Relativistic Effects for NMR Shielding Constants in Transition Metal Oxides Using the Zeroth-Order Regular Approximation

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Relativistic effects for NMR shielding constants have been calculated using the zero order regular approximation (ZORA) for relativistic effects. Isotropic NMR shielding constants were obtained using density functional theory with gauge including atomic orbitals (GIAO) in a spin-free formalism for the metal nuclei in transition metal oxides MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and carbonyl complexes $M(CO)_6$ (M = Cr, Mo, W). The ZORA isotropic shieldings are compared with results from an extended version of the relativistic method employing the Pauli Hamiltonian developed earlier by Schreckenbach and Ziegler. Comparison between ZORA and Pauli shieldings, employing the restrictions necessary for the Pauli approach—frozen cores, restricted basis sets in the core region—show the ZORA shieldings to be significantly different from Pauli ones, but the chemical shifts of the metal oxides with respect to the carbonyl complexes do not differ much. However, extending the ZORA calculations (no frozen core, extended basis sets) gives significant changes, proving the limitation to frozen cores and restricted basis sets of the Pauli method to be unwarranted. Comparison to experiment shows that the errors of the most precise ZORA chemical shifts are ca. 10% (in the order of a few 100 ppm) for both the light and heavy transition metals. Error sources may be, apart from deficiencies of the density functional, the neglect of spin−orbit coupling and the neglect of solvent effects.

1. Introduction

NMR spectroscopy is widely applied in chemistry and biochemistry. Calculations in this field are important for correlating measurements of the chemical shift with the molecular structure. The theoretical determination of NMR parameters is of general interest, but lately special attention is also being given to relativistic effects in NMR shielding of heavy nuclei.[1−8] The relativistic effects are not only important for the NMR shielding of the heavy atom themselves but also for light ligands. For the chemical shifts of the latter especially, the spin−orbit coupling turned out to be important.[9−13] For the heavy atoms, the scalar relativistic effects are particularly important.[4] In order to enable applications to large systems containing heavy atoms, an accurate and efficient method is required, for which DFT-based methods offer good prospects. Significant progress in the application of DFT for shielding tensor calculations has been made by Schreckenbach and Ziegler using a density functional theory (DFT) method with gauge including atomic orbitals (GIAO),[14,5] by Malkin, Malkina, and Salahub,[15−17] also using DFT methods but with independent gauge for localized orbitals (IGLO) and by Wolff and Ziegler,[11] who also include spin−orbit coupling.

Malkin and co-workers used relativistic pseudopotentials and did therefore not calculate heavy atom shieldings. Schreckenbach and Ziegler treat relativistic effects using the so-called quasi-relativistic method based on the Pauli Hamiltonian, which has some well-known problems coming from the use of an expansion parameter that becomes singular close to the nuclei. This makes all-electron calculations on heavy systems impossible, because the Pauli Hamiltonian has no lower bound and the necessary tight functions will lead to variational collapse. The quasi-relativistic method can therefore only be applied with a frozen core approximation that avoids variational collapse by the orthogonality constraint on the core. In addition, the basis set needs to be restricted, in the sense that, in a heavy metal complex for instance, tight functions are to be avoided at the metal nucleus as well as large flexible basis sets on the ligands.

The zeroth-order regular approximation (ZORA)[18,19] presents a good alternative, giving a two-component relativistic method which is variationally stable and can be used in all-electron calculations. A first application of the ZORA NMR method has already been published by Wolff et al.[8]

We will make a detailed comparison between the application of the quasi-relativistic Pauli method for NMR and the ZORA, which we use in its spin-free (one-component) form. First, in section 2, the derivation of the expressions for the shielding tensors will be treated for both the quasi-relativistic Pauli method and the ZORA method. We will identify some relativistic terms in the Pauli method which were neglected by Schreckenbach

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and Ziegler. These terms have been included to make a fair assessment of the Pauli method. In section 3, applications are presented for a series of transition metal oxides MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os), as well as for the hexacarbonyl complexes $M(CO)_6$. A detailed comparison between ZORA and Pauli shieldings and chemical shifts is made in section 3.2. This comparison has necessarily to be performed within the restrictions imposed by the Pauli method (frozen cores, restricted basis sets). Although the differences for the shieldings are not negligible, they tend to be similar for different complexes such as the oxides and carbonyl complexes investigated here. This implies that the ZORA and Pauli chemical shifts are not so different. However, the results are, due to the restrictions on the basis sets, not close to the basis set limit. A distinct advantage of the ZORA method is the possibility to perform all-electron calculations in extended basis sets, including special tight functions to describe the core orbitals and particularly the core tails of valence orbitals accurately. Extensive ZORA investigations of the frozen core approximation and basis set effects are presented in section 3.3. Section 4 summarizes the results.

2. Theory

We begin by deriving relativistic Hamiltonians for an electron moving in a molecule that is a placed in an external magnetic field. We then follow the procedure outlined by Schreckenbach and Ziegler[5,14,20] and obtain the shielding tensor as the second derivative of the electronic energy with respect to both the external and the internal (arising from the nuclear magnetic moments) magnetic field. The resulting expressions are formulated in a Hamiltonian-independent way, which allows us to treat the nonrelativistic, Pauli, and ZORA Hamiltonians within the same formalism. In this formalism, we use the GIAO method to avoid unphysical dependencies on the gauge-origin of the external magnetic field and allow for the definition of frozen core orbitals (section 2.3).

2.1. Relativistic Hamiltonians. As a starting point for our relativistic calculations, we use the Dirac equation for a one-electron system in atomic units

$$\begin{pmatrix} V & c\vec{\sigma}\cdot\vec{p} \\ c\vec{\sigma}\cdot\vec{p} & V - 2c^2 \end{pmatrix}\begin{pmatrix}\phi\\ \chi\end{pmatrix} = E\begin{pmatrix}\phi\\ \chi\end{pmatrix} \tag{1}$$

which contains the large component ϕ and the small component χ. The effective one-electron potential V in our density functional calculations is the sum of the external nuclear potential, the Hartree (Coulomb) potential from the electron density, and the exchange-correlation potential.

The traditional reduction of the four-component Dirac formalism to an approximate (or exact, see Foldy–Wouthuysen transformation[21]) two-component one starts with elimination of the small component χ to give the following equation for the large component ϕ

$$V\phi + \frac{1}{2}\vec{\sigma}\cdot\vec{p}\left(1 + \frac{E - V}{2c^2}\right)^{-1}\vec{\sigma}\cdot\vec{p}\phi = E\phi \tag{2}$$

Since the large component is not normalized we introduce a two-component normalized function $\Psi = O\phi$ with O a normalization operator, which can be chosen as

$$O = \sqrt{1 + X^{+}X} \tag{3}$$

with

$$X = \frac{1}{2c}\left(1 + \frac{E - V}{2c^2}\right)^{-1}\vec{\sigma}\cdot\vec{p} \tag{4}$$

The textbook approach[22,23] now is to expand these equations in $(E - V)/2c^2$ resulting in the first-order Pauli Hamiltonian

$$H^{\mathrm{Pauli}} = V + \frac{p^2}{2} - \frac{p^4}{8c^2} + \frac{\Delta V}{8c^2} + \frac{1}{4c^2}\vec{\sigma}\cdot[\vec{\nabla}V \times \vec{p}] \tag{5}$$

consisting of the nonrelativistic Hamiltonian, the mass–velocity term, the Darwin term and the spin–orbit coupling term. This expansion is, however, only valid if the velocity of the electrons is everywhere small compared to the velocity of light ($E - V \ll 2mc^2$). This condition is not satisfied for a Coulombic potential like the nuclear potential. The singularities that arise in approximate two-component theories in a Coulomb potential have been discussed by Kutzelnigg and others.[24–27]

Following van Lenthe et al.,[18,28] the problems are avoided by using an expansion in $E/(2c^2 - V)$ which is regular even near the singularity of a Coulombic potential. Up to zeroth order this regular approximation (ZORA)[18] gives for the Hamiltonian

$$H^{\mathrm{ZORA}} = V + \vec{\sigma}\cdot\vec{p}\frac{K}{2}\vec{\sigma}\cdot\vec{p} = V + \vec{p}\cdot\frac{K}{2}\vec{p} + \vec{\sigma}\cdot\left[\vec{\nabla}\left(\frac{K-1}{2}\right) \times \vec{\mathrm{p}}\right] \tag{6}$$

where

$$K = \frac{1}{1 - \dfrac{V}{2c^2}} \tag{7}$$

The scalar relativistic effects are incorporated in the first two terms $V + \vec{p}\cdot(K/2)\vec{p}$. This Hamiltonian was derived earlier by Chang et al.[29] and Heully et al.[30] Notice that in the case $K = 1$ we get the nonrelativistic Hamiltonian.

Although the spin–orbit coupling can be quite considerable for heavy elements, and in fact affects the shielding of light ligand nuclei,[10,11] we will in this paper concentrate on the scalar relativistic effects on NMR shielding of heavy metal nuclei using the spin-free relativistic theory. The terms in the Hamiltonian linear in the spin are therefore ignored.

We now include the magnetic field in the Hamiltonian by means of minimal substitution

$$\vec{p} \rightarrow \vec{p} + \frac{\vec{A}}{c} \tag{8}$$

The vector field $\vec{A}$ is given by

$$\vec{A} = \frac{1}{2}(\vec{B}^{\mathrm{ext}} \times \vec{r}_{\mathrm{g}}) + \frac{\vec{\mu} \times \vec{r}_N}{r_N^{\,3}} \tag{9}$$

containing the applied external magnetic field $\vec{B}^{\mathrm{ext}}$, the nuclear magnetic moment $\vec{\mu}$ of the atom under consideration, the position $\vec{r}_N$ relative to the considered atom and the position $\vec{r}_{\mathrm{g}}$ relative to the gauge origin $\vec{R}_{\mathrm{g}}$ of the vector potential of the external magnetic field. The vectorfield satisfies the Coulomb gauge, i.e., $\vec{\nabla}\cdot\vec{A} = 0$.

