal to the U−F bond axis, and one principal component parallel to it. Thus, the chemical shift tensor is entirely characterized by the isotropic chemical shift and the chemical shift anisotropy, i.e., the difference between orthogonal and parallel principal components. Calculated and experimental values for these properties are given in Table 2.

TABLE 2: Calculated and Experimental ^{19}F Chemical Shift Tensor in UF_6 (ppm)

method	chemical shift[a]	anisotropy[b]
experiment	764[c]	1210 ± 30[d]
Pauli scalar	813	1217
Pauli spin−orbit	846	1229
ZORA scalar	852	1246
ZORA spin−orbit	831	1270

[a] Relative to $CFCl_3$. Calculated ^{19}F shieldings are (optimized geometry): 130.8 ppm (nonrelativistic; Pauli scalar), 130.6 (Pauli spin−orbit), 125.9 (ZORA scalar), 130.7 (ZORA spin−orbit). [b] Chemical shift anisotropy: $\Delta\delta = \delta_\perp - \delta_\parallel$ [c] Reference 86. $CFCl_3$ solution. The same chemical shift value of $\delta = -764.0$ (5) ppm had also been obtained earlier by Seppelt and Bartlett.[90] [d] Reference 87. Polycrystalline UF_6 at low temperature.

Comparing scalar and spin−orbit relativistic calculations, we observe that spin−orbit effects are of a modest influence only. This follows also from a direct inspection of the respective calculations. Spin−orbit chemical shifts require strong s-type bonding contributions at the NMR nucleus.[19,88] This is not the case for the U−F bond where the fluorine atoms will bind primarily through p-orbitals (p_σ and p_π).[89] Hence, one would not expect prominent spin−orbit chemical shifts in this example.

The agreement between the experimental ^{19}F chemical shift, 764 ppm,[86,90] and the calculated values is reasonable although there are still considerable deviations with all the theoretical methods overestimating this value, Table 2. Interestingly, the spin−orbit correction goes in the wrong direction for the Pauli method, i.e., away from the experimental value and opposite to the ZORA case. As has been mentioned above in section 2, part of the problem might also be the calculated ^{19}F shielding of the reference compound, $CFCl_3$, rather than that of UF_6. In any case, it is well-known that the ^{19}F NMR is a particularly difficult case for all existing DFT methods.[27,66,91] These difficulties might be related to the extremely compact nature of the fluorine orbitals, or perhaps also to the neglected contributions from the current density.[64−66] We will discuss more calculated ^{19}F NMR shieldings and chemical shifts below and in Paper II.

The experimental shielding anisotropy[87] is well reproduced by all theoretical methods employed; the calculated values are within or close to the experimental error range. Thus, the shielding tensor as a whole is reasonably well reproduced by our DFT calculations. This is a clear success of the methods, giving confidence into their accuracy. Note that the orthogonal tensor components ($\delta_\perp$) are the most downfield ones, Table 2.

(B) Relativity: Pauli or ZORA? In this paper and in Paper II, we use principally two different approaches to relativity, the QR (Pauli) and the ZORA methods, section 3. Then, the question arises which one might be superior for the given set of molecules.

We have done many—indeed, most—of the calculations with both Pauli and ZORA. Hence, we will come back to the comparison of the two approaches in Paper II. At this point, we shall present a general discussion and a limited comparison.

ZORA is clearly superior over Pauli on purely theoretical grounds, because it avoids rather than circumvents the fundamental stability problems of the Pauli operator, sections 2 and 3. Furthermore, it has been found that ZORA is also more accurate in practical calculations. For instance, ZORA was shown to be superior for the ^{13}C chemical shifts in methyl derivatives CH_3X and CX_4 (X = Br, I),[17,20] as well as for ^{183}W and ^{207}Pb metal chemical shifts.[92] The deviations between the ZORA and the QR approaches may be partly due to the different

TABLE 3: Calculated and Experimental ^{19}F Chemical Shifts[a] in $UF_{6-n}Cl_n$ Compounds

