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The accuracy of hyperfine integrals in relativistic NMR computations based on the zeroth-order regular approximation

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Abstract. The accuracy of the hyperfine integrals obtained in relativistic NMR computations based on the zeroth–order regular approximation (ZORA) is investigated. The matrix elements of the Fermi contact operator and its relativistic analogs for *s* orbitals obtained from numerical nonrelativistic, ZORA, and four–component Hartree–Fock–Slater calculations on atoms are compared. It is found that the ZORA yields very accurate hyperfine integrals for the valence shells of heavy atoms, but performs rather poorly for the innermost core shells. Because the important observables of the NMR experiment—chemical shifts and spin–spin coupling constants—can be understood as "valence properties" it is concluded that ZORA computations represent a reliable tool for the investigations of these properties. On the other hand, absolute shieldings calculated with the ZORA might be substantially in error. Because applications to molecules have so far exclusively been based on basis set expansions of the molecular orbitals, ZORA hyperfine integrals obtained from atomic Slater-type basis set computations for mercury are compared with the accurate numerical values. It is demonstrated that the core part of the basis set requires functions with Slater exponents only up to 10^4 in the case where errors in the hyperfine integrals of a few percent are acceptable.

Keywords: NMR calculations – relativistic quantum chemistry – atomic hyperfine integrals

1 Introduction

The zeroth–order regular approximation (ZORA) has been introduced as a well investigated and computationally effective approximation to the (not explicitly known) exact two-component relativistic Hamiltonian [1–4]. The ZORA approach is by now the most frequently applied methodology in order to carry out relativistic computations of heavy-nucleus NMR chemical shifts and spin–spin coupling constants in molecules [5, 6], however, the results obtained with the ZORA represent approximations to the fully relativistic values. So far, it has remained an open question how large the errors in the NMR hyperfine integrals are that are introduced by the ZORA. The present work was carried out in order to investigate this problem.

The ZORA Hamiltonian has been studied in detail by van Lenthe and coworkers [1, 2, 4, 7] as well as by others [8–11]. For instance, it is known that regarding orbital energies or radii expectation values the ZORA performs very well for valence and auto core orbitals of heavy atoms. Because the chemical properties of heavy atomic molecules depend almost exclusively on these orbitals, the ZORA approach has, in connection with Kohn–Sham density functional theory (DFT), been found to yield binding energies, molecular geometries, and also NMR chemical shifts and spin–spin coupling constants that compare well with experimental data. Generally, the ZORA is a good approximation for states with large magnitudes of the potential localized in a rather small region of space, and comparatively small energies. This is exactly the case for valence orbitals of heavy atoms, but not for their core orbitals. Consequently, errors in core orbital energies, radii expectation values, etc., have been found to be substantial in heavy atoms (but of little or no consequence for their chemical properties).

However, NMR nuclear shielding and in particular spin–spin coupling constants are properties that are strongly influenced by the electronic structure in the vicinity of the nuclei under consideration [6]. Typically, in relativistic computations the hyperfine integrals depend on the electronic structure in the spatial *K* shell of the heavy atom, up to a radius of the order of magnitude $1/Z$ [12]. In the ZORA case, in calculations for PbH_4 with point nuclei it was previously shown that a substantial portion of the relativistic contributions to the Pb–H spin–spin coupling constant is in fact obtained from distances of about 10^{-4} Å around the Pb center

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[13], which is of the same order of magnitude as the radius of the Pb nucleus. Because of this, and the fact that this very spatial region exerts the strongest influence on relativistic effects and the various relativistic approximations, it is important to assess the principal quality of the ZORA approach for the computation of NMR properties, as well as the influence of a basis set expansion of the orbitals. So far it has been somewhat unclear whether the success of the ZORA–DFT method for NMR observables might be due to a fortuitous error cancellation.