The gauge origin can in principle be chosen arbitrarily, since this choice does not affect the magnetic field. The calculated shielding tensor does, however, depend on the chosen gauge unless a complete basis set is used. Since we will consider a finite basis set consisting of atomic orbitals (AOs), this may result in a gauge origin dependence of the calculated shielding tensor. This problem is overcome by using gauge including atomic orbitals (GIAOs), also called London orbitals, introduced in NMR by Ditchfield[31] and first used by London.[32] With this choice of basis set the calculated shielding tensor becomes invariant for the change of gauge origin. For convenience we choose the gauge origin to be equal to the origin of the coordinate system and drop the subscript g in the following.

After minimal substitution the scalar relativistic Hamiltonians become

$$H_{\mathrm{SR}}^{\mathrm{Pauli}}(\vec{A}) = V + \frac{p^2}{2} + \frac{\vec{p}\cdot\vec{A}}{2c} + \frac{\vec{A}\cdot\vec{p}}{2c} + \frac{A^2}{2c^2} - \frac{p^4}{8c^2} + \frac{\Delta V}{8c^2} - \frac{1}{8c^2}\left(2p^2\left(\vec{p}\cdot\frac{\vec{A}}{c}\right) + 2\left(\vec{p}\cdot\frac{\vec{A}}{c}\right)p^2 + \frac{A^2}{c^2}p^2 + p^2\frac{A^2}{c^2} + 4\left(\vec{p}\cdot\frac{\vec{A}}{c}\right)^2\right) \quad (10)$$

and

$$H_{\mathrm{SR}}^{\mathrm{ZORA}}(\vec{A}) = V + \vec{p}\cdot\frac{K}{2}\vec{p} + \frac{K}{2c}\vec{A}\cdot\vec{p} + \vec{p}\cdot\vec{A}\frac{K}{2c} + \frac{K}{2c^2}A^2 \quad (11)$$

In the Pauli Hamiltonian we ignored terms higher than quadratic in the vector field that come from the mass−velocity operator. The Darwin term gives no extra terms when applying minimal substitution.

We derived the spin-free Pauli Hamiltonian (10) by applying minimal substitution to the one-component field-free equations. This is the simplest approach that directly gives a spin-free formalism. A more rigorous approach would be to apply the minimal substitution to the original Dirac equation before carrying out the transformation to a two-component form. We will not include the resulting extra, mainly spin-dependent, terms in our present spin-free calculations. A more extensive discussion of these and other relativistic terms in the Pauli Hamiltonian can be found in the paper by Fukui et al.[7]

2.2. Shielding Tensor. At a nucleus, an applied external magnetic field $\vec{B}^{\mathrm{ext}}$ is shielded by the electrons moving around the nucleus. The effective field the nucleus experiences can be written as[33]

$$\vec{B}^{\mathrm{eff}} = \vec{B}^{\mathrm{ext}}(1 - \vec{\vec{\sigma}}) \quad (12)$$

where $\vec{\vec{\sigma}}$ is the nuclear magnetic shielding tensor.

In practice one usually measures the chemical shift δ, which is related to the resonance frequencies of the sample ν_{s} and of a reference sample ν_{ref}

$$\delta/\mathrm{ppm} = 10^6\frac{\nu_{\mathrm{s}} - \nu_{\mathrm{ref}}}{\nu_{\mathrm{ref}}} \quad (13)$$

The resonance frequencies are determined by the Zeeman splitting caused by the nuclear magnetic moment. Since a resonance frequency ν is linear with $1 - \sigma$, where σ is the isotropic shielding $\mathrm{Tr}(\vec{\vec{\sigma}})/3$, the chemical shift will be for small shieldings ($\sigma \ll 1$)

$$\delta/\mathrm{ppm} = 10^6(\sigma_{\mathrm{ref}} - \sigma_{\mathrm{s}}) \quad (14)$$

To calculate the magnetic shielding tensor we use that in lowest order the energy of the system is linear in both the external magnetic field and the nuclear magnetic moment. Therefore, the shielding tensor is in lowest order

$$\sigma_{\mathrm{st}} = \frac{\partial^2 E}{\partial B_{\mathrm{s}}^{\mathrm{ext}}\partial\mu_t}\Big|_{\vec{B}^{\mathrm{ext}}=\vec{\mu}=0} \quad (15)$$

which by means of the generalized Hellmann−Feynman theorem[34] can be written as

$$\sigma_{\mathrm{st}} = \frac{\partial}{\partial B_{\mathrm{s}}^{\mathrm{ext}}}\left\langle \Psi(\vec{B}^{\mathrm{ext}})\left|\frac{\partial H(\vec{B}^{\mathrm{ext}},\vec{\mu})}{\partial\mu_t}\right|_{\vec{\mu}=0}\left|\Psi(\vec{B}^{\mathrm{ext}})\right.\right\rangle_{\vec{B}^{\mathrm{ext}}=0} \quad (16)$$

where the Hamiltonian contains the applied external magnetic field $\vec{B}^{\mathrm{ext}}$ and the nuclear magnetic moment $\vec{\mu}$ of the atom under consideration. $\Psi(\vec{B}^{\mathrm{ext}})$ depends only on the external magnetic field and is the ground-state eigenfunction of

$$H(\vec{B}^{\mathrm{ext}})\Psi(\vec{B}^{\mathrm{ext}}) = \epsilon(\vec{B}^{\mathrm{ext}})\Psi(\vec{B}^{\mathrm{ext}}) \quad (17)$$

where there is no term dependent on the nuclear magnetic moment in the Hamiltonian.

One generally splits the shielding tensor (eq 16) in a diamagnetic shielding σ^{d} and a paramagnetic shielding σ^{p}, where the diamagnetic shielding contains the zeroth order (with respect to the magnetic field) wave function and the paramagnetic shielding contains the first order wave function. The terms can be individually kept gauge invariant.

For the magnetic shielding we need to know the first-order response to the magnetic field of the wave function $\Psi(\vec{B}^{\mathrm{ext}})$. We suppose we already solved the eigenvalue problem (eq 17) for $\vec{B}^{\mathrm{ext}} = 0$, i.e., no magnetic field included, giving solutions Ψ_i^0, written as a linear combination of atomic orbitals

$$\Psi_i^0 = \sum_\nu d_{\nu i}\chi_\nu \quad (18)$$

To avoid gauge-origin dependence we introduce gauge including atomic orbitals (GIAO), also called London orbitals

$$\chi_\nu(\vec{B}^{\mathrm{ext}}) = \mathrm{e}^{-(i/2c)(\vec{B}^{\mathrm{ext}} \times \vec{R}_\nu)\cdot\vec{r}}\chi_\nu \quad (19)$$

where $\vec{R}_\nu$ is the position of the nucleus at which χ_ν is centered. By using GIAOs the choice of the origin will not affect the shielding tensor.

As a basis for the eigenfunctions of $H(\vec{B}^{\mathrm{ext}})$ we use the solutions (18) of the nonmagnetic equation, where the atomic orbitals are now replaced by the GIAOs

$$\Phi_j(\vec{B}^{\mathrm{ext}}) = \sum_\nu d_{\nu j}\chi_\nu(\vec{B}^{\mathrm{ext}})$$

Following Pople et al.[35] the wave function can now be written as

$$\Psi_i(\vec{B}^{\mathrm{ext}}) = \sum_j u_{ji}\Phi_j(\vec{B}^{\mathrm{ext}}) \quad (20)$$

which is up to first order in the magnetic field equal to

$$\Psi_i(\vec{B}^{\mathrm{ext}}) = \Psi_i^0 + \sum_\nu \frac{i}{2c}d_{\nu i}\vec{B}^{\mathrm{ext}}\cdot(\vec{r} \times \vec{R}_\nu)\chi_\nu + \sum_j i\vec{B}^{\mathrm{ext}}\cdot u_{ji}^1\Psi_j^0 \quad (21)$$

This first-order wave function is normalized to first order in the magnetic field. Since the operators depending on B are imaginary we took $u_{ji}^{1,s} = (\partial/\partial iB_s^{\mathrm{ext}})u_{ji}$ to make the first-order coefficients real.

We get for the *s*-component of u_{ji}

$$u_{ii}^{1,s} = -\frac{1}{2}S_{ii}^{1,s} \quad (22)$$

$$u_{ji}^{1,s} = \frac{F_{ji}^{1,s} - \epsilon_i^0 S_{ji}^{1,s}}{\epsilon_i^0 - \epsilon_j^0}, \quad \text{for } j \neq i \tag{23}$$

with

$$S_{ji}^{1,s} = \frac{\partial}{\partial i B_{\mathrm{s}}^{\mathrm{ext}}} \langle \Phi_j | \Phi_i \rangle_{\vec{B}^{\mathrm{ext}}=0} \tag{24}$$

$$F_{ji}^{1,s} = \frac{\partial}{\partial i B_{\mathrm{s}}^{\mathrm{ext}}} \langle \Phi_j | H(\vec{B}^{\mathrm{ext}}) | \Phi_i \rangle_{\vec{B}^{\mathrm{ext}}=0} \tag{25}$$

If we write out the expressions for $S_{ji}^{1,s}$ and $F_{ji}^{1,s}$, we obtain

$$S_{ji}^{1,s} = \frac{1}{c} \sum_{\mu,\nu}^{M} d_{\mu j} d_{\nu i} \left\langle \chi_\mu \middle| \left[\frac{\vec{r}}{2} \times (\vec{R}_\nu - \vec{R}_\mu) \right]_s \middle| \chi_\nu \right\rangle \tag{26}$$

$$F_{ji}^{1,s} = \frac{1}{c} \sum_{\mu,\nu}^{M} d_{\mu j} d_{\nu i} \left\langle \chi_\mu \middle| H(0) \left(\frac{\vec{r}}{2} \times \vec{R}_\nu \right)_{\mathrm{s}} - \left(\frac{\vec{r}}{2} \times \vec{R}_\mu \right)_{\mathrm{s}} H(0) \middle| \chi_\nu \right\rangle + \left\langle \Psi_j^0 \middle| \frac{\partial H(\vec{B}^{\mathrm{ext}})}{\partial i B_{\mathrm{s}}^{\mathrm{ext}}} \middle|_{\vec{B}^{\mathrm{ext}}=0} \middle| \Psi_i^0 \right\rangle \tag{27}$$

where M is the number of molecular orbitals, both occupied and virtual and $H(0)$ is the field free Hamiltonian. The S^1 matrix is a consequence of the introduction of GIAOs, just as the first term in the F^1 matrix and the second term in the wave function (eq 21). In the limit of a complete basis the net effect of these terms will be zero.