			NMR Chemical Shift (ppm)[a]					
molecule	NMR system		experiment[b]	Pauli scalar	Pauli spin−orbit	ZORA scalar	ZORA spin−orbit	ECP−B3LYP scalar
UF_6	A_6		764.0	812.6	846.5	852.2	831.0	1030.3
UF_5Cl	A_4X	A_4	762.0	792.6	824.9	832.6	813.3	986.5
		X	781.5	757.9	797.8	798.0	780.2	1000.3
trans-UF_4Cl_2	A_4		755.5	782.5	813.0	823.4	805.0	950.4
cis-UF_4Cl_2	A_2X_2	A_2[c]	760.0	779.2	810.9	820.3	803.3	955.7
		X_2[c]	785.8	741.8	779.6	783.0	767.3	967.6
mer-UF_{3Cl3}	A_2X	A_2	753.0	773.4	803.9	813.9	798.0	918.9
		X	782.6	731.1	767.2	772.5	759.0	925.6
fac-UF_3Cl_3	A_3		786.4	727.9[d]	763.2[d]	770.2[d]	758.0[d]	926.7[d]
trans-UF_2Cl_4	A_2		746.1	769.8	799.3	809.1	795.0	888.9
cis-UF_2Cl_4	A_2		781.0	724.1	757.6	765.9	755.3	896.6
$UFCl_5$	A		774.3	718.2	750.9	758.4	750.8	858.1

[a] Relative to $CFCl_3$. Calculated ^{19}F shieldings are (optimized geometry): 130.8 ppm (nonrelativistic; Pauli scalar), 130.6 ppm (Pauli spin−orbit), 126.2 ppm (ZORA scalar), 130.7 ppm (ZORA spin−orbit), 155.0 ppm (ECP−B3LYP). [b] Downs and Gardner, ref 94. [c] $A_2-{}^{19}$F site trans to a fluorine; $X_2-{}^{19}$F site trans to a chlorine. [d] Averaged value; the three fluorine sites are not all equivalent in the optimized structure.

basis sets used (double-ζ vs single-ζ core type basis for ZORA and QR, respectively, cf. above), rather than to the different treatment of relativity alone.[93]

Here, we would like to investigate whether the practical superiority of ZORA over Pauli holds for the very heavy actinide molecules also.

As a first example, we have collected in Table 3 calculated and experimental ^{19}F chemical shifts in UF_6 derivatives $UF_{6-n}Cl_n$, $n = 0-5$. Let us, for the moment, ignore the ECP calculations and concentrate on the comparison of Pauli and ZORA results. The comparison of scalar and spin−orbit calculations, i.e., the importance of spin−orbit, shall be discussed in more detail below. Here, we note that (Pauli) Fermi-contact shielding contribution amounts to about −27 ppm for fluorine nuclei situated trans to another fluorine, and −35 to −41 ppm for sites trans to a chlorine. Interestingly, the sign of the spin−orbit correction is just reversed for the ZORA case. The magnitude of the correction is decreasing along the series. In summary, the spin−orbit effects are not negligible but result, in the Pauli case, in a fairly constant positive shift of the calculated (Pauli) chemical shifts. Similarly, they result in a comparatively small negative shift for the ZORA chemical shifts. (Recall the opposite sign between shieldings and chemical shifts, eq 1.)

When comparing calculated and experimental chemical shifts,[94] we note considerable differences between theory and experiment, Table 3. While some experimental trends are reproduced by both the ZORA and Pauli methods (e.g., the small increase in chemical shift in going from $UFCl_5$ to *cis*-UF_2Cl_4), other trends are not matched. In particular, the relative ordering between magnetically inequivalent fluorine sites is consistently predicted wrong by both ZORA and Pauli, scalar or spin−orbit. We will briefly come back to this somewhat disappointing result below in the discussion of the XC functionals. We note, for now, that the results in Table 3 do not allow for a discrimination between the ZORA and QR (Pauli) methods; there is no point in calculating such statistical measures as standard or mean absolute deviations.

As the next test, we have considered the ^{1}H and ^{19}F NMR chemical shifts in methoxy compounds $UF_{6-n}(OCH3)_n$. Experimental solution data (CH_2Cl_2 solution) is available in these cases,[95] see also Paper II. Both Pauli and ZORA spin−orbit calculations have been done for the first few members of the series ($n = 0-3$). We will discuss the methoxy series in more detail in Paper II. Here, we will use it only to determine the practical accuracy of the relativistic methods.

Starting with the proton NMR (^{1}H), we find that ZORA consistently overestimates the chemical shift by a fairly constant amount. Calculated Pauli chemical shifts are, on the other hand, spread to either side of the experimental data. Comparing theory and experiment for these compounds [$UF_{6-n}(OCH_3)_n$, $n = 1-3$], we obtain for the Pauli method an average absolute deviation of 0.27 ppm and a weighted average absolute deviation of 0.25 ppm. The degeneracy of the different methoxy sites has been used as the weighing factor in the latter value. The same numbers for the ZORA method are 0.68 ppm for the simple average, and 0.70 ppm for the weighted average. Thus, based on the absolute deviation, Pauli is, in this case, the more accurate method of the two, the difference being mostly due to the constant offset in the ZORA numbers.