In this work the *s* orbital matrix elements of the Fermi–contact (FC) term and its relativistic analogs (collectively referred to as FC-type integrals) are studied because they can be expected to be most sensitive with respect to relativistic effects. It is demonstrated in Sect. 2 that the ZORA yields very accurate hyperfine integrals for heavy atomic valence orbitals, whereas the relativistic effects of the core shells are not very well represented. Van Lenthe et al. [14] have previously compared electron paramagnetic resonance (EPR) A-tensors for atoms obtained from the ZORA and the four–component formalism [14] and also observed very good agreement. Reference [14] contains some exact relationships between the ZORA and the Dirac picture for the respective matrix elements for one–electron (hydrogen-like) atoms. The ZORA errors were shown to decrease rapidly for states with high principal quantum numbers and low energy.

From a comparison of accurate numerical results for Hg with basis set computations it will further be shown in this work that it is possible to obtain hyperfine integrals correctly within a few percent of error or better from basis set computations including Slater exponents up to about 10^4. All the results were obtained from Hartree–Fock–Slater calculations (Xα, with $\alpha = 0.7$). Calculations which employ more modern density functionals can be expected to yield similar accuracy for the hyperfine integrals for heavy atoms, in comparison with four–component results obtained with the same density functional.

2 Hyperfine integrals in the different formalisms

In the following, dimensionless Hartree atomic units with $m_e = 1, e = 1, 4\pi\varepsilon_0 = 1, h = 2\pi$ and $c = 137.0359895$ are employed. Equations were converted to atomic units from SI units.

2.1. Relativistic atomic s orbitals

Throughout this work the discussion will be restricted to *s* orbitals because they generally yield the largest (nonrelativistically the only) contributions to the FC-type matrix elements. They are characterized by the quantum numbers n, k, and m_j, with $k = -1$, $l = 0$, $j = l + 1/2 = |k| - 1/2 = 1/2$. (In general, $k = -1, -2, -3, \ldots$ for $s_{1/2}$, $p_{3/2}$, $d_{5/2}$, $\ldots$ orbitals, and $+1, +2, +3, \ldots$ for $p_{1/2}$, $d_{3/2}$, $f_{5/2}$, $\ldots$ orbitals [15].) For the following discussion, only the quantum numbers k and m_j will be of importance. The external potential is $V^{\mathrm{ext}}(r) = -Z/r$ (point nucleus of charge Z). In the four-component Dirac picture, an atomic *s* orbital $|k; m_j\rangle = |-1; \pm 1/2\rangle$ for an electron has the form

$$\varphi_+^{\mathrm{D}} = \frac{1}{\sqrt{4\pi}} \begin{pmatrix} g^{\mathrm{D}}(r) \\ 0 \\ if^{\mathrm{D}}(r) \cdot \cos\theta \\ if^{\mathrm{D}}(r) \cdot \sin\theta \mathrm{e}^{i\phi} \end{pmatrix};$$

$$\varphi_-^{D} = \frac{1}{\sqrt{4\pi}} \begin{pmatrix} 0 \\ g^{\mathrm{D}}(r) \\ if^{\mathrm{D}}(r) \cdot \sin\theta \mathrm{e}^{-i\phi} \\ -if^{\mathrm{D}}(r) \cdot \cos\theta \end{pmatrix} \tag{1}$$

where the subscripts + and − denote the sign of $m_j = \pm 1/2$ [16, 17]. The real radial functions for the upper (g^{D}) and lower (f^{D}) component can, for instance, be determined numerically to high precision, or can be obtained from a basis set expansion, from the following coupled set of radial equations for $G^{\mathrm{D}} = r \cdot g^{\mathrm{D}}$ and $F^{\mathrm{D}} = r \cdot f^{\mathrm{D}}$:

$$\frac{\mathrm{d}}{\mathrm{d}r} F^{\mathrm{D}} - \frac{k}{r} \cdot F^{\mathrm{D}} - \left(\frac{V - \varepsilon^{\mathrm{D}}}{c}\right) \cdot G^{\mathrm{D}} = 0 \ , \tag{2a}$$

$$\frac{\mathrm{d}}{\mathrm{d}r} G^{\mathrm{D}} + \frac{k}{r} \cdot G^{\mathrm{D}} + \left(\frac{V - \varepsilon^{\mathrm{D}}}{c} - 2c\right) \cdot F^{\mathrm{D}} = 0 \ . \tag{2b}$$