2.3. Frozen Core Approximation. To save computing time it is often desirable to use a frozen core approximation. The MOs close to a nucleus are believed to change only very little in going from a free atom to an atom in a molecule and have a negligible overlap with each other. In addition one can assume that the response of the tightly bound core electrons to the applied magnetic field is negligible, so that their paramagnetic contribution to the shielding can be ignored. With these assumptions we can keep the core AOs frozen during the molecular calculation so that they can be excluded from the matrix equations that are to be solved. In the quasi-relativistic method based on the Pauli Hamiltonian the frozen core approach has to be used anyway, when dealing with heavy atoms, since otherwise variational collapse will occur.

Since only the valence orbitals need to be represented in a frozen core approximation the basis set can be reduced to a set of M_{val} valence functions χ_ν^{val} only. These functions are in general, however, not orthogonal to the frozen core orbitals. This can be remedied by introducing core orthogonalization functions χ_ν^{core}. The new valence functions $\lambda_\nu^{\mathrm{val}}$ then become

$$\lambda_\nu^{\mathrm{val}} = \chi_\nu^{\mathrm{val}} + \sum_{\mu}^{M_{\mathrm{core}}} b_{\nu\mu} \chi_\mu^{\mathrm{core}} \tag{28}$$

where M_{core} is the number of core orbitals (and the number of χ_ν^{core}) and the coefficients $b_{\mu\nu}$ are taken such that these new functions in the valence basis set are orthogonal to the frozen core AOs. Note that the core orthogonalization functions are single STOs that are not identical to the original core AOs that are expressed in a large atomic basis set. In the Pauli molecular calculations we have the additional complication that we always have to use nonrelativistic atomic core orbitals, since the Pauli approach precludes the determination of Pauli core orbitals. For the Coulomb and exchange-correlation potentials that feature in the Hamiltonian, the fully relativistic Dirac density is used.

By using GIAOs the orthogonalization coefficients $b_{\mu\nu}$ become dependent on the external magnetic field $\vec{B}^{\mathrm{ext}}$, introducing extra terms in the shielding tensor, the S^1 matrix and the F^1 matrix. The introduction of GIAOs in NMR shielding tensors and the effects of it on the frozen core approximation have been treated earlier by Schreckenbach and Ziegler.[14,5]

The extra terms caused by the frozen core approximation follow easily from the definitions of the S^1 and F^1 matrix and the shielding tensor, using the first-order correction coming from the b coefficients in the orthogonalized valence functions (eq 28). We define the function

$$\Psi_{l,s}^{(1,b^1)}(i) = \sum_{\mu}^{M_{\mathrm{val}}} d_{\mu l} \sum_{\tau}^{M_{\mathrm{core}}} b_{\mu\tau}^{1,s} \chi_\tau^{\mathrm{core}}(i) \tag{29}$$

which is the first-order response of the wave function to the external magnetic field in the b coefficients only. From the definition of the S^1 matrix (24) follows

$$S_{ji}^{1,s} = \frac{\partial}{\partial i B_s^{\mathrm{ext}}} \langle \Phi_j | \Phi_i \rangle_{\vec{B}^{\mathrm{ext}}=0} - \langle \Psi_{j,s}^{(1,b^1)} | \Psi_i^0 \rangle + \langle \Psi_j^0 | \Psi_{i,s}^{(1,b^1)} \rangle \tag{30}$$

with the first term given by (26). From (25) we get

$$F_{ji}^{1,s} = \frac{\partial}{\partial i B_s^{\mathrm{ext}}} \langle \Phi_j | H(\vec{B}^{\mathrm{ext}}) | \Phi_i \rangle_{\vec{B}^{\mathrm{ext}}=0} - \langle \Psi_{j,s}^{(1,b^1)} | H(0) | \Psi_i^0 \rangle + \langle \Psi_j^0 | H(0) | \Psi_{i,s}^{(1,b^1)} \rangle \tag{31}$$

with the first term given by (27).

2.4. Nonrelativistic Shielding Tensor. By introducing the nonrelativistic Hamiltonian

$$H^{\mathrm{NR}}(\vec{A}) = V + \frac{p^2}{2} + \frac{\vec{p}\cdot\vec{A}}{c} + \frac{A^2}{2c^2} \tag{32}$$

one gets for the magnetic shielding tensor

$$\sigma_{\mathrm{st}} = \sigma_{\mathrm{st}}^{\mathrm{d}} + \sigma_{\mathrm{st}}^{\mathrm{p}} \tag{33}$$

The diamagnetic core contribution is the only core contribution in the total shielding and is given by

$$\sigma_{\mathrm{core}_{\mathrm{st}}}^{\mathrm{d}} = \frac{1}{2c^2} \sum_{A}^{N_{\mathrm{Nuc}}} \int \mathrm{d}\tau\, \rho_{\mathrm{core}}^{\mathrm{A}} \frac{1}{r_N^{\,3}} (\vec{r}_N \cdot \vec{r}_A \delta_{st} - r_{N_{\mathrm{s}}} r_{A_{\mathrm{t}}}) \tag{34}$$

where $\rho_{\mathrm{core}}^{\mathrm{A}}$ is the core density located at nucleus A.

The diamagnetic valence part is

$$\sigma_{\mathrm{val}_{\mathrm{st}}}^{\mathrm{d}} = \frac{1}{c^2} \sum_{i}^{\mathrm{occ}} n_i \sum_{\nu}^{M} d_{\nu i} \left\langle \Psi_i \middle| \frac{1}{2 r_N^{\,3}} (\vec{r}_N \cdot \vec{r}_\nu \delta_{st} - r_{N_s} r_{\nu_t}) \middle| \chi_\nu \right\rangle + \frac{1}{c} \sum_{i}^{\mathrm{occ}} n_i \sum_{\mu,\nu}^{M} d_{\mu i} d_{\nu i} \left\langle \chi_\mu \middle| \left[\frac{\vec{r}_\nu}{2} \times (\vec{R}_\nu - \vec{R}_\mu) \right]_s i h_t^{01\mathrm{NR}} \middle| \chi_\nu \right\rangle \tag{35}$$

with

$$h_t^{01\mathrm{NR}} = \frac{\partial}{\partial \mu_t} H^{\mathrm{NR}}(\vec{A})|_{\vec{B}^{\mathrm{ext}}=\vec{\mu}=0} = \frac{1}{c} \left[\frac{\vec{r}_N}{r_N^{\,3}} \times \vec{p} \right]_t \tag{36}$$

The diamagnetic shielding is determined by the zeroth-order wave function. The summations over the occupied orbitals are over the valence orbitals only. The introduction of GIAO orbitals, securing gauge invariance, leads to the second term. This term gives no further diamagnetic core contribution, since it comes from the first-order magnetic response of the orbitals and we assumed the core orbitals to be independent of the magnetic field. For the same reason there will be no contribution from the core orbitals to the paramagnetic shielding, since it is determined by the first-order wave function in the magnetic field. The first term in eq 35 is inversely proportional to the distance to the NMR nucleus and will therefore be determined by the most localized orbitals around the NMR nucleus.

The nonrelativistic paramagnetic shielding is

$$\sigma_{\mathrm{st}}^{\mathrm{p}} = \frac{1}{c}\sum_{i}^{\mathrm{occ}} n_i \sum_{\mu,\nu}^{M} d_{\mu i} d_{\nu i} \left\langle \chi_\mu \middle| \left[\frac{1}{2}\vec{R}_\mu \times \vec{R}_\nu\right]_s ih_t^{01\mathrm{NR}} \middle| \chi_\nu \right\rangle + \sigma_{\mathrm{st}}^{\mathrm{p,oc-oc}} + \sigma_{\mathrm{st}}^{\mathrm{p,oc-vir}} + \sigma_{\mathrm{st}}^{\mathrm{p},b^1} \quad (37)$$

which is determined by the first-order wave function and in which the first term comes from the GIAO introduction. The occupied−occupied part in the paramagnetic shielding is also a gauge correction

$$\sigma_{\mathrm{st}}^{\mathrm{p,oc-oc}} = \sum_{i,j}^{\mathrm{occ}} n_i S_{ij}^{1,s} \langle \Psi_i | ih_t^{01\mathrm{NR}} | \Psi_j \rangle \quad (38)$$

The S^1 matrix is independent of the Hamiltonian and is given by (eq 30) and is completely due to the GIAOs. The occupied−virtual part is the most important term since this is the only term that is not a result from the introduction of the GIAOs. It is given by

$$\sigma_{st}^{\mathrm{p,oc-vir}} = 2\sum_{i}^{\mathrm{occ}} n_i \sum_{a}^{\mathrm{vir}} u_{ai}^{1,s} \langle \Psi_i | ih_t^{01\mathrm{NR}} | \Psi_a \rangle \quad (39)$$

and the frozen core contribution is

$$\sigma_{st}^{\mathrm{p},b^1} = -\sum_{i}^{\mathrm{occ}} n_i \langle \Psi_{i,s}^{(1,b^1)} | ih_t^{01\mathrm{NR}} | \Psi_i \rangle \quad (40)$$

which contains the first-order response of the orthogonalization coefficients $b_{\mu\nu}$ that also come from the GIAO introduction. The u^1 coefficients have been defined earlier in eq 23 with F^1 following from (31)

$$F_{ji}^{1,s} = \frac{1}{c}\sum_{\nu}^{M} d_{\nu i} \left\langle \Psi_j \middle| \left[-\frac{\vec{r}_\nu}{2} \times \vec{\nabla}\right]_s \middle| \chi_\nu \right\rangle + \frac{1}{c}\sum_{\mu,\nu}^{M} d_{\mu j} d_{\nu i} \left\langle \chi_\mu \middle| \left[\frac{\vec{r}}{2} \times (\vec{R}_\nu - \vec{R}_\mu)\right]_s \left(\frac{p^2}{2} + V\right) \middle| \chi_\nu \right\rangle - \left\langle \Psi_{j,s}^{(1,b^1)} \middle| \frac{p^2}{2} + V \middle| \Psi_i \right\rangle + \left\langle \Psi_j \middle| \frac{p^2}{2} + V \middle| \Psi_{i,s}^{(1,b^1)} \right\rangle \quad (41)$$

In the derivation equal occupation numbers for all occupied orbitals were assumed. The relations

$$i(\vec{r}_N \times \vec{p})_t (\vec{r} \times \vec{R})_s - i(\vec{r} \times \vec{R})_s (\vec{r}_N \times \vec{p})_t = -\vec{r}_N \cdot \vec{R} \delta_{\mathrm{st}} + r_{N_s} R_t \quad (42)$$

$$(u_{ji}^{1,s})^* + u_{ij}^{1,s} = -S_{ij} \quad (43)$$

have also been used. Furthermore, the summations over the occupied orbitals are again over the valence orbitals. The frozen core orbitals enter only via the change in orthogonalization coefficients (the last two terms of (41)).