The situation is different for the fluorine NMR (^{19}F). In this case, all the calculated chemical shifts are larger than their experimental counterparts. Such a constant offset might be due to the calculated shielding of the reference compound, at least in part (eq 1; see also below). As has been mentioned before, the ^{19}F nucleus is a rather difficult case for any DFT-NMR method. In any case, let us compare the calculated and experimental ^{19}F NMR chemical shifts for the first few compounds of the methoxy series [$UF_{6-n}(OCH_3)_n$, $n = 0-3$]. Then, we obtain for the Pauli (ZORA) method an average deviation of 125.7 ppm (115.3 ppm), and a weighted average deviation of 122.7 ppm (111.7 ppm). Thus, ZORA is slightly but clearly superior over Pauli for this case.

In summary, we found, quite surprisingly, that it is not as easy here as in earlier studies[17,20,92,93] to prove the practical superiority of the ZORA method over the Pauli (QR) approach. Nevertheless, we still consider the ZORA approach to be the more accurate method of the two, even for the given molecules. This assertion is based on the mentioned experience and theoretical arguments but also on the fact that better basis sets can be—and have been—used with ZORA. Furthermore, in Paper II, we shall discuss another case where ZORA is superior in practical calculations (ligand NMR in uranyl compounds $[UO_2L_n]^{\pm q}$), and we will present arguments according to which the Pauli approach appears to be at or beyond its limits for the NMR of the very heavy uranium nucleus (^{235}U).

(C) ZORA: To Scale or Not To Scale? In the ZORA approach to relativity, one has the option of using the scaled or unscaled ZORA MO energies (eigenvalues), eqs 14 to 16 and Table 1. We have tested the influence of this option and compared NMR shielding and chemical shift results for the two methods. The calculated ^{19}F and ^{235}U NMR in the series

TABLE 4: To Scale or Not to Scale: Comparison of Calculated (ZORA Spin−Orbit) ^{19}F and ^{235}U Absolute Shieldings (σ) and ^{235}U Chemical Shifts[a] (δ) in $UF_{6-n}Cl_n$ Molecules (ppm)

molecule	^{19}F NMR system		$\sigma(^{19}F)$		$\sigma(^{235}U)$		$\delta(^{235}U)$	
			unscaled	scaled	unscaled	scaled	unscaled	scaled
UF_6	A_6		−700.4	−700.3	−2434	678	0	0
UF_5Cl	A_4X	A_4	−682.6	−682.6	−5049	−1934	2614	2612
		X	−649.1	−649.5				
trans-UF_4Cl_2	A_4		−674.4	−674.3	−7707	−4589	5273	5268
cis-UF_4Cl_2	A_2X_2	A_2[b]	−672.6	−672.6	−7325	−4206	4891	4884
		X_2[b]	−636.3	−636.6				
mer-UF_3Cl_3	A_2X	A_2	−667.4	−667.3	−9664	−6541	7229	7219
		X	−628.1	−628.3				
fac-UF_3Cl_3	A_3		−626.9[c]	−627.3[c]	−9362	−6239	6928	6918
trans-UF_2Cl_4	A_2		−664.3	−664.3	−11757	−8631	9323	9309
cis-UF_2Cl_4	A_2		−624.3	−624.6	−11516	−8388	9081	9066
$UFCl_5$	A		−619.9	−620.1	−13409	−10275	10975	10954
UCl_6					−15198	−12057	12764	12736

[a] ^{235}U chemical shifts taken relative to UF_6, see also Paper II. [b] A_2−^{19}F site trans to a fluorine; X_2−^{19}F site trans to a chlorine. [c] ^{19}F NMR shieldings averaged over the three fluorine nuclei.

$UF_{6-n}Cl_n$ ($n = 0-6$) has been chosen as the test case. Results have been collected in Table 4.

The scaling procedure has practically no effect on the ligand (^{19}F) shieldings and hence chemical shifts. Here, the differences between scaled and unscaled ZORA NMR calculations amount to 0.4 ppm at most, much less than the errors that have been discussed in the previous sections. We conclude that the unscaled ZORA approach is entirely sufficient if only ligand NMR parameters are of interest.