Here, $\varepsilon^{\mathrm{D}} = E^{\mathrm{D}} - c^2$, with E^{D} being the Dirac orbital energy including the rest-mass energy of $m_e c^2$. For a many-electron system, the potential V is assumed to include an effective potential for the electronic interaction, in addition to V^{ext}. The normalization is chosen in the usual way such that

$$\int_0^\infty \mathrm{d}r \cdot r^2 (g^2 + f^2) = 1 \ . \tag{3}$$

For one–electron atoms, the two-component ZORA orbitals were shown [2] to be the upper components of the Dirac orbitals with a scaled coordinate $\mathbf{r}' = \mathbf{r}/\lambda$, $\lambda = (2c^2 + \varepsilon^{\mathrm{D}})/2c^2$. Likewise, it could be shown that for a one–electron system with two nuclei the ZORA eigenfunction corresponds to the scaled upper Dirac component solved for a different, scaled, internuclear distance. The A-tensor work by van Lenthe et al. [14] was already mentioned in the Introduction. The ZORA EPR hyperfine matrix elements of hydrogen-like systems were shown to be a factor of λ^{-3} too large. For a more general self-consistent potential in a many–electron atom or molecule no such simple relations hold. It should be noted that for valence orbitals, λ is very close to unity.

2.2. Relativistic and nonrelativistic hyperfine operators

In the nonrelativistic NMR theory [18–23] one obtains the FC (and also the spin–dipole, SD) one–electron operator(s) as the derivative of the nonrelativistic many-electron Hamiltonian with respect to the u component ($u \in \{x, y, z\}$) of a nuclear spin–magnetic moment $\boldsymbol{\mu}_A$ of a nucleus A, i.e.

$$\left.\frac{\partial \hat{H}^{\mathrm{nrel}}}{\partial \mu_{\mathrm{A},u}}\right|_{\mu_{\mathrm{A},u}=0} = \sum_i \hat{h}_u^{\mathrm{nrel\text{-}FC+SD}}(i) \tag{4}$$

with

$$\hat{h}_u^{\mathrm{nrel\text{-}FC}} = \frac{4\pi}{3c^2}\sigma_u \delta(\mathbf{r}_\mathrm{A}) \ . \tag{5}$$

Here, σ_u is the Pauli spin matrix for direction u. The four–component (Dirac) analog of $\hat{h}^{\mathrm{nrel-FC}}$ is [24–27]

$$\hat{h}_u^{\mathrm{D}} = -\frac{1}{c}\left[\boldsymbol{\alpha} \times \frac{\mathbf{r}_\mathrm{A}}{r_\mathrm{A}^3}\right]_u \ , \tag{6}$$

with α being the 3–vector of the 4×4 Dirac matrices. It also contains implicitly the contributions due to the paramagnetic orbital term of the nonrelativistic theory, as well as the SD term. For atomic s-shells, however, only the FC part yields a nonvanishing contribution. The ZORA analog of the sum of the FC– and the SD–type operators is [13, 28, 29, 30]

$$\left.\frac{\partial \hat{H}^{\mathrm{ZORA}}}{\partial \mu_{\mathrm{A},u}}\right|_{\mu_{\mathrm{A},u}=0} = \sum_i \hat{h}_u^{\mathrm{Z-FC+SD}}(i) \ , \tag{7}$$

with

$$\hat{h}_u^{\mathrm{Z-FC+SD}} = \frac{1}{2c^2}\left[\sigma_u \boldsymbol{\nabla}\left(\mathscr{K}\frac{\mathbf{r}_\mathrm{A}}{r_\mathrm{A}^3}\right) - \boldsymbol{\sigma}\nabla_u\left(\mathscr{K}\frac{\mathbf{r}_\mathrm{A}}{r_\mathrm{A}^3}\right)\right] \ . \tag{8}$$

