

Effects of finite size nuclei in relativistic four-component calculations of hyperfine structure

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The effect of a finite size model for both the nuclear charge and magnetic moment distributions on calculated EPR hyperfine structure have been studied using a relativistic four-component method based on density functional theory. This approach employs a restricted kinetically balanced basis (mDKS-RKB) and includes spin-polarization using noncollinear spin-density exchange-correlation functionals in the unrestricted fashion. Benchmark calculations have been carried out for a number of small molecules containing Zn, Cd, Ag, and Hg. The present results are compared with those obtained at the Douglas–Kroll–Hess second order (DKH-2) method. The dependence of the results on the quality of the orbital and auxiliary basis sets has been studied. It was found that some basis sets contain irregularities that deteriorate the results. Especial care has to be taken also on the construction of the auxiliary basis for fitting the total electron and spin-densities.

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I. INTRODUCTION

The EPR spectroscopy provides us with ultimate information on the electronic structure at the position and the vicinity of a nucleus possessing a magnetic moment. It also gives a challenge for theoreticians to calculate accurately EPR parameters (hyperfine structure, g-tensor and zero-field-splitting) and also provides an opportunity to test the precision of quantum-chemical methods. In particular, the EPR hyperfine structure constant, which in the nonrelativistic case is usually defined via the Fermi-contact operator at the position of the nucleus, is known as especially difficult to calculate. Besides, the electronic structure in the vicinity of a nucleus is primarily affected by relativistic effects. Even for relatively light elements relativistic effects should be taken into account for accurate evaluation of the hyperfine operator.¹ Going to heavier elements one has to abolish even such basic models as the nuclear point charge and point magnetic dipole because these models become too crude: they have to be replaced with more physical finite size (FN) models for both nuclear charge and nuclear magnetic moment distributions. Although FN model for charge distribution in the form of a Gaussian function is widely used in relativistic calculations (see, e.g., a thorough review by Andrae,² and references therein), so far only a few studies dealing with a FN model for the magnetic moment has been reported for atoms (Refs. 3–9, and cited

therein) and for calculation of NMR shielding¹⁰ and spin–spin coupling.¹¹

Recently, we have studied the effect of a finite size nuclear model for both charge and moment distributions on the calculated hyperfine coupling constants (HFCC).¹² The results, obtained at the second order scalar Douglas–Kroll–Hess (DKH-2) DFT level showed remarkable effect for ¹⁹⁹Hg HFCC. That time two points remained open. First, the biggest drawback of that approach was the limited accuracy of DFT. The second question is connected with quality of the DKH-2 transformation itself. In that study it was difficult to separate the effects of these two sources of errors on the calculated results. Nowadays, when the DKH second order transformation is quickly becoming outdated (especially in calculations of molecular properties such as NMR and EPR parameters), it would be interesting to see to which extent DKH-2 is able to reproduce the results of a fully relativistic four-component method. To answer these questions an efficient implementation of a FN model in calculations of HFCC at a post-Hartree-Fock four-component level of theory is required. Although this work (which is currently in progress) is much more involved than implementation at the DFT level, in the present paper we are answering only the second question by presenting results for hyperfine structure obtained with the Dirac–Kohn–Sham (DKS) method. This method is based on the use of restricted-kinetically balanced (RKB) basis and includes spin-polarization using noncollinear spin-density exchange-correlation functionals in the unrestricted fashion.

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The paper is organized as follows. The basic equations for unrestricted noncollinear relativistic four-component calculations of HFCC within the mDKS-RKB method are given in Sec. II. Computational details are described in Sec. III. Section IV is devoted to benchmark calculations and discussions of the results on a series of two- and three-atomic molecules. Finally, conclusions are summarized.

II. THEORY

Throughout the paper we will use the Hartree system of atomic units. Summation over repeated indices is assumed. The following index notation is employed: i, j denote occupied positive energy orbitals and λ, τ are basis function indices. Cartesian directions are indexed by u, v . Superscripts L and S denote the large and the small components, respectively. We will use subscripts 2×2 and 4×4 to stress that the corresponding matrices are two- and four-component, respectively. For the nuclear charge and nuclear magnetic moments we will consider point models and Gaussian-type distributions,¹³ i.e., the same models as were employed in our previous work.¹²

We start with the following definition of the hyperfine coupling (HFC) tensor of the M th nucleus (for a detailed discussion of the definitions and related issues see Refs. 14, 15, and works cited therein)

$$A_{uv}^M = \frac{1}{\langle \tilde{S}_v \rangle} \left. \frac{dE(J_v, \vec{I}^M)}{dI_u^M} \right|_{\vec{I}^M=0}, \quad (1)$$

where $\langle \tilde{S}_v \rangle$ is an effective spin used to characterize the system under study, \vec{J} is the total magnetization vector, \vec{I}^M is the spin of the M th nucleus and E is the Dirac–Kohn–Sham electronic energy.