The situation is more complex for the heavy ^{235}U nucleus, Table 4. Inclusion of the scaled eigenvalues leads to enormous changes in the calculated absolute shieldings. The differences between the scaled and unscaled ZORA calculations are as large as 3141 ppm (for UCl_6). Most of that cancels out in relative chemical shifts where the differences amount to less than 30 ppm for the molecules studied, Table 4.

We conclude that the ZORA scaling should influence core orbitals only. This point of view is supported by a direct inspection of the calculated MO energies for the uranium atom, cf. Table 1 and the accompanying discussion. In this way, the effects of the scaling are largely independent from the chemical environment of the heavy nucleus and should cancel out in relative chemical shifts, as is indeed observed in the calculations, Table 4.

Similar effects have been observed earlier for the somewhat lighter ^{199}Hg nucleus.[20,96] For the mercury nucleus, there are also large differences in the absolute shieldings between unscaled and scaled ZORA calculations. Again, this cancels out in relative chemical shifts. The remaining differences were found to be as small as 1 ppm, even smaller than for the case of ^{235}U NMR. The conclusion for the earlier ^{199}Hg studies[20] was that the ZORA scaling procedure is not necessary.

Regarding the calculated ^{235}U NMR, we have decided to keep the ZORA energy scaling (eqs 14 to 16) in our calculations. As has been discussed above, some small but noticeable effects of the scaling procedure survive even in the relative chemical shifts, Table 4. What is more important, though, is that ^{235}U NMR is not yet known experimentally, apart from a single observation of a ^{235}U resonance for UF_6.[97] Hence, accurately calculated chemical shifts *and* absolute shieldings might be helpful to guide future NMR experiments. The calculated ^{235}U NMR shieldings and chemical shifts will be discussed in greater detail in Paper II.[10]

(D) Spin−Orbit Effects. As has been mentioned above in sections 2 and 3, spin−orbit effects can be included or excluded. The question arises whether such spin−orbit effects (eqs 10 and 13, respectively) are relevant, or whether the computationally less demanding scalar relativistic approximation might suffice. In the following, we would like to discuss by way of some examples the importance of spin−orbit for the ligand NMR. We will postpone the discussion of spin−orbit effects in the ^{235}U metal NMR to Paper II.

TABLE 5: Calculated Ligand Absolute Shieldings in $UF_5(OCH_3)$ (Values in ppm)

	calculated shielding			
	Pauli (QR)		ZORA	
nucleus[a]	scalar	spin−orbit	scalar	spin−orbit
^{19}F (A_4 site)	−586.4	−618.0	−627.7	−605.7
^{19}F (X site)	−593.4	−633.2	−634.4	−616.5
^{17}O	−534.9	−570.8	−563.5	−568.3
^{13}C	79.1	76.6	79.1	79.8
^{1}H	26.00	19.17	25.92	18.39

[a] An average has been taken in cases where more than one nucleus belongs to a given site (^{1}H, ^{19}F−A_4).

We have seen before that spin−orbit effects are of modest relevance only for the calculated ^{19}F NMR chemical shifts along the uranium fluoride chloride series, Table 3. Given the magnitude of the errors for these compounds, spin−orbit effects could, in principle, be neglected in this case.

The situation is different for the methoxy derivatives of UF_6, $UF_{6-n}(OCH_3)_n$ that have also been discussed already in the previous section. As an example, we have compiled calculated ligand shieldings for the first member of the series ($n = 1$), $UF_5(OCH_3)$, in Table 5. The situation is very similar for the other members of the series (i.e., for $n > 1$).

We note from this table that spin−orbit has only a moderate influence on the calculated ^{19}F shieldings. This influence is very similar to the case of the fluoride chlorides, Table 3. In particular, we note that in either case, scalar and spin−orbit calculations give the same relative ordering for inequivalent sites (A_4 vs X in this case). Additionally, we observe again that the spin−orbit corrections do not have the same sign for the Pauli and ZORA methods, Tables 3 and 5. The reason for these differences is not at all clear at the moment. We note, however, that the spin−orbit chemical shifts are defined in different ways for the two methods.[19,20]

Spin−orbit has a very small influence on the calculated ^{13}C shielding in $UF_5(OCH_3)$. Indeed, it is practically negligible. The influence on the ^{17}O NMR can be characterized as being small (ZORA) to modest (Pauli), Table 5.

The situation is very different for the proton NMR. Here, we observe large spin−orbit chemical shifts of almost 7 ppm, Table 5. Thus, spin−orbit is essential for a correct representation of the proton NMR.