In Eq. (8), $\mathscr{K} = 2c^2/[2c^2 - V(\mathbf{r})]$. The FC–only contribution in Eq. (8) is [13]

$$\hat{h}_u^{\mathrm{Z}} = \frac{1}{3c^2}\left[\sigma_u \boldsymbol{\nabla}\left(\mathscr{K}\frac{\mathbf{r}_\mathrm{A}}{r_\mathrm{A}^3}\right)\right] \ . \tag{9}$$

2.3. *Matrix elements of the hyperfine operators*

For simplicity the z–direction is chosen for u in Eqs. (5), (6), and (7). Let the radial part of a normalized nonrelativistic spin–up (+) or spin–down (−) s orbital $\varphi_\pm^{\mathrm{nrel}}(\mathbf{r})$ be $g^{\mathrm{nrel}}(r)$, with $\int_0^\infty \mathrm{d}r \cdot r^2 g^{\mathrm{nrel}}(r)^2 = 1$. The radial part of a corresponding two–component ZORA s orbital $\varphi_\pm^{\mathrm{Z}}(\mathbf{r})$ will be denoted with $g^{\mathrm{Z}}(r)$.

In the nonrelativistic case, the well–known expectation value of $\hat{h}_z^{\mathrm{nrel-FC}}$ for s orbitals is simply

$$\langle \varphi_\pm^{\mathrm{nrel}} | \hat{h}_z^{\mathrm{nrel}} | \varphi_\pm^{\mathrm{nrel}} \rangle = \pm \frac{1}{3c^2} g^{\mathrm{nrel}}(0)^2 \ . \tag{10}$$

The factor of 4π in Eq. (5) is canceled by the normalization factor of $\varphi(\mathbf{r})$ from the integration over the angles θ and ϕ. By applying partial integration to Eq. (10) after using the identity $\boldsymbol{\nabla}(\mathbf{r}_\mathrm{A}/r_\mathrm{A}^3) = 4\pi\delta(\mathbf{r}_\mathrm{A})$, it can be recast into the form

$$\langle \varphi_\pm^{\mathrm{nrel}} | \hat{h}_z^{\mathrm{nrel}} | \varphi_\pm^{\mathrm{nrel}} \rangle = \mp \frac{2}{3c^2} a_{-1;-1}^{\mathrm{nrel}} \ , \tag{11}$$

with the nonrelativistic hyperfine integral

$$a_{k;k'}^{\mathrm{nrel}} = \frac{1}{2}\int_0^\infty \mathrm{d}r \cdot \left[\frac{\mathrm{d}g_k^{\mathrm{nrel}}}{\mathrm{d}r} g_{k'}^{\mathrm{nrel}} + g_k^{\mathrm{nrel}} \frac{\mathrm{d}g_{k'}^{\mathrm{nrel}}}{\mathrm{d}r}\right] \ . \tag{12}$$

Of course, no different results are obtained with Eq. (11) than with Eq. (10).

In the four–component case, one obtains instead from Eq. (1) with Eq. (6)

$$\langle \varphi_\pm^{\mathrm{D}} | \hat{h}_z^{\mathrm{D}} | \varphi_\pm^{\mathrm{D}} \rangle = \mp \frac{2}{3c^2} a_{-1;-1}^{\mathrm{D}} \ , \tag{13}$$

with the four–component hyperfine integral

$$a_{k;k'}^{\mathrm{D}} = c \cdot \int_0^\infty \mathrm{d}r \cdot (g_k f_{k'} + f_k g_{k'}) \ . \tag{14}$$