2.5. Pauli Shielding Tensor. To include scalar relativistic effects the shielding tensor has to be based on the scalar relativistic Hamiltonian (eq 10). Schreckenbach and Ziegler[20] argue that relativistic terms only have to be taken into account explicitly in the first-order magnetic orbitals. This means that relativistic contributions to most shielding terms only enter indirectly through the relativistic change in orbitals (hence density) and orbital energies. In particular, all relativistic contributions to the diamagnetic shielding would only arise indirectly from the use of relativistic orbitals. There is then only an explicit relativistic correction to the F^1 matrix appearing in the expression for the occupied−virtual part of the paramagnetic shielding (eq 39). This procedure is substantiated by statements in the literature[36] that one can either use third-order perturbation theory with one of the perturbations being the relativistic terms in the Pauli Hamiltonian, or second-order perturbation theory (magnetic fields only) with relativistic orbitals. This would be correct if the perturbations were truly independent and the Hamiltonian would consist of pure relativistic and pure magnetic terms. Equation 10 has also some mixed relativistic-magnetic terms, however, and they give additional scalar relativistic contributions to the shielding tensor (eq 16). Schreckenbach and Ziegler[20] include the mixed relativistic-(external magnetic field) term but exclude others. We will include all scalar terms that contribute to first order in the relativistic perturbation.

For the Pauli relativistic corrections to the F^1 matrix we refer to Schreckenbach and Ziegler.[37,20] The additional terms that we obtain for the shielding tensor when using the Pauli Hamiltonian in eq 16 are for the diamagnetic shielding

$$\Delta\sigma_{st}^{\mathrm{d,rel}} = \sum_{i}^{\mathrm{occ}} n_i \left\langle \Psi_i(0) \middle| \frac{\partial}{\partial B_s^{\mathrm{ext}}} \frac{\partial}{\partial \mu_t} \left(-\frac{1}{8c^4} (A^2 p^2 + p^2 A^2 + 4(\vec{p}\cdot\vec{A})^2) \right) \Big|_{\vec{\mu}=0,\vec{B}^{ext}=0} \middle| \Psi_i(0) \right\rangle$$
$$= -\frac{1}{8c^4} \sum_{i}^{\mathrm{occ}} n_i \left\langle \Psi_i(0) \middle| \frac{1}{r_N^{\;3}} (\vec{r}_N \cdot \vec{r} \delta_{st} - r_{N_s} r_t) p^2 + p^2 \frac{1}{r_N^{\;3}} (\vec{r}_N \cdot \vec{r} \delta_{\mathrm{st}} - r_{N_s} r_t) + 2\left(\frac{\vec{r}_N}{\vec{r}_N^{\;3}} \times \vec{p}\right)_t (\vec{r} \times \vec{p})_s + 2(\vec{r} \times \vec{p})_s \left(\frac{\vec{r}_N}{\vec{\mathrm{r}}_N^{\;3}} \times \vec{p}\right)_t \middle| \Psi_i(0) \right\rangle \quad (44)$$

and for the paramagnetic shielding

$$\Delta\sigma_{st}^{\mathrm{p,rel}} = \sum_{i}^{\mathrm{occ}} n_i \left\langle \frac{\partial}{\partial B_s^{\mathrm{ext}}} \Psi_i(\vec{B}^{\mathrm{ext}}) \Big|_{\vec{B}^{ext}=0} \middle| \frac{\partial}{\partial \mu_t} \left(-\frac{1}{4c^3} (p^2 (\vec{p}\cdot\vec{A}) + (\vec{p}\cdot\vec{A}) p^2) \right) \Big|_{\vec{\mu}=0,\vec{B}^{ext}=0} \middle| \Psi_i(0) \right\rangle + \mathrm{cc}$$
$$= -\frac{1}{4c^3} \sum_{i}^{\mathrm{occ}} n_i \left\langle \frac{\partial}{\partial B_s^{\mathrm{ext}}} \Psi_i(\vec{B}^{\mathrm{ext}}) \Big|_{\vec{B}^{ext}=0} \middle| p^2 \left(\frac{\vec{r}_N}{r_N^{\;3}} \times \vec{p}\right)_t + \left(\frac{\vec{r}_N}{r_N^{\;3}} \times \vec{p}\right)_t p^2 \middle| \Psi_i(0) \right\rangle + cc \quad (45)$$

which can be included in the paramagnetic shielding (h_t^{01} also has to be changed in eq 35 for the diamagnetic shielding) given earlier (eqs 37−40) by changing $h_t^{01\mathrm{NR}}$ (eq 36) to

$$h_t^{01,\mathrm{Pauli}} = \frac{\partial}{\partial \mu_t} H^{\mathrm{Pauli}}(\vec{A})|_{\vec{B}^{ext}=\vec{\mu}=0} = \frac{1}{c}\left(\left(\frac{\vec{r}_N}{r_N^{\,3}} \times \vec{p}\right)_t - \frac{1}{4c^2}\left(p^2\left(\frac{\vec{r}_N}{\vec{r}_N^{\,3}} \times \vec{p}\right)_t + \left(\frac{\vec{r}_N}{r_N^{\,3}} \times \vec{p}\right)_t p^2\right)\right) \quad (46)$$

This makes the inclusion of these extra terms in the paramagnetic shielding very straightforward. The core density enters in eq 34 and gives a constant contribution to the shielding that drops out in the calculated chemical shifts. Although this contribution is therefore not relevant for most applications, it is of interest when comparing methods that calculate the absolute shielding. In the quasi-relativistic Pauli method one cannot calculate this term directly because the core density cannot be obtained with the Pauli Hamiltonian. We use the four-component Dirac atomic density in this expression, so this term will also include relativistic effects.

2.6. ZORA Shielding Tensor. We start from the ZORA Hamiltonian (eq 11), which for $K = 1$ is equal to the nonrelativistic Hamiltonian. The expressions will therefore look very similar to those of the nonrelativistic shielding tensor from section 2.4, but contain a K that damps the singularities near the nuclei.

The shielding tensor is again split in a diamagnetic and a paramagnetic part

$$\sigma_{\mathrm{st}} = \sigma_{st}^{\mathrm{d}} + \sigma_{st}^{\mathrm{p}} \quad (47)$$

Here the diamagnetic part consists of a core part

$$\sigma_{\mathrm{core}_{st}}^{\mathrm{d}} = \frac{1}{2c^2}\sum_A^{N_{\mathrm{Nuc}}}\int d\tau\, \rho_{\mathrm{core}}^{\mathrm{A}} \frac{K}{r_N^{\,3}}(\vec{r}_N\cdot\vec{r}_A\delta_{\mathrm{st}} - r_{N_s} r_{A_t}) \quad (48)$$

where $\rho_{\mathrm{core}}^{\mathrm{A}}$ is the core density located at nucleus A, and a valence part

$$\sigma_{st}^{\mathrm{d}} = \frac{1}{c^2}\sum_i^{\mathrm{occ}} n_i \sum_\nu^M d_{\nu i}\left\langle \Psi_i \left| \frac{K}{2r_N^{\,3}}(\vec{r}_N\cdot\vec{r}_\nu\delta_{\mathrm{st}} - r_{N_s} r_{\nu_t}) \right| \chi_\nu \right\rangle + \frac{1}{c^2}\sum_i^{\mathrm{occ}} n_i \sum_{\mu,\nu}^M d_{\mu i} d_{\nu i}\left\langle \chi_\mu \left| \frac{iK}{2r_N^{\,3}}[\vec{r}_\nu \times (\vec{R}_\nu - \vec{R}_\mu)]_s (\vec{r}_N \times \vec{p})_t \right| \chi_\nu \right\rangle \quad (49)$$

which is again determined by the zeroth-order wave function. The last term comes from the introduction of GIAO orbitals to make the diamagnetic shielding gauge-independent. Like in the Pauli approximation the other possible core contributions vanish when using the orthogonality between core and valence orbitals and the assumption that the core orbitals of different atoms do not overlap.