We conclude that the scalar relativistic approximation is sufficient for the ligand NMR shieldings and chemical shifts in some cases but entirely insufficient in others. Proton (^{1}H) NMR is a prominent example in the latter category.

(E) Effective Core Potentials. It is not possible, by construction, to get meaningful NMR parameters from ECP calculations for the heavy nucleus proper, see above. However, relativistic NMR calculations for light ligand atoms in transition metal complexes have been performed very successfully. In this type of calculations, relativistic effects are described by an ECP at the transition metal center, whereas all electron basis sets are employed for the (light) NMR nuclei.[7,9,36,37]

We have tested the applicability of this approach for some of the heavy uranium compounds that are the subject of the given study. We used an ECP at uranium[79] and the B3LYP functional[57,59,82] to calculate the ^{19}F NMR chemical shift for the uranium fluoride chloride series. The results are compiled in Table 3. Comparing the ECP results to the experimental NMR data,[94] we notice that the chemical shift is strongly overestimated in all cases. The deviation amounts to between about 80 and 270 ppm for the different molecules. Experimental trends along the series, such as the relative chemical shift between different compounds (e.g., UF_5Cl vs *cis*-UF_4Cl_2), are generally not well reproduced. Thus, we conclude that the ECP approach is beyond its limits for the NMR of the very heavy actinide compounds.

(F) XC Functionals. As has been discussed above, the choice of model XC functional can, at times, have a *dramatic* (Bühl[61]) effect on the calculated NMR shieldings and chemical shifts.[8] In particular, it has been found that hybrid functionals such as B3LYP[57,59,82] are strongly superior over GGAs for, e.g., ^{57}Fe and ^{103}Rh chemical shifts[61] but inferior for other cases such as ^{17}O NMR[62] in transition metal complexes MO_4^{n-}.

Thus, we found it appropriate to test the performance of hybrid functionals for the given systems. A technical difficulty arises in that such functionals are currently not available in the ADF program[69−75] that has been the basis for most of the calculations in the given study and in Paper II. Therefore, we had to resort to the Gaussian program.[80] However, this means that we had to rely on ECPs for the description of the (scalar) relativistic effects, and an adequate relativistic description is not possible, cf. the preceding section. Hence, only limited conclusions can be drawn in the following.

We have chosen the ^{19}F NMR of the uranium fluoride chloride series as the test case. This appears to be a reasonable choice since, on one hand, the GGA description is somewhat deficient, see above. On the other hand, the effects of spin−orbit are comparatively small, so that their neglect in the ECP calculations does not introduce large additional errors.

Results of ECP NMR calculations with the B3LYP hybrid functional[57,59,82] are shown in Table 3. While the absolute values of the chemical shifts are not very good, we notice that these calculations reproduce certain experimental trends that were missed by the (QR or ZORA) GGA calculations. For instance, the calculated difference in chemical shift between the two inequivalent ^{19}F sites in UF_5Cl, A_4 and X, 14.1 ppm (ECP-B3LYP) compares reasonably well to the experimental value of 19.5 ppm, Table 3. GGA calculations with either the ZORA or QR relativistic methods get the opposite sign for this difference. (This applies to both the PW91[58] and BP86 functionals;[55,56] recall that the two GGAs gave very similar results.) This is also true for the ECP approach: ECP−BPW91 calculations[55,58] give chemical shifts of 1010.2 ppm for the A_4 sites and 977.3 for the X site of UF_5Cl. Other cases where the GGAs miss the experimental order of inequivalent sites include *cis*-UF_4Cl_2 (A_2 versus X_2), mer-UF_3Cl_3 (A_2, X), and *trans*- versus *cis*-UF_2Cl_4, Table 3. ECP−B3LYP gets at least the right ordering in all of these cases; even though, of course, neither the absolute values of the calculated chemical shifts nor the shifts between the different members of the series are too impressive. Interestingly, GGA based ECP calculations (ECP-BPW91[55,58]) give again the wrong sign for every one of these cases. This *may* indicate that hybrid functionals are required for a correct description of the ^{19}F NMR in the uranium fluoride chloride systems. However, it is not possible to pursue this any further at the moment, and a test of this assertion will only be possible once a reliable relativistic DFT-NMR method *and* hybrid XC functionals become available in one and the same program system.