Analytical expressions for Eq. (14) for hydrogen-like atoms were given in Ref. [12]. Equation (13) is consistent with the general expression previously derived by Lipas et al. [31], which reads in the notation chosen in this work

$$\begin{aligned}
&\langle k; m_j | \hat{h}_z^{\mathrm{D}} | k'; m_j' \rangle \\
&\quad = \frac{1}{c^2}(-1)^{l+j-m_j'}\sqrt{2(2j+1)(2j'+1)} \\
&\quad \begin{pmatrix} j & 1 & j' \\ 1/2 & -1 & 1/2 \end{pmatrix}\begin{pmatrix} j & 1 & j' \\ m_j & 0 & -m_j' \end{pmatrix} a_{k;k'}^{\mathrm{D}}
\end{aligned} \tag{15}$$

for $l + l'$ even, and is zero otherwise. For $j = j' = 1/2$ and $m_j = m_j' = 1/2$, the $3j$ symbols have the values $-1/\sqrt{3}$ and $1/\sqrt{6}$, respectively. Please note that the four–component hyperfine integral defined by Pyykkö in Ref. [25] differs from Eq. (14) by not containing the factor of c.

For the ZORA FC operator (Eq. 9) one obtains instead for an s orbital [13, 29]

$$\langle \varphi_\pm^{\mathrm{Z}} | \hat{h}_z^{\mathrm{Z}} | \varphi_\pm^{\mathrm{Z}} \rangle = \mp \frac{2}{3c^2} a_{-1;-1}^{\mathrm{Z}} \ , \tag{16}$$

with the ZORA hyperfine integral

$$a_{k;k'}^{\mathrm{Z}} = \frac{1}{2}\int_0^\infty \mathrm{d}r \cdot \left[\frac{\mathrm{d}g_k^{\mathrm{Z}}}{\mathrm{d}r}\mathscr{K} g_{k'}^{\mathrm{Z}} + g_k^{\mathrm{Z}}\mathscr{K}\frac{\mathrm{d}g_{k'}^{\mathrm{Z}}}{\mathrm{d}r}\right] \ . \tag{17}$$

In the last equation, partial integration was applied in order to avoid derivatives of $\mathscr{K}$. It should be noted that the contact term itself vanishes for finite values of c in the last equation [13, 28, 32].

2.4. *The nonrelativistic limit*

For the ZORA FC operator, (Eq. 9), the nonrelativistic limit is simply obtained by letting $\mathscr{K} \to 1$, in which case the differentiation of the remaining $\mathbf{r}_\mathrm{A}/r_\mathrm{A}^3$ term yields $4\pi\delta(\mathbf{r}_\mathrm{A})$ and thus the operator Eq. (5). At the same time, $g^{\mathrm{Z}} \to g^{\mathrm{nrel}}$. Another way of obtaining the nonrelativistic limit for the matrix elements of the ZORA FC operator is to set $\mathscr{K} = 1$ in Eq. (17) which then yields $-(1/2)g^{\mathrm{nrel}}(0)^2$ upon integration. It can also be seen that $a^{\mathrm{nrel}}_{-1;-1}$ and $a^{\mathrm{Z}}_{-1;-1}$ only differ by the factor of $\mathscr{K}$ in the integrand.

For the four–component case, the nonrelativistic limit must be obtained from the nonrelativistic limit for the coupled pair of radial equations for g and f (Eqs. 2a, 2b). For $c \to \infty$, the $(V - \varepsilon^{\mathrm{D}})/c$ term in Eq. (2b) can be neglected and thus

$$F^{\mathrm{nrel}} = \frac{1}{2c}\left(\frac{\mathrm{d}G^{\mathrm{nrel}}}{\mathrm{d}r} + \frac{k}{r} \cdot G^{\mathrm{nrel}}\right) \ . \tag{18}$$

For s orbitals, $k = -1$, one obtains

$$f^{\mathrm{nrel}} = \frac{1}{2c}\frac{\mathrm{d}g^{\mathrm{nrel}}}{\mathrm{d}r} \ . \tag{19}$$

Substituting the last expression in the hyperfine integral, Eq. (14) yields exactly Eq. (12), i.e. $-(1/2)g^{\mathrm{nrel}}(0)^2$; thus the nonrelativistic limit Eq. (10) is properly obtained from Eq. (13). See also Ref. [25].