In order to evaluate the derivative of the energy, we can apply the Hellmann–Feynman theorem. Thus the HFC tensor can be written in the following form

$$A_{uv}^M = \frac{1}{\langle \tilde{S}_v \rangle} \langle \varphi_i^{(J_v,0)} | D^{(1)uM} | \varphi_i^{(J_v,0)} \rangle, \quad (2)$$

where $\varphi_i^{(J_v,0)}$ is the i th unperturbed MO, the superscript $(J_v, 0)$ denotes the dependence on the total magnetization vector oriented along v -axis and independence on the spin of the nucleus, operator $D^{(1)uM}$ is defined as follows

$$D^{(1)uM} \equiv \left. \frac{\partial(\vec{\alpha} \cdot \vec{A})}{\partial I_u^M} \right|_{\vec{I}^M=0}, \quad (3)$$

where $\vec{\alpha}$ is the vector composed of the Dirac matrices ($\vec{\sigma}$ are the Pauli matrices)

$$\vec{\alpha} = \begin{pmatrix} 0_{2 \times 2} & \vec{\sigma} \\ \vec{\sigma} & 0_{2 \times 2} \end{pmatrix}. \quad (4)$$

The vector potential \vec{A} can be written either with the point nuclear magnetic moment

$$\vec{A}_{\vec{I}^M, \text{PN}} = \gamma^M \frac{\vec{I}^M \times \vec{r}_M}{r_M^3}, \quad (5)$$

or with a finite magnetic moment of nucleus

$$\vec{A}_{\vec{I}^M, \text{FN}} = -\gamma^M \vec{I}^M \times \vec{\nabla} \iiint \frac{G_\eta(|\vec{R} - \vec{R}_M|)}{|\vec{r} - \vec{R}|} d^3 \vec{R}, \quad (6)$$

where γ^M is the gyromagnetic ratio for nucleus M , $\vec{r}_M = \vec{r} - \vec{R}_M$, \vec{r} is the electron coordinate, \vec{R} is the nuclear magnetic moment distribution coordinate, \vec{R}_M is the position of the M th nucleus and G_η refers to the normalized s -type Gaussian function

$$G_\eta(|\vec{R} - \vec{R}_M|) = \left(\frac{\eta}{\pi}\right)^{3/2} e^{-\eta(|\vec{R} - \vec{R}_M|)^2}. \quad (7)$$

The unperturbed MOs $\varphi_i^{(J_v,0)}$ [see Eq. (2)] can be obtained from the three SCF procedures solving the equations

$$\left(D_{kin} + V_{4 \times 4}^{(J_v,0)} \right) \varphi_i^{(J_v,0)} = \varepsilon_i \varphi_i^{(J_v,0)}, \quad (8a)$$

$$D_{kin} \equiv (\beta - 1_{4 \times 4}) c^2 + c \vec{\alpha} \cdot \vec{p}, \quad (8b)$$

$$V_{4 \times 4}^{(J_v,0)} \equiv \begin{pmatrix} V_{2 \times 2}^{(J_v,0)} & 0_{2 \times 2} \\ 0_{2 \times 2} & V_{2 \times 2}^{(J_v,0)} \end{pmatrix}.$$

Here ε_i is the one-electron energy, c is the speed of light, \vec{p} is the momentum operator, matrix β has the following form

$$\beta = \begin{pmatrix} 1_{2 \times 2} & 0_{2 \times 2} \\ 0_{2 \times 2} & -1_{2 \times 2} \end{pmatrix} \quad (9)$$

and $1_{2 \times 2}$, $1_{4 \times 4}$ are identity matrices.

The potential $V_{2 \times 2}^{(J_v,0)}$ is defined as $V_{2 \times 2}^{(J_v,0)} \equiv V_{\text{nuc}} + V_{\text{ee}}^{(J_v,0)} + V_{\text{xc}}^{(J_v,0)}$, where the Coulomb electron–electron repulsion potential $V_{\text{ee}}^{(J_v,0)}$ and the exchange–correlation potential $V_{\text{xc}}^{(J_v,0)}$ have their usual forms

$$V_{\text{ee}}^{(J_v,0)} \equiv \int \frac{\rho_0^{(J_v,0)}(\vec{r}')}{|\vec{r} - \vec{r}'|} dV' 1_{2 \times 2}, \quad (10)$$

$$V_{\text{xc}}^{(J_v,0)} \equiv \frac{\delta E_{\text{xc}}[\rho_k^{(J_v,0)}]}{\delta \rho_k^{(J_v,0)}} \sigma_k, \quad k = 0, x, y, z, \quad (11)$$

where E_{xc} is the Kohn–Sham exchange–correlation energy and $\rho_k^{(J_v,0)}$ represents the relativistic electron density ($k = 0$) and three spin densities ($k = x, y, z$)

$$\rho_k^{(J_v,0)} \equiv \varphi_i^{(J_v,0)\dagger} \Sigma_k \varphi_i^{(J_v,0)}, \quad (12)$$

$$\Sigma_0 \equiv 1_{4 \times 4}, \quad \vec{\Sigma} \equiv \begin{pmatrix} \vec{\sigma} & 0_{2 \times 2} \\ 0_{2 \times 2} & \vec{\sigma} \end{pmatrix}.$$