The paramagnetic part is

$$\sigma_{st}^{\mathrm{p}} = \frac{1}{c^2}\sum_i^{\mathrm{occ}} n_i \sum_{\mu,\nu}^M d_{\mu i} d_{\nu i}\left\langle \chi_\mu \left| \frac{iK}{4r_N^{\,3}}[\vec{R}_\mu \times \vec{R}_\nu]_s (\vec{r}_N \times \vec{p})_t \right| \chi_\nu \right\rangle + \sigma_{st}^{\mathrm{p,oc-oc}} + \sigma_{st}^{\mathrm{p,oc-vir}} + \sigma_{st}^{\mathrm{p},b^1} \quad (50)$$

The paramagnetic shielding is determined by the first-order wave function and also contains some GIAO terms. The occupied−occupied part in the paramagnetic shielding is a gauge correction

$$\sigma_{st}^{\mathrm{p,oc-oc}} = -\sum_{i,j}^{\mathrm{occ}} n_i S_{ij}^{1,s}\left\langle \Psi_i \left| \frac{iK}{2cr_N^{\,3}}(\vec{r}_N \times \vec{p})_t \right| \Psi_j \right\rangle \quad (51)$$

the occupied−virtual part is

$$\sigma_{st}^{\mathrm{p,oc-vir}} = -\sum_i^{\mathrm{occ}} n_i \sum_a^{\mathrm{vir}} u_{ai}^{1,s}\langle \Psi_i | i h_t^{01,\mathrm{ZORA}} | \Psi_a \rangle \quad (52)$$

and the frozen core contribution

$$\sigma_{st}^{\mathrm{p}.b^1} = -\sum_i^{\mathrm{occ}} n_i \langle \Psi_{i,s}^{(1,b^1)} | i h_t^{01,\mathrm{ZORA}} | \Psi_i \rangle \quad (53)$$

with

$$h_t^{01,\mathrm{ZORA}} = \frac{\partial}{\partial \mu_t} H^{\mathrm{ZORA}}(\vec{A})|_{\vec{B}^{ext} = \vec{\mu} = 0} = \frac{K}{2cr_N^{\,3}}(\vec{r}_N \times \vec{p})_t + (\vec{r}_N \times \vec{p})_t \frac{K}{2cr_N^{\,3}} \quad (54)$$

Again we take in the summations over the occupied orbitals only the valence orbitals.

The S^1 matrix in (51) has been given earlier (eq 30) and is independent of the Hamiltonian. The F^1 matrix, however, does depend on the Hamiltonian and is now given by

$$F_{ji}^{1,s} = \frac{1}{c}\sum_{\mu,\nu}^M d_{\mu j} d_{\nu i}\left\langle \chi_\mu \left| \frac{iK}{4}[-\vec{r}_\mu \times \vec{p}]_s + [-\vec{r}_\nu \times \vec{p}]_s \frac{iK}{4} \right| \chi_\nu \right\rangle + \frac{1}{c}\sum_{\mu,\nu}^M d_{\mu j} d_{\nu i}\left\langle \chi_\mu \left| \frac{V}{2}[\vec{r} \times (\vec{R}_\nu - \vec{R}_\mu)]_s + \vec{p}\cdot\frac{K}{4}[\vec{r} \times (\vec{R}_\nu - \vec{R}_\mu)]_s \vec{p} \right| \chi_\nu \right\rangle - \left\langle \Psi_{j,s}^{(1,b^1)} \left| V + \vec{p}\cdot\frac{K}{2}\vec{p} \right| \Psi_i \right\rangle + \left\langle \Psi_j \left| V + \vec{p}\cdot\frac{K}{2}\vec{p} \right| \Psi_{i,s}^{(1,b^1)} \right\rangle \quad (55)$$

following from (31). In this derivation we used that the wave functions are real.

The core contribution to the diamagnetic shielding contains the core density. Like in the Pauli approximation this term could be calculated directly from the Dirac equation without using the ZORA core orbitals. However, when comparing all-electron and frozen core calculations it will be necessary for consistency to use the ZORA orbitals also for the calculation of the core density.

Furthermore, it can be checked that taking $K = 1$ indeed gives the nonrelativistic shielding tensor, as we stated earlier. In practice, the nonrelativistic terms in the Pauli shielding tensor and the nonrelativistic terms in the ZORA shielding tensor (with $K = 1$) are not equal when using numerical integration even though they can be shown to be equal analytically by means of partial integration. To compare the different approximations discussed, numerical integration errors should thus be minimized. For the calculations we make use of the Amsterdam Density Functional package (ADF98) developed in our research group.[38−42] The default integration accuracy in this program, which approaches an accuracy of 4 significant digits in all integrals (AccInt 4 in ADF), is insufficient in this case. The differences in the total isotropic shieldings of the metals for the two discussed alternatives, due to numerical integration error, go as high as 12 ppm for the heaviest molecules. On a total shielding of a few thousand ppm for the heavy molecules this is not very much, so for most purposes this default integration accuracy will suffice. However, for comparing the different approximations as we do here, a higher integration accuracy is needed. When we approach an accuracy of 7 significant digits in all integrals (AccInt 7 in ADF) the observed numerical differences between the two ways of calculating the nonrelativistic result diminish dramatically. They are all at most 0.02 ppm. This integration accuracy will be used for all calculations involving a comparison of different NMR methods, thereby making sure that the differences coming from the numerical integrations are negligible.

3. Isotropic Shieldings of Transition Metal Oxides

The theory of the previous sections will be used in calculations on the shieldings of the metal nuclei in the transition metal oxides MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os). We will first make an assessment of the magnitude of the relativistic effects on the NMR shielding, where direct and indirect relativistic effects may be distinguished. The direct relativistic effects are associated with explicit relativistic terms in the expressions for the NMR shielding (eq 16). However, relativity is also known to considerably affect the energies and the shapes of the atomic orbitals.[36,43] These changes alone will already affect the NMR shielding, even if the relativistic terms in the shielding would not be taken into account. These may be called indirect effects. It is interesting to know to what extent these direct and indirect contributions are important for the NMR shielding.

Next, the two relativistic methods, Pauli and ZORA, are compared. Before actually comparing the results, the additional terms in the Pauli NMR shielding that we have identified ((44) and (45)) are studied. As it turns out, these terms cannot be neglected. The results quoted as "Pauli" will therefore contain, apart from the terms implemented by Schreckenbach and Ziegler,[5,14,20] these additional relativistic terms. The two contributions to the total isotropic shielding, the diamagnetic and the paramagnetic shielding, are considered separately. This makes comparison simpler because the diamagnetic shielding is mostly determined by the core orbitals, while the paramagnetic shielding is mostly determined by the valence orbitals. Chemical shifts of the metals in the metal oxides with respect to metal carbonyls are also considered.

A distinct advantage of the ZORA method over the quasi-relativistic Pauli method is the variational stability of the former. It is therefore possible to perform all-electron calculations and to use extended basis sets, including very tight functions. Such calculations will be performed in order to investigate the effectiveness of the frozen core approximation. Basis set extension is also important to obtain a better description of the core tails of the valence orbitals. It has been argued[5] that the frozen core approximation is adequate, but that a high-quality representation of the core tails of the valence orbitals is important.

For our calculations we used experimental geometries as also used by Kaupp, Malkina, and Malkin.[44] For iron oxide we will use their prediction for the Fe–O distance of 1.58 Å. For the calculation of the chemical shifts we used as a reference the isotropic shieldings of the transition metal carbonyls $M(CO)_6$ with experimental geometries.[45] The experimental chemical shifts, which are used later, are from measurements on molecules in a solvent. Gas-phase data do not exist to our knowledge. We will ignore the possible solvent effects. This is a second reason that makes a direct comparison with experimental results difficult. We already mentioned that we ignore the spin–orbit coupling.

All calculations were performed using the Amsterdam Density Functional package (ADF98) developed by Baerends et al.[38–40] ADF uses the numerical integration scheme by te Velde et al.[41,42] Added to ADF98 were the modified NMR code from Schreckenbach and Ziegler[5,14,20] and our ZORA NMR code. Unless stated otherwise, basis sets are used that are triple-ζ for the upper valence orbitals and double-ζ in the subvalence region. These basis sets are included in the ADF package (basis set IV). Note that the basis sets used in the Pauli and the ZORA calculations will be different as both of them were optimized separately. The Pauli calculations employ nonrelativistic basis sets. Both the Pauli and ZORA basis set contain a single STO core orthogonalization function per frozen core orbital. These STOs describe the core tails of the valence orbitals. For the 5d metals the ZORA basis sets contain an extra tight 1s STO, in order to describe the core tails of the valence orbitals better. The accuracy of the numerical integration used has been discussed earlier (AccInt 7 in ADF). The density functional used has been based on the local density approximation with density-gradient corrections to the exchange according to Becke (Becke88)[46] and density-gradient corrections to the correlation energy according to Perdew.[47]

3.1. Relativistic Effects Using ZORA. The relativistic effects on the NMR shielding can be large for the heavy atoms in the molecule, but also for their ligands.[4,36,37,44] For the ligands this is mainly a consequence of spin–orbit coupling.[10] Since we consider only scalar relativistic calculations, we will focus our attention on the NMR shielding of the heavy atoms only.[20]

Here we will investigate the order of magnitude of these relativistic effects as well as their origin. They can come either from a change in the molecular orbitals and their energies determined during the SCF calculation (indirect relativistic effect), or from using a relativistic Hamiltonian in the shielding tensor (eq 16) (direct relativistic effect). In the calculations the approximation used in the SCF part can be chosen independent from the approximation used in the NMR shielding calculation, thereby separating the indirect and the direct contributions. The following cautioning remark should however be made.

The generalized Hellmann–Feynman theorem, used to get to eq 16, assumes the wave function to be optimized for the zeroth-order Hamiltonian. If we take the SCF and the NMR method to be different this requirement is not fulfilled. As a consequence, expression (16) for the NMR shielding is not complete in that case. Although a rigorous analysis is now formally not possible, we can still make a qualitative analysis in order to know how significant the direct relativistic effects are that come from the use of a relativistic Hamiltonian in eq 16, leading to explicit relativistic terms in the expression for the shielding. These effects can be compared to the effect of using a relativistic (either Pauli or ZORA) versus a nonrelativistic SCF procedure.