2.5. *Numerical and basis set results*

The computation of the hyperfine integrals was for this work implemented into the numerical Dirac–Hartree–Fock–Slater code DIRAC that accompanies the Amsterdam density functional (ADF) program package [33]. Van Lenthe [2] previously implemented atomic ZORA calculations in this code. The nonrelativistic limit was obtained by scaling the speed of light by a factor of 10^4 in the numerical calculations. The Xα parameter was set to 0.7.

Additionally, nonrelativistic and ZORA basis set Xα calculations for the mercury atom were carried out with the ADF program. The hyperfine integrals were then computed with the ZORA code for spin–spin coupling constants previously developed by Autschbach and Ziegler [13, 29]. The numerical integration parameter in ADF was set to 10 (12 for the inner core region) in order to minimize errors due to the numerical integration.

The results obtained with the numerical DIRAC code for the series Zn, Cd, Hg, Eka–Hg, and the rare-gas atoms are collected in Table. 1. Presented are c^2 times the results of Eqs. (11), (13), and (16), respectively. It can be seen that for the valence shells of the heaviest atoms the ZORA approach yields very accurate results for the hyperfine integrals. At the same time, huge relativistic effects can be found, for instance a relativistic increase of the Hg 6s hyperfine integral of about a factor of 3. Such drastic effects are already known from relativistic scaling factors for hyperfine integrals tabulated by Pyykkö et al. [12].

For the innermost core shells, substantial errors are obtained, which suggests that a ZORA calculation might not yield very accurate results for properties that depend on the core orbitals themselves. For instance, when evaluating absolute shielding constants for heavy atomic systems the ZORA approach will contain errors from the contributions due to the core orbitals. However, these errors can be expected to cancel almost entirely when the chemical shifts are determined. This explains why reasonable to good agreement with experimental chemical shifts has so far been obtained with the ZORA-DFT approach [28, 34–43].

Regarding spin–spin coupling constants, which are most sensitive to the accuracy of the FC–type matrix elements, also the valence orbitals almost exclusively determine the coupling to another atom. The reason is that in order to yield a sizeable contribution to the coupling constant, an orbital must have comparatively large values at both nuclei. This picture holds for an orbital–based formalism in which each valence orbital must be orthogonal to the other atom's cores. The orthogonalization tails of a heavy atom's core orbitals on another atom's core are usually too small to be of any substantial influence on the coupling constant. This also explains why spin–spin coupling constants obtained from the ZORA–DFT approach have been found to be in good to very good agreement with experimental data for a variety of heavy atomic systems [5, 13, 29, 30, 41, 44–48] — even though there is no systematic cancellation of errors between a probe and a reference as is the case for chemical shifts.

Molecular ZORA NMR computations were so far exclusively carried out with basis set expansions of the molecular orbitals. The 1s and 6s hyperfine integrals for the Hg atom that were calculated for the present work using various Slater–type basis sets are listed in Table 2. It is obvious from the results in Table 2 that the use of an incomplete basis introduces nonnegligible errors to the hyperfine integrals. The relativistic basis sets do not reproduce well the nonrelativistic hyperfine integrals, and vice versa. Regarding the relativistic corrections, in particular the region very close to the Hg nuclear radius (around 10^{-4} a.u.) was previously shown in Ref. [13] to yield substantial contributions to the FC–type matrix elements. The orbital density has to be properly modeled in this spatial region, which requires the use of 1s basis functions with exponents that are much higher than what is required to yield accurate ZORA energies and orbital energies. This is visible from the data in Table 2. However, it should be kept in mind that the present study has focused on point like nuclei, whereas a very accurate computational result must take finite–nucleus effects into consideration. Thus it seems that the less than 3% error in the Hg 6s hyperfine integral which is obtained by limiting the largest 1s exponent to 5×10^3 is acceptable when such effects are neglected. In fact, it can be expected that the truncation of the basis set near the nucleus compensates to some extent for the error that is made by not adopting a realistic finite-nucleus model [13]. In summary, the errors due to a limited basis size are comparable or smaller in magnitude than finite–nucleus effects, the influence of temperature and molecular vibrations, and other approximations in the computational model. The ZORA itself, on the other hand, does not seem to cause much error for valence-shell hyperfine integrals.