Recently, we have analyzed in some detail[98] how the inclusion of exact Hartree−Fock exchange in hybrid functionals influences the calculated ^{57}Fe NMR shielding and chemical shift in ferrocene and other compounds of iron. Ferrocene was the case that showed the most dramatic influence of the hybrid functionals.[61] In our study, we found three major differences between NMR shieldings (chemical shifts) from hybrid functionals and pure DFT (GGAs), respectively.[98] These are (i) a change (increase) in occupied-virtual separation that is due to a strong stabilization of occupied MOs, accompanied by a slight destabilization of the virtuals, (ii) the more diffuse nature of at least one important virtual MO, the LUMO in this case, and (iii) the coupling due to the Hartree−Fock exchange that is not present for pure DFT. It is difficult to assess which of these influences might be responsible for the observed differences between ECP based hybrid and GGA calculations for the uranium chloride fluorides. However, it is obvious that, in UF_5Cl for instance, different pairs of occupied and virtual MOs will be responsible for the calculated shielding of the A_4 and X sites, respectively. Hence, the first point, the change in MO energies and energy separations due to exact exchange, ought to be important here, too. It is less clear how the presence or absence of coupling could have a very different influence on the shielding of the different fluorine sites, making the third point an unlikely candidate. Likewise, one can test the importance of the second point by direct inspection of, e.g., the QR calculations. Taking as the example again the A_4 and X sites in UF_5Cl, it appears that their ^{19}F NMR shieldings are due to couplings that comprise roughly the same set of virtuals. Then, the shape of some particular virtual MO cannot have an influence on the *relative* ordering for the two distinct sites. To summarize, it appears that, in the given case, the change in MO energies due to Hartree−Fock exchange might be the determining factor for the possible superiority of the hybrid functional. A more detailed and less speculative discussion is not possible at the moment.

(G) Reference Compound, Geometry Dependence of the NMR Shielding. As has been discussed above in section 2, the calculated shielding of the reference compound for some nucleus is relevant for the discussion of chemical shift results: It can either hide or introduce systematic errors into the calculations. Here, we would like to discuss and illustrate the influence of the reference compound by way of example.

The experimentally used reference compound for ^{1}H (proton) NMR is tetramethylsilane, TMS. We have calculated the ^{1}H absolute shielding for TMS. Nonrelativistic DFT as well as the different relativistic approaches have been used, Table 6. In this

TABLE 6: Calculated ^{1}H Absolute Shieldings in TMS (Values in ppm)

method	Calculated ^{1}H Shielding		difference
	exptl geometry[a]	optimized geometry[b]	
nonrelativistic	30.922	31.444	0.522
Pauli scalar	30.913	31.435	0.522
Pauli spin−orbit	30.931	31.452	0.521
ZORA scalar	30.872	31.406	0.534
ZORA spin−orbit	30.872	31.406	0.534

[a] Reference 99, electron-diffraction data. [b] Optimized with the Gaussian program[80] at the 6-31+G*/B3LYP level of theory.

way, we are able to compare calculated proton chemical shifts directly to experiment.

For TMS, high-quality experimental geometrical parameters are available from electron-diffraction studies.[99] In this case, the question arises anew whether to use the experimental structure or an optimized structure.

To decide this question, we have compared the calculated proton absolute shielding of TMS for the two geometries. As is evident from Table 6, the optimized structure results in absolute shieldings that are 0.52 to 0.53 ppm larger than those based on the experimental geometry. This difference is due to deviations in the structures: The optimized (6-31+G*/B3LYP) Si−C and C−H bond lengths, 1.897 and 1.098 Å, respectively, are both off by about 0.02 Å as compared to their experimental counterparts,[99] 1.876 and 1.115 Å, respectively.

We have further calculated the proton (^{1}H) chemical shifts in the methoxyuranium series $UF_{6-n}(OCH_3)_n$, $n = 1-5$. Using the optimized geometry for TMS results in an average deviation between theory and experiment[95] of 1.14 ppm (ZORA spin−orbit), and the proton chemical shift is uniformly overestimated. The average deviation is almost cut in half by using the experimental TMS geometry, and amounts to only 0.61 ppm for the same set of molecules. Thus, we find it reasonable to use the experimental geometry for TMS as a basis of our ^{1}H chemical shift calculations. The $UF_{6-n}(OCH_3)_n$ molecules will be discussed in more detail in Paper II.[10]

In the literature, it has been suggested that geometry optimizations should employ at least a triple-ζ basis set with polarization functions if they are to be used as the basis for NMR calculations.[100] The structural and NMR data for TMS presented above underlines the point: a double-ζ basis set such as 6-31+G* appears to be insufficient. At that point, we had the choice of either using the experimental geometry or a higher level basis set. Such basis sets would, however, not be affordable for the rather large actinide complexes. Given both the quality of the experimental TMS structure[99] and the ^{1}H chemical shift results cited above, we decided to use the experimental structure for this molecule.