In Table 1 the total isotropic shieldings of the metals in some transition metal oxides MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) are shown using for the SCF and NMR method (SCF/NMR) either the nonrelativistic (NR) limit or the ZORA method. The frozen core approximation was used and the table shows up to which orbital the orbitals are kept frozen for the metals. For the oxygen atoms (and the carbon atoms in the carbonyl complexes), only the 1s orbital is kept frozen. The sizes of the frozen cores will be the same in all frozen core calculations. We start by comparing the results in Table 1 from

TABLE 1: Isotropic Shielding (in ppm) of M in MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and of M in $M(CO)_6$ (M = Cr, Mo, or W) Using for the SCF and the NMR Method Both the Nonrelativistic (NR) and the ZORA Method

SCF		NR		ZORA	
NMR	frozen core	NR	ZORA	NR	ZORA
CrO_4^{2-}	2p	−2358	−2375	−2285	−2303
MnO_4^-	2p	−3515	−3533	−3440	−3460
FeO_4	2p	−4010	−4030	−3952	−3974
MoO_4^{2-}	3d	−357	−372	−215	−239
TcO_4^-	3d	−1066	−1070	−929	−952
RuO_4	3d	−1668	−1693	−1654	−1690
WO_4^{2-}	4d	798	119	2028	1898
ReO_4^-	4d	−282	−1030	1125	1011
OsO_4	4d	−922	−1718	421	263
$Cr(CO)_6$	2p	−535	−548	−487	−501
$Mo(CO)_6$	3d	1479	1393	1671	1571
$W(CO)_6$	4d	4275	3359	6641	5100

completely nonrelativistic calculations (NR/NR) with completely ZORA calculations (ZORA/ZORA). For the 3d metals (Cr, Mn, and Fe) the relativistic effects are relatively small, less than 100 ppm. For the 4d metals (Mo, Tc, and Ru) they are only a little larger, but for the 5d metals (W, Re, and Os) the relativistic effects are large, on the order of 1000 ppm. One has to keep in mind that the total chemical shielding is the sum of two large contributions with opposite sign, the diamagnetic and paramagnetic shielding which approach for the 5d metals plus and minus 10000 ppm, respectively (see below). The resulting total NMR shielding is much smaller than each individual contribution. A small relative change in either contribution due to relativity can result in a large relative change in the total chemical shielding, which is observed in Table 1.

If we include the results from calculations with the SCF and the NMR method chosen differently (NR/ZORA and ZORA/NR), in particular those for the "relativistic" 5d elements, the following observations can be made. In the first place, the change to a relativistic (ZORA) SCF calculation is large, i.e., indirect relativistic effects are very significant, up to 2000 ppm. In the second place, comparing for a given SCF method the ZORA with the NR NMR calculation, we see that the direct relativistic effects are large (up to 800 ppm) in the case of a NR SCF, and for the oxides smaller but nonnegligible (larger than 100 ppm) for ZORA SCF. We have not further analyzed this difference between the magnitude of the direct relativistic effects for the two SCF methods, but leave it at the conclusion that, while the indirect relativistic effects are clearly larger than the direct effects, neither of them can be neglected for 4d and particularly 5d metals.

In the next section, the ZORA method for the calculation of relativistic effects on the NMR shielding is compared to the Pauli (quasi-)relativistic method.

3.2. ZORA Method versus the Pauli Approximation. In section 2 we discussed two possible relativistic approximations, the Pauli approximation and the ZORA method. The isotropic shieldings obtained with these methods for the metal oxides will be compared as well as the chemical shifts with respect to the metal carbonyl complexes. Just as in the last section, different combinations of SCF and NMR methods will be considered. We will start, however, with a discussion regarding the Pauli approximation.

TABLE 2: Valence Contribution to Diamagnetic Isotropic Shieldings (in ppm) of M in MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and of M in $M(CO)_6$ (M = Cr, Mo, or W) Using Pauli SCF with Pauli NMR, Excluding and Including the Extra Relativistic Term in the Diamagnetic Shielding (Eq 44)

	$\sigma^{d,Excl}$	$\sigma^{d,Incl}$	$\Delta\sigma^d$	SCF	$\sigma^{d,Excl}$	$\sigma^{d,Incl}$	$\Delta\sigma^d$
CrO_4^{2-}	265	264	−1.3	WO_4^{2-}	716	709	−7.0
MnO_4^-	304	303	−1.5	ReO_4^-	754	746	−7.9
FeO_4	346	344	−1.8	OsO_4	795	786	−8.7
MoO_4^{2-}	215	213	−2.0	$Cr(CO)_6$	282	281	−1.2
TcO_4^-	240	237	−2.2	$Mo(CO)_6$	226	224	−1.9
RuO_4	267	264	−2.6	$W(CO)_6$	725	718	−7.0

TABLE 3: Paramagnetic Isotropic Shieldings (in ppm) of M in MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and of M in $M(CO)_6$ (M = Cr, Mo, or W) Using Pauli SCF with Pauli NMR, Excluding and Including the Extra Relativistic Term in the Paramagnetic Shielding (Eq 45)

	$\sigma^{p,Excl}$	$\sigma^{p,Incl}$	$\Delta\sigma^p$	SCF	$\sigma^{p,Excl}$	$\sigma^{p,Incl}$	$\Delta\sigma^p$
CrO_4^{2-}	−4095	−4076	19	WO_4^{2-}	−7581	−6788	793
MnO_4^-	−5360	−5338	22	ReO_4^-	−8989	−8118	871
FeO_4	−5985	−5961	24	OsO_4	−10088	−9225	862
MoO_4^{2-}	−4219	−4098	121	$Cr(CO)_6$	−2308	−2297	10
TcO_4^-	−5075	−4948	126	$Mo(CO)_6$	−2416	−2324	92
RuO_4	−5830	−5715	115	$W(CO)_6$	−4238	−3651	587

We have discussed some relativistic terms (eqs 44 and 45) in the NMR shielding which Schreckenbach and Ziegler did not include in their calculations. As a result, the only relativistic contributions were in the first-order response of the molecular orbitals to the external magnetic field, resulting in only a change of the u^1 matrix. In this treatment, the diamagnetic shielding therefore only contained indirect relativistic contributions, whereas the paramagnetic shielding contained both indirect and direct relativistic contributions. To investigate the relevance of the extra terms the Pauli NMR implementation of Schreckenbach and Ziegler has been extended with the terms (44) and (45). Table 2 and Table 3 show the results of calculations with and without these terms for the diamagnetic and paramagnetic parts, respectively. Clearly, the effect of the extra terms on the valence contribution to the diamagnetic shielding in Table 2 is small (we will comment below on the omitted core contribution to the diamagnetic shielding). The magnitude of the additional term (45) on the paramagnetic shielding, however, is much larger, about 800 ppm for the 5d metals. This is quite large compared to the total shieldings as given in Table 1. We conclude that the additional terms should therefore be taken into account in calculations of absolute shieldings using the Pauli approximation. A fair assessment of the Pauli approximation in a comparison with, e.g., the ZORA method will also require inclusion of these terms.

We have not included in Table 2 the core contribution to the diamagnetic shielding. This contribution is large (on the order of 10 000 ppm for the 5d metals, see Table 7), and the effect of the additional term (eq 44) is also large (ca. −2000 ppm for the 5d metals). These contributions come mostly from the inner core orbitals, which remain practically unaltered (exactly so in the frozen core approximation). These diamagnetic core contributions are therefore irrelevant for chemical shifts. It is interesting to observe in Table 2, by comparing the Cr, Mo, and W shieldings of the oxides with those of the carbonyl complexes, that the valence contributions to the diamagnetic shieldings exhibit only small shifts (10−20 ppm), while the relativistic term $\Delta\sigma^d$ is practically equal in the oxides and the carbonyl complexes, yielding a negligible contribution to the chemical shift. However, the paramagnetic shielding (Table 3) is evidently very important for the chemical shifts, exhibiting differences of a few thousand ppm between oxides and carbonyls. Also the relativistic term $\Delta\sigma^d$ has a nonnegligible contribution to the chemical shift. Indeed, we see a small difference (less than 1 ppm) between the additional relativistic

TABLE 4: Valence Contribution to Diamagnetic Shielding (in ppm) of M in MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and of M in $M(CO)_6$ (M = Cr, Mo, or W) Using for the SCF and the NMR Method Both the Pauli Approximation and the ZORA Method

SCF	Pauli	Pauli	ZORA	SCF	Pauli	Pauli	ZORA
NMR	Pauli	ZORA	ZORA	NMR	Pauli	ZORA	ZORA
CrO_4^{2-}	263.8	264.6	263.8	WO_4^{2-}	708.6	713.7	712.6
MnO_4^-	302.9	303.9	302.9	ReO_4^-	746.2	751.9	750.4
FeO_4	343.8	345.0	343.8	OsO_4	786.3	792.6	791.0
MoO_4^{2-}	212.7	213.9	209.7	$Cr(CO)_6$	280.9	281.7	281.0
TcO_4^-	237.3	238.7	233.7	$Mo(CO)_6$	224.5	225.6	222.7
RuO_4	264.3	265.9	262.0	$W(CO)_6$	717.8	722.9	725.8

TABLE 5: Paramagnetic Shielding (in ppm) of M in MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and of M in $M(CO)_6$ (M = Cr, Mo, or W) Using for the SCF and the NMR Method Both the Pauli Approximation and the ZORA Method

SCF	Pauli	Pauli	ZORA	SCF	Pauli	Pauli	ZORA
NMR	Pauli	ZORA	ZORA	NMR	Pauli	ZORA	ZORA
CrO_4^{2-}	−4076	−4088	−4095	WO_4^{2-}	−6788	−7234	−6871
MnO_4^-	−5338	−5351	−5360	ReO_4^-	−8118	−8593	−7925
FeO_4	−5961	−5976	−5985	OsO_4	−9225	−9680	−8843
MoO_4^{2-}	−4098	−4172	−4209	$Cr(CO)_6$	−2297	−2304	−2310
TcO_4^-	−4948	−5026	−5051	$Mo(CO)_6$	−2324	−2383	−2412
RuO_4	−5715	−5785	−5921	$W(CO)_6$	−3651	−3969	−3682

TABLE 6: Diamagnetic, Paramagnetic, and Total Chemical Shifts (in ppm) of M in MO_4^{2-} Relative to $M(CO)_6$ (M = Cr, Mo, or W) for the SCF and the NMR Method Both the Pauli Approximation and the ZORA Method[a]

	SCF	Pauli	Pauli	ZORA	
	NMR	Pauli	ZORA	ZORA	experiment[48]
CrO_4^{2-}	diamagnetic	17	17	17	
	paramagnetic	1779	1784	1785	
	total	1796	1801	1802	1795
MoO_4^{2-}	diamagnetic	12	12	13	
	paramagnetic	1774	1789	1797	
	total	1786	1801	1810	1857
WO_4^{2-}	diamagnetic	9	9	13	
	paramagnetic	3137	3265	3189	
	total	3147	3274	3202	3505

[a] As an indication some experimental results are given.

diamagnetic contributions $\Delta\sigma^d$ for the metals in the different molecules, but a difference of up to 200 ppm between the additional paramagnetic contributions $\Delta\sigma^d$ for tungsten.