Table 1. Numerically calculated hyperfine integrals ($-2/3$ times Eqs. (12), (14), and (17)) for the s orbitals $|n; -1; 1/2\rangle$ of the atoms Zn, Cd, Hg, Eka–Hg (Uub), and the rare gas atoms He–Rn, in atomic units. All calculations based on Hartree–Fock–Slater calculations (Xα, with $\alpha = 0.7$). The factor of c^{-2} in Eqs.(11), (13), and (16) has not been included. Nonrelativistic results were obtained from four–component calculations with a large speed of light (Dirac– and Zeroth order regular approximation (ZORA) – calculations yielded the same nonrelativistic results within the displayed number of digits)

Atom/shell	nrel.	Dirac	ZORA	Error/%[a]
Zn				
1*s*	0.3474974×10^5	0.3740329×10^5	0.3857595×10^5	3.1352
2*s*	0.3284919×10^4	0.3646748×10^4	0.3664363×10^4	0.4830
3*s*	0.4859469×10^3	0.5442031×10^3	0.5446763×10^3	0.0870
4*s*	0.2684037×10^2	0.3043327×10^2	0.3042713×10^2	−0.0202
Cd				
1*s*	0.1440583×10^6	0.1758837×10^6	0.1914724×10^6	8.8631
2*s*	0.1491092×10^5	0.1976127×10^5	0.2006116×10^5	1.5176
3*s*	0.2810212×10^4	0.3754415×10^4	0.3768236×10^4	0.3681
4*s*	0.5462829×10^3	0.7357665×10^3	0.7362748×10^3	0.0691
5*s*	0.3868055×10^2	0.5435522×10^2	0.5433639×10^2	−0.0346
Hg				
1*s*	0.6727451×10^6	0.1324240×10^7	0.1735135×10^7	31.029
2*s*	0.7452473×10^5	0.1887951×10^6	0.1989677×10^6	5.3882
3*s*	0.1671006×10^5	0.4297198×10^5	0.4362344×10^5	1.5160
4*s*	0.4173350×10^4	0.1100035×10^5	0.1104751×10^5	0.4287
5*s*	0.8392472×10^3	0.2266142×10^4	0.2267078×10^4	0.0413
6*s*	0.6551365×10^2	0.2020647×10^3	0.2018691×10^3	−0.0968
Eka−Hg				
1*s*	0.1853252×10^7	0.2094892×10^8	0.4080311×10^8	94.774
2*s*	0.2117183×10^6	0.4434898×10^7	0.5075296×10^7	14.440
3*s*	0.5079108×10^5	0.1094293×10^7	0.1139439×10^7	4.1256
4*s*	0.1478285×10^5	0.3198698×10^6	0.3240658×10^6	1.3118
5*s*	0.4372390×10^4	0.9642374×10^5	0.9671521×10^5	0.3023
6*s*	0.9670271×10^3	0.2352428×10^5	0.2349986×10^5	−0.1038
7*s*	0.8137886×10^2	0.2713729×10^4	0.2705483×10^4	−0.3039
He				
1*s*	0.7393698×10^1	0.7395910×10^1	0.7396414×10^1	0.0068
Ne				
1*s*	0.1220830×10^4	0.1230457×10^4	0.1234021×10^4	0.2896
2*s*	0.6929871×10^2	0.7011968×10^2	0.7013692×10^2	0.0246
Ar				
1*s*	0.7359462×10^4	0.7552022×10^4	0.7630797×10^4	1.0431
2*s*	0.5860302×10^3	0.6080286×10^3	0.6088560×10^3	0.1361
3*s*	0.6546627×10^2	0.6800073×10^2	0.6801134×10^2	0.0156
Kr				
1*s*	0.6036323×10^5	0.6722745×10^5	0.7036373×10^5	4.6652
2*s*	0.5936913×10^4	0.6916659×10^4	0.6968786×10^4	0.7536
3*s*	0.9625452×10^3	0.1131200×10^4	0.1132957×10^4	0.1553
4*s*	0.1150442×10^3	0.1354177×10^3	0.1354296×10^3	0.0088
Xe				
1*s*	0.2055918×10^6	0.2664610×10^6	0.2974435×10^6	11.627
2*s*	0.2165651×10^5	0.3118513×10^5	0.3181664×10^5	2.0250
3*s*	0.4292881×10^4	0.6231963×10^4	0.6264353×10^4	0.5197
4*s*	0.9389574×10^3	0.1370429×10^4	0.1372066×10^4	0.1195
5*s*	0.1329676×10^3	0.1965856×10^3	0.1965736×10^3	−0.0061
Rn				
1*s*	0.8365342×10^6	0.1921799×10^7	0.2653621×10^7	38.080
2*s*	0.9334817×10^5	0.2895494×10^6	0.3084836×10^6	6.5392
3*s*	0.2127532×10^5	0.6712433×10^5	0.6837643×10^5	1.8653
4*s*	0.5503302×10^4	0.1774418×10^5	0.1784173×10^5	0.5498
5*s*	0.1273283×10^4	0.4142075×10^4	0.4145479×10^4	0.0822
6*s*	0.1928948×10^3	0.6547230×10^3	0.6543090×10^3	−0.0632