The dependence of the ^{1}H NMR in TMS on the structure is an example where uniform systematic errors are introduced from the reference compound into the calculated chemical shifts. Additionally, it is a clear example for the strong geometry dependence of (calculated) NMR shieldings. We will discuss one more example for such geometry dependencies next.

We have calculated the NMR shieldings of all the nuclei in the pentaaquo uranyl (VI) complex, $[UO_2(H_2O)_5]^{2+}$. The optimized ground-state structure possesses D_5 symmetry at the chosen B3LYP/ECP/6-31+G* level of theory. The water molecules are tilted from an idealized D_{5h} geometry by 25.07°. On the other hand, properties (other than the NMR shieldings) of this and related molecules have been studied before based on an idealized D_{5h} geometry.[101] The question arises whether such a simplification is useful for the very sensitive NMR shieldings.

TABLE 7: Calculated NMR Shieldings in $[UO_2(H_2O)_5]^{2+}$ for the Ground State (D_5) Geometry as Well as for an Idealized D_{5h} Geometry

nucleus	calculated shielding (ppm)			
	Pauli		ZORA	
	scalar	spin−orbit	scalar	spin−orbit
D_5 Ground-State Structure				
^{235}U	3330	3399	−82	8954
^{17}O (uranyl)	−726.0	−716.5	−738.1	−756.1
^{17}O (water)	240.0	212.3	233.4	217.8
^{1}H	24.6	24.2	24.4	23.9
D_{5h} Structure				
^{235}U	3283	3355	−145	8855
^{17}O (uranyl)	−722.3	−712.8	−733.9	−752.8
^{17}O (water)	231.3	202.9	223.7	207.7
^{1}H	24.5	24.0	24.2	23.6

We have calculated NMR shieldings for the $[UO_2(H_2O)_5]^{2+}$ complex in its ground-state D_5 symmetry as well as for an idealized D_{5h} structure. The results are shown in Table 7. At this point, we will not discuss the large difference in absolute shielding for the ^{235}U nucleus between the different methods. As will be explained in detail in Paper II, most of these differences are due to inclusion or neglect of certain core effects. Accordingly, they cancel out in relative chemical shifts. Here, we will mostly concentrate on the difference between the two structures for a given method.

Starting with the water protons, we note that the structural differences amount to rather small changes of 0.3 ppm or less. This should not be too surprising, given that the immediate vicinity of these nuclei, i.e., the water ligands, are hardly changed from one structure to the other. Likewise, only a modest geometry influence is observed for the uranyl oxygen atoms where the calculated shieldings (and chemical shifts) change by about 4 ppm only. The picture is different for the remaining two sites, the water oxygen and the metal. The tilting of the water molecules from the D_{5h} structure to the ground-state D_5 structure is seen to result in a decrease in shielding (increase in chemical shift) of about 10 ppm for the water oxygen site. Finally, the calculated ^{235}U NMR shieldings change the most in absolute terms, by about 100 ppm for the ZORA spin−orbit approach. We conclude that, overall, the use of an idealized D_{5h} structure appears to be questionable if NMR parameters are of interest.

6. Conclusions

In this paper and the subsequent Paper II,[10] relativistic DFT has been applied to the heaviest part of the periodic table, the actinide block. Diamagnetic uranium compounds have been chosen as a representative example.

In the given first paper of the series, we have compiled, discussed and evaluated various issues related to the calculation of NMR shieldings and chemical shifts in such systems.

We found the relativistic DFT-QR (Pauli) and DFT-ZORA methods to be applicable for the calculation of metal and ligand chemical shifts in such heavy element compounds. On the other hand, relativistic DFT-ECP methods appear to be beyond their limit, even for the NMR of neighboring light nuclei. (ECP NMR calculations are intrinsically impossible for the heavy element proper.)

Comparing ZORA and Pauli, we did not unambiguously confirm the earlier observation[17,20,92,93] that ZORA is the more reliable approach of the two. Thus, we found Pauli to be clearly superior for the ^{1}H (proton) NMR in $UF_{6-n}(OCH_3)_n$ compounds ($n = 1-3$) where the calculated ZORA chemical shifts are too large by a fairly uniform amount, see also Paper II. Nevertheless, ZORA is seen to be more accurate for the same set of compounds if other nuclei (notably ^{19}F) are considered. Besides, ZORA is clearly superior on theoretical grounds. Additionally, better basis sets can be used in the ZORA case.[93] This is particularly important for heavy nuclei with large cores, including the ^{235}U nucleus, Paper II. We conclude that, overall, ZORA is the more accurate approach of the two, even for the heaviest part of the periodic table.