In the rest of the calculations the additional relativistic terms of eqs 44 and 45 will be included in the Pauli calculations to get a consistent comparison with the ZORA method.

In Tables 4−6, the Pauli approximation and the ZORA method can be compared at the level of full Pauli (Pauli/Pauli) and full ZORA (ZORA/ZORA) calculations, i.e., the same approximation is used for both the SCF and the NMR calculation. These results will also be compared with calculations using Pauli SCF with ZORA NMR (Pauli/ZORA). Performing ZORA SCF with Pauli NMR (ZORA/Pauli) gives poor results, since the ZORA basis sets contain tight functions. These functions are localized around nuclei where the Pauli approximation breaks down. In SCF calculations with the Pauli Hamiltonian such tight functions cannot be used since they lead to variational collapse, and apparently the problematic nature of the Pauli approximation in the nuclear neighborhood also adversely affects the Pauli NMR calculation with tight basis functions. These functions are needed, however, in the ZORA SCF calculations for a good description of the core tails of the valence orbitals. Beside the possibility to do all-electron calculations, the ability to use tight basis functions for an accurate description of core tails is another point in favor of the ZORA method. We will come back to this point in the next section where even more tight functions are included in the basis set.

We will start by considering the isotropic valence diamagnetic shielding for the transition metal oxides MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os) and the transition metal hexacarbonyls $M(CO)_6$ (with M = Cr, Mo, W). The results are given in Table 4. The ZORA shieldings are quite close to the Pauli ones (less than 5 ppm difference, with 8 ppm for $W(CO)_6$ as the only exception). We do not include core contributions, since in the Pauli case we cannot calculate quasi-relativistic Pauli core orbitals due to the variational stability problem. The choice of core orbital and density ($\Psi_i(0)$ in eq 44 and ρ^A_{core} in eq 34) therefore becomes arbitrary (options are: nonrelativistic or ZORA, or, for ρ^A_{core}, the atomic Dirac core density). The core contributions are irrelevant for the chemical shifts anyway.

The direct relativistic effect on the valence contributions to the diamagnetic shielding was already shown to be small (Table 2) in the Pauli case. In the ZORA method the direct relativistic contribution can be calculated as the difference with shieldings obtained with $K = 1$ in the expressions for the shielding tensor, while still using the ZORA orbitals and energies. The direct relativistic effect has been found to be also small for ZORA calculation. The observations we made concerning the small contribution in the Pauli case of the valence diamagnetic shieldings to the chemical shifts of the metal nuclei in the oxides with respect to the carbonyls can be extended to the ZORA case. These valence diamagnetic chemical shifts are given in Table 6, which reveals very small contributions to the chemical shifts of up to 20 ppm in both the Pauli and ZORA cases.

Since the diamagnetic contributions to the chemical shifts are very small, the total chemical shifts are almost entirely determined by the paramagnetic contributions to the shieldings. For the metals in the oxo and carbonyl complexes these are given in Table 5. This time there are large differences caused by the different NMR methods (compare Pauli/Pauli with Pauli/ZORA) and also large differences caused by the different SCF methods (compare Pauli/ZORA with ZORA/ZORA). So even if the orbitals and energies are the same (from the Pauli SCF for instance, comparing Pauli/Pauli and Pauli/ZORA), the ZORA equations for the NMR shielding yield significantly different results from the Pauli equations. This, we feel, implies an important caveat against the Pauli NMR shielding expressions. When the ZORA shielding expressions are used, Table 5 displays a significant difference between Pauli and ZORA SCF calculations. The reason for this is that, since the relativistic contributions arise mainly in the nuclear neighborhood,[43] the core tails of the valence orbitals become important for the relativistic effects on the paramagnetic shielding. The ZORA SCF uses a different basis set than the Pauli SCF, in particular for the 5d metals, since the ZORA basis sets for these atoms contain an extra tight 1s STO, in order to describe the core tails of the valence orbitals better. The Pauli basis sets cannot include such tight basis functions, as we mentioned earlier.

The large differences in the paramagnetic contributions to the shieldings between the various cases, as displayed in Table 5, cancel for a large part in the chemical shifts, just as for the diamagnetic shieldings. Table 6 gives the paramagnetic contributions to the chemical shifts for the three metals in MO_4^{n-} relative to $M(CO)_6$, from which we see that a full Pauli and a full ZORA calculation only gives a maximum difference of about 50 ppm. The total chemical shifts are given in Table 6, together with experimental data. The differences in the chemical shifts using the Pauli approximation or the ZORA method are at this point rather small. The theoretical results are in quite reasonable, but not excellent, agreement with experiment for both approximations.

At this point we cannot yet draw definite conclusions. Of course, from this very limited set of examples it is not possible to jump to the conclusion that the observed cancellation of the shielding differences between the various methods for the oxo and carbonyl complexes will always happen, i.e., that Pauli/Pauli will always give chemical shifts close to ZORA/ZORA. In this case, however, the results are close and a comparison with experiment cannot be used to decide on a preference for one method over the other. However, we should keep in mind that the ZORA/ZORA results are not converged with respect to the basis set size. As we will see in the next section, the basis set limit results for ZORA still differ considerably from the present ones. As a matter of fact, the important advantage of the ZORA method is precisely that it allows to remove approximations that are inherent to the Pauli method. The basis sets in the Pauli method cannot be extended, so a basis set limit result cannot be obtained. Nevertheless, an accurate representation of core tails of the valence orbitals is crucial. In the second place the frozen core approximation cannot be lifted in the Pauli approximation. In the next section, the possibility offered by the ZORA method to investigate the significance of these approximations will be exploited.

3.3. All-Electron versus Frozen Core Calculations. In this section we will consider all-electron (ae) and frozen core (fc) calculations. We first comment on the core densities $\rho_{\text{core}}^{\text{A}}$ to be used in the frozen core approximation. In a relativistic calculation the core densities and the core potentials are calculated from densities $\rho_{\text{core}}^{\text{A}}$ that have been obtained in atomic Dirac calculations, but it is also possible to use the ZORA method in these atomic calculations. Since the core contribution to the diamagnetic shielding contains the core density (see eq 34), this contribution to the shielding is directly affected by the method used to obtain the core density. The paramagnetic shielding only experiences indirect effects from the resulting changes in the SCF calculation.

A few calculations were performed using the ZORA method for the core density. As expected, using the ZORA core densities instead of Dirac core densities has practically no effect on the orbital energies of the valence orbitals and on the valence orbitals themselves. The resulting change in the paramagnetic shielding is only a few ppm for the three heaviest atoms (W, Re, and Os). The effect on the diamagnetic shielding is, however, not negligible. For the heaviest atoms, the diamagnetic shielding increases with about 80 ppm on a total of close to 10 000 ppm. Since the increase is caused by the core, the used core method has a totally negligible effect on the chemical shifts. However, to study the frozen core approximation, i.e., to compare frozen core and all-electron calculations with the ZORA method, the core density will in the following be calculated using the ZORA method, since this is necessary to get a consistent comparison between all-electron and frozen core calculations.

TABLE 7: Diamagnetic ZORA Shielding (in ppm) of the Transition Metals from All-electron and Frozen Core Calculations[a]

basis set	ZORA fc IV-val	ZORA ae IV-ae	ZORA fc TZ/QZ-ae	ZORA ae TZ/QZ-ae
CrO_4^{2-}	1796	1799	1789	1789
MnO_4^-	1905	1909	1905	1906
FeO_4	2016	2021	2018	2019
MoO_4^{2-}	3990	3993	3975	3974
TcO_4^-	4120	4123	4108	4107
RuO_4	4254	4258	4242	4242
WO_4^{2-}	8852	8851	8837	8837
ReO_4^-	9022	9021	9010	9010
OsO_4	9195	9193	9183	9183
$Cr(CO)_6$	1813	1821	1798	1801
$Mo(CO)_6$	4003	4010	3992	3990
$W(CO)_6$	8865	8863	8854	8855

[a] Used were a triple-ζ basis set IV and a large basis set TZ/QZ. Additional frozen core calculations were performed using the all-electron basis for the valence orbitals (valence basis TZ/QZ-ae).

TABLE 8: Paramagnetic ZORA Shielding (in ppm) of the Transition Metals from All-electron and Frozen Core Calculations[a]

basis set	ZORA fc IV val	ZORA ae IV-ae	ZORA fc IV-ae	ZORA fc TZ/QZ-ae	ZORA ae TZ/QZ-ae
CrO_4^{2-}	−4094	−4108	−4113	−4348	−4342
MnO_4^-	−5359	−5367	−5370	−5724	−5719
FeO_4	−5984	−5992	−5995	−6362	−6358
MoO_4^{2-}	−4208	−4711	−4734	−4790	−4766
TcO_4^-	−5049	−5683	−5721	−5757	−5730
RuO_4	−5919	−6617	−6654	−6759	−6720
WO_4^{2-}	−6874	−7970	−8260	−8415	−8102
ReO_4^-	−7929	−9223	−9512	−9667	−9340
OsO_4	−8847	−10341	−10631	−10861	−10523
$Cr(CO)_6$	−2309	−2329	−2328	−2427	−2419
$Mo(CO)_6$	−2412	−2722	−2758	−2782	−2746
$W(CO)_6$	−3684	−4318	−4588	−4670	−4340

[a] Used were a triple-ζ basis set IV and a large basis set TZ/QZ. Additional frozen core calculations were performed using the all-electron basis for the valence orbitals (valence basis IV-ae and TZ/QZ-ae).