[a] Percentage deviation of ratio of ZORA and Dirac value from 1

3. Concluding remarks

The good performance of the ZORA to obtain relativistic hyperfine integrals for valence shells in heavy many–electron atoms was perhaps not to be expected a priori. The reason for this is that the core tails of the valence orbitals should somewhat depend on the shape of the innermost core orbitals because of the orthogonality requirement. Since the latter afford large relativistic errors due to the ZORA, the former might also suffer from these errors. As it turns out from the present numerical analysis this is hardly the case for the types of integrals that were investigated.

Table 2. Comparison of numerical ZORA hyperfine integrals of the $1s$ and $6s$ orbitals of Hg with approximate ones from Slater–type basis set atomic calculations and numerical integration [49]. The factor of c^{-2} is not included, as in Table 1

Basis/shell	nrel	ZORA
nrel.TZP[a]		
$1s$	672825.1	964021.6
$6s$	66.83272	114.6450
ZORA TZP[b]		
$1s$	672361.8	1359656.
$6s$	76.41098	163.0920
ZORA TZP + steep 1s + 2p[c]		
$1s$	671277.2	1650413.
$6s$	70.12537	196.5137
Numerical results (Tab.1)		
$1s$	672745.1	1735135
$6s$	65.51365	201.8691

[a] Nonrelativistic triple–ζ polarized basis set from the ADF AE basis set library. Double ζ for core shells. Highest $1s$ exponent is 91.85.
[b] Triple–ζ polarized basis set from the ADF ZORA/TZP basis set library for use with ZORA computations. Double ζ for core shells. Highest $1s$ exponent is 781.0
[c] ZORA–TZP basis augmented with even–tempered set of $1s$ and $2p$ functions with exponents up to 5×10^3. See Ref. [13]

Taking the present–day accuracy of ZORA–DFT computations on heavy atomic systems into consideration, i.e. the prevalent errors due to the approximate treatment of the electron correlation as well as simplified computational models of the real systems, the ZORA does not appear to be a source of large errors for computations of chemical shifts and spin–spin coupling constants. Errors might arise for properties that depend on the core orbitals, such as absolute shieldings. Because of the strong relativistic increase of the hyperfine matrix elements, some care has to be taken that a molecular basis set has enough functions with high exponents at the heavy nuclei in order to give a good description of the valence orbital's core tails.

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