We have discussed the influence of spin−orbit effects on the calculated ligand NMR in uranium compounds. The neglect of such effects (leading to the simpler and cheaper scalar relativistic methods) was found to be a reasonable approximation in some cases, for example, the ^{19}F NMR in $UF_{6-n}L_n$ compounds, Tables 3 and 5. In other cases, however, spin−orbit chemical shifts were found to be essential for a correct representation of the NMR shieldings and chemical shifts. In particular, we found large spin−orbit chemical shifts for the proton (^{1}H) NMR shieldings and consequently chemical shifts. These spin−orbit chemical shifts turned out to be as large as 7 ppm in our example $UF_5(OCH_3)$, Table 5. The origin of the spin−orbit chemical shifts has been discussed in detail in the literature.[20,88] The consensus is that the dominant mechanism can be understood as follows. The relativistic spin−orbit effects, in the presence of a magnetic field, produce spin polarization at the heavy nucleus.[19,88] This spin polarization is transferred through the bond to the NMR nucleus where it is picked up by means of a Fermi-contact mechanism. One consequence is that spin−orbit chemical shifts are only relevant if there are strong s bond contributions at the NMR nucleus. (Otherwise, the Fermi-contact mechanism is not important.) This explains why we found large spin−orbit chemical shifts for the ^{1}H NMR but less so for other nuclei, Table 5: A hydrogen atom will bind primarily through its s orbitals, and strong spin−orbit chemical shifts should be expected in this case. The other nuclei (in our case carbon, oxygen, fluorine) will, however, bind mostly through their p orbitals. We will come back to the discussion of spin−orbit effects in Paper II.

Regarding a technical detail, we observed that the ZORA scaling procedure (eqs 14−16, Table 1) has practically no influence on the ligand NMR shieldings and chemical shifts. On the other hand, its influence on the absolute shielding of the heavy metal is rather large, Table 4. Core effects that cancel out in relative chemical shifts (Table 1) are the biggest part of this, and only a very modest influence of the scaling procedure survived in relative chemical shifts. Thus, it is essential to use the full scaled ZORA approach if the metal *shielding* is required rather than the relative chemical shift alone. Otherwise, unscaled ZORA or Pauli should be a reasonable alternative. However, we will conclude in Paper II that Pauli is at or beyond its limit for the NMR chemical shifts of the very heavy actinide nuclei.

We have discussed, by way of example, the influence of the reference compound and the strong geometry dependence of the calculated NMR shieldings and chemical shifts. This dependence makes the use of idealized geometries questionable (e.g., a D_{5h} geometry for the uranyl water complex, Table 7).

We have applied the DFT-QR and DFT-ZORA approaches to the ^{19}F NMR in mixed uranium chloride fluorides, $UF_{6-n}Cl_n$ where experimental data is available.[94] While the agreement between theory and experiment[86,87] is satisfactory for the ^{19}F chemical shift tensor of UF_6 (Table 2), it is less good for the ^{19}F chemical shifts along the entire series, Table 3. Here, only some experimental trends have been reproduced, and other important trends have been missed by the calculations.

We have discussed possible reasons for these shortcomings of the theoretical methods. On the basis of test calculations with an ECP at the uranium atom, we found that the XC functionals *might* be responsible for these problems. In this case, we used GGAs[55,58] and hybrid functionals[57,59,82] as model functionals. Thus, while ECP calculations gave rather bad results in general, they did reproduce certain experimental trends if a hybrid model functional (B3LYP[57,59,82]) was employed instead of a GGA. Hence, it appears that hybrid functionals *could* be required for the ^{19}F NMR in the $UF_{6-n}Cl_n$ molecules. These conclusions will remain preliminary for the moment. A decisive test will require that a proper treatment of relativity beyond the use of ECPs (e.g., ZORA or QR) *and* hybrid DFT functionals be available in one and the same program. Currently, this is not the case. Besides, it will be interesting to apply new model XC functionals to this demanding test case. Potentially interesting developments in this regard include modern GGAs (e.g., the PBE functional[102]) or meta-GGAs (see, e.g., ref 103; the meta-GGAs include the so-called kinetic energy functionals, e.g., ref 104).

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