In Tables 7 and 8 the two contributions to the total isotropic shielding, the diamagnetic and the paramagnetic shieldings, are given for the calculated transition metal complexes for both the frozen core and the all-electron calculations using several basis sets. The standard basis set IV for ZORA frozen core calculations (basis IV-val) is triple-ζ in the valence region, double-ζ in the subvalence, and single-ζ in the core region, except for an additional very tight 1s function in the 5d metals. The core functions only have to describe the core wiggles of the valence orbitals, not the (frozen) core orbitals themselves. The latter are taken from separate atomic calculations using very large (converged) basis sets. The all-electron basis ae (IV-ae) has the same STOs in the valence space but is double-ζ in the core. Frozen core calculations with the ae basis (IV-ae) simply have more tight functions available to describe the core wiggles of the valence orbitals. The frozen core orbitals themselves are the same atomic orbitals as in the frozen core calculations with the basis IV-val. An extended basis set TZ/QZ, which is quadruple-ζ in the valence region and triple-ζ in the core region, has also been used. This basis also contains additional polarization functions, such as a 4f set on the 3d and 4d metals, and a 5f set on the 5d metals. Frozen core calculations with the TZ/QZ-ae basis employ the same frozen core orbitals, but have three STOs available for each core wiggle of the valence orbitals.

Table 7 shows that the all-electron and the frozen core calculations using basis set IV give practically the same diamagnetic shielding. This indicates that for the diamagnetic shielding the frozen core approximation is justified. The lack of significant change between the frozen core and all-electron calculations, which effectively employ somewhat different basis sets for the valence orbitals, also suggests that basis IV-ae is adequate for the diamagnetic shielding. These inferences are corroborated by the calculations with the larger TZ/QZ basis. The frozen core calculations and the all-electron calculations using the same extended basis set TZ/QZ-ae are virtually

TABLE 9: ZORA Chemical Shifts (in ppm) of M in MO_4^{2-} Relative to $M(CO)_6$ (M = Cr, Mo or W) Using Frozen Core and All-Electron Calculations[a]

basis set	ZORA fc IV-val	ZORA fc IV-ae	ZORA ae IV-ae	ZORA fc TZ/QZ-ae	ZORA ae TZ/QZ-ae	expt[48]
CrO_4^{2-}	1802	1801	1801	1930	1935	1795
MoO_4^{2-}	1809	1991	2007	2025	2036	1857
WO_4^{2-}	3203	3683	3664	3762	3780	3505

[a] For the valence orbitals both the frozen core basis and the all-electron basis was used. Used were a triple-ζ basis set IV and a large basis set TZ/QZ.

identical, and very close to the results obtained with basis IV. For the diamagnetic shielding basis IV appears to be practically converged, and the frozen core approximation is well justified.

The paramagnetic shielding (Table 8) exhibits, in contrast to the diamagnetic shielding, large differences between the fc (basis IV-val) and ae (basis IV-ae) calculations, up to 1500 ppm for OsO_4. A possible cause is that the frozen cores have been chosen too large, but this would also have reflected itself in the diamagnetic shielding. Another possibility is that the paramagnetic shielding is sensitive to the basis set, and the increased flexibility of the basis set IV-ae as compared to IV-val for the (core tails of the) valence orbitals induces the observed large changes. In order to investigate this possibility frozen core calculations were performed using as the basis set the all-electron basis set (IV-ae), while the frozen core is treated as before. The results (ZORA fc, basis IV-ae) are given in the third data column in Table 8. Compared to the earlier frozen core calculations, the only difference is the larger basis set used for the valence orbitals in the core region, such that now two STOs are available for each core wiggle of the valence orbitals. The paramagnetic shieldings are seen to change very much from the fc calculations in basis IV-val, and are now much closer to the all-electron results. Apparently, it is not primarily the frozen core approximation but the quality of the valence basis that is the crucial factor here. We have noted that the all-electron basis set allows a better description of the core tails of the valence orbitals. Since relativity becomes mainly important close to the nuclei, these core tails are important for the relativistic contributions to the paramagnetic shielding. Tight functions should therefore always be included in basis sets when performing relativistic NMR calculations on heavy systems. With respect to the frozen core approximation we make the following observation. The fc results are very close to the all-electron results in the same basis (IV-ae) for the 3d metals. For the 4d metals there are differences in the range 20−40 ppm, and for the 5d metals on the order of 300 ppm. For the 5d metals the chosen frozen core (up to 4d) apparently is too large. On the other hand, very similar changes in going from fc to ae calculations in the IV-ae basis are observed for the carbonyl complexes. The chemical shifts of the oxo complexes with respect to the carbonyl complexes will therefore differ only little between the fc and ae calculations, cf. Table 9.

The large changes in going from the IV-val to IV-ae basis indicate strong basis set sensitivity of notably the paramagnetic shieldings. We therefore extend the basis set further, to a basis set that is triple-ζ for the core orbitals, and quadruple-ζ for the valence orbitals (TZ/QZ). The TZ/QZ basis has also been extended with additional polarization functions, such as a set of 4f functions on the 3d and 4d metals, 5f functions on the 5d metals, and extra polarization functions on C and O. With the all-electron basis sets both frozen core and all-electron calculations have been performed; see the last two columns in Table 8. Compared to the calculations with the basis IV-ae we find changes in the shielding of −100 to −200 ppm, for the transition metals from each row, in both the fc and the ae calculations. The basis set IV-ae is therefore not yet converged for NMR shielding calculations. We note that the difference between frozen core and all-electron calculations is very similar for the present TZ/QZ-ae calculations as found earlier for the IV-ae calculations, i.e., no difference for 3d metals and ca. −300 ppm change from fc to ae for the 5d metals. This confirms that the chosen fc approximation (up to 4d) is too severe for the 5d metals.

The differences between the different calculations (basis set IV to basis set TZ/QZ; fc to ae) are similar for the metal shieldings in the oxo and carbonyl complexes. There will therefore be considerable cancellation in the chemical shifts. This is evident from Table 9. Nevertheless, the basis set IV-val has considerable deviation (200 ppm for Mo, 580 ppm for W) in the chemical shift from the best results (TZ/QZ-ae). For the IV-ae basis this deviation has been reduced to ca. 30 ppm for Mo and ca. 100 ppm for W. It is clear that not only for the absolute shieldings but also for chemical shifts a large basis set, with sufficient flexibility in the core region (tight functions), is required for precise results. Given a sufficiently flexible basis set, the frozen core approximation appears to be acceptable in chemical shift calculations; compare the ZORA fc and ZORA ae calculations in the TZ/QZ-ae basis.

As for the comparison to experiment, we note that our most precise results (ZORA ae, TZ/QZ-ae) for the chemical shifts in Table 9 exhibit discrepancies with respect to experiment on the order of 200 ppm. This is already a quite useful accuracy. Further improvement would require investigation of several possible influences. In the first place we note that effects of spin−orbit coupling have been neglected, as well as environmental (solvent) effects. In the second place the dependency of the results on the density functional would have to be considered.

4. Summary

Relativistic effects on NMR shieldings and chemical shifts have been studied using the zero-order regular approximation (ZORA) in the spin-free form for transition metal oxides MO_4^{n-} (M = Cr, Mn, Fe, Mo, Tc, Ru, W, Re, Os), and transition metal carbonyls $M(CO)_6$ (M = Cr, Mo or W). The implementation follows the strategy (GIAOs, numerical integration) of the earlier implementation of Schreckenbach and Ziegler[5,37] based on the Pauli Hamiltonian for the relativistic effects. The relativistic effects are large, on the order of +1000 ppm on nonrelativistic shieldings that range from +800 to −900 for W−Os. This confirms the importance of the use of relativistic theory when calculating NMR shielding parameters. The Pauli based method that was developed by Schreckenbach and Ziegler neglected some relativistic terms that were here shown to contribute significantly to the isotropic shieldings. A comparison of the Pauli approach including these additional relativistic terms with the ZORA approach was made using a frozen core approximation and restricted basis sets, which is imperative for the quasi-relativistic Pauli calculations. There were only small differences in the valence contributions to the diamagnetic shieldings. However, the differences in the paramagnetic shieldings went up to 400 ppm for the heaviest atoms considered. Since these differences in going from Pauli to ZORA were similar in the metal oxides and in the carbonyl complexes, there was considerable cancellation in the chemical shifts computed for the oxides with respect to the carbonyl complexes. Still, the ZORA chemical shift for tungsten differed by about 50 ppm from the Pauli chemical shift.

Although the differences in the chemical shifts for the Pauli and ZORA approaches are relatively small in frozen core calculations with restricted basis sets, this need not be the case in all-electron calculations with large basis sets. Such calculations are not feasible with the Pauli Hamiltonian due to its variational instability. In contrast, the ZORA method is variationally stable. As a consequence, all-electron calculations are possible and the basis sets can be extended to include tight basis functions. These tight basis functions are necessary for a correct description of the core tails of the valence orbitals, which are important for the paramagnetic shielding. Removing the frozen core approximation and extending the basis sets beyond what is possible in Pauli calculations proved to have considerable effect. The following conclusions can be formulated regarding the basis set effects and the frozen core approximation, respectively. Basis set effects are rather important. A triple-ζ valence basis set with only a single-ζ description of the core wiggles of the valence orbitals is definitely inadequate. For the 5d elements even a triple-ζ valence basis set with a double-ζ core description is insufficient, yielding chemical shifts that differ on the order of 100 ppm from shifts with more complete basis sets. The frozen core approximation affects the absolute shieldings significantly (on the order of 300 ppm for the 5d metals), but the chemical shifts are much less sensitive, the effects of the frozen core approximation being very similar in the oxides and in the reference compounds (carbonyl complexes). It is therefore possible to obtain reliable chemical shifts with frozen core calculations, provided the valence basis set is sufficiently flexible in the core region so that it can describe the core wiggles of the valence orbitals accurately.

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