Here we would like to note that (1) we do not employ any relativistic current-dependent exchange–correlation functionals (i.e., we use nonrelativistic LDA or GGA functionals; the extension to the hybrid functionals is straightforward) and (2) the exchange–correlation part $V_{\text{xc}}^{(J_v,0)}$ of the potential $V_{2 \times 2}^{(J_v,0)}$ is implemented in the “noncollinear” fashion.^{14, 16}

The nuclear Coulomb potential V_{nuc} can be also used with the point charge

$$V_{\text{nuc,PN}} \equiv - \sum_M \frac{Z_M}{r_M} 1_{2 \times 2}, \quad (13)$$

or with the finite charge distribution

$$V_{\text{nuc, FN}} = - \sum_M Z_M \iiint \frac{G_\theta(|\vec{R} - \vec{R}_M|)}{|\vec{r} - \vec{R}|} d^3 \vec{R} \quad 1_{2 \times 2}, \quad (14)$$

and Z_M is the charge of the M th nucleus.¹⁷

To get the final equations for the HFC tensor in the matrix form, one has to express MOs [in Eq. (2)] as a linear combination of basis functions. The choice of the basis set in the four-component calculations is crucial: a not properly balanced basis set for the small component might lead to a variationally unstable SCF procedure. The use of the restricted kinetically balanced basis, in the absence of a magnetic field, reduces the variational instability to the order c^{-4} (see Refs. 18 and 19 for more details) and therefore stabilizes the whole SCF procedure

$$\varphi_i^{L(J_v, 0)} = C_{\lambda i}^{L(J_v, 0)} \chi_\lambda, \quad (15a)$$

$$\varphi_i^{S(J_v, 0)} = C_{\lambda i}^{S(J_v, 0)} \frac{1}{2c} \vec{\sigma} \cdot \vec{p} \chi_\lambda. \quad (15b)$$

Here χ_λ is an λ th basis function, $C_{\lambda i}^{L(J_v, 0)}$ and $C_{\lambda i}^{S(J_v, 0)}$ represent the expansion coefficients for the large and the small component, respectively, for a system with magnetization vector \vec{J} oriented along ν -axis.

Substituting this expansion in Eq. (2), we obtain the final expression for the HFC tensor of the M th nucleus

$$A_{uv}^M = \frac{1}{\langle \vec{S}_v \rangle} \left(\mathbf{C}_{(i)}^{L(J_v, 0)\dagger} \mathbf{C}_{(i)}^{S(J_v, 0)\dagger} \right) \begin{pmatrix} \mathbf{0} & \mathbf{\Lambda}_{I_u}^{P\dagger} \\ \mathbf{\Lambda}_{I_u}^P & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^{L(J_v, 0)} \\ \mathbf{C}_{(i)}^{S(J_v, 0)} \end{pmatrix}. \quad (16)$$

For the sake of simplicity, below we will employ the matrix notation $C_{\lambda i}^{(J_v, 0)} = \mathbf{C}_{(i)}^{(J_v, 0)}$. We keep the subscript (i) , to stress that $\mathbf{C}_{(i)}^{(J_v, 0)}$ are coefficients for the i th MO. The matrix $\mathbf{\Lambda}_{I_u}^P$ can be written either for the point nuclear magnetic moment distribution [Eq. (5)]

$$\left(\mathbf{\Lambda}_{I_u}^P, \text{PN} \right)_{\lambda\tau} \equiv \gamma^M \left\langle \chi_\lambda \left| \vec{\sigma} \cdot \vec{p} \left(\frac{\vec{r}_M \times \vec{\sigma}}{r_M^3} \right) \right| \chi_\tau \right\rangle, \quad (17)$$

or for the finite nuclear magnetic moment distribution [Eq. (6)]

$$\begin{aligned} & \left(\mathbf{\Lambda}_{I_u}^P, \text{FN} \right)_{\lambda\tau} \\ & \equiv \gamma^M \left\langle \chi_\lambda \left| \vec{\sigma} \cdot \vec{p} \left(\vec{\sigma} \times \vec{\nabla} \iiint \frac{G_\eta(|\vec{R} - \vec{R}_M|)}{|\vec{r} - \vec{R}|} d^3 \vec{R} \right) \right| \chi_\tau \right\rangle. \end{aligned} \quad (18)$$

The evaluation of all final expressions for HFC tensor is straightforward and fast as one may expect from the calculation of a first-order property (they take only a fraction of the SCF computation time).

III. COMPUTATIONAL DETAILS

All calculations have been carried out with the ReSpect code²⁰ (including the property module MAG-ReSpect). Fully

relativistic calculations were done with a new four-component module of ReSpect developed in Bratislava.^{21–23} Molecular structures have been taken the same as in Ref. 12. The calculations have been done at the DFT level with the gradient-corrected Becke exchange²⁴ and Perdew correlation²⁵ functionals (BP86). In all four-component calculations grid for numerical calculations with 256 radial and 194 angular points have been employed. For calculations at the scalar DKH-2 level, we have taken grid with 128 radial points. The number of angular points in the radial shell depended on the distance of this shell from the integration center (with a denser grid in the valence area) that resulted in about 12,000 grid points per atom. In the DKH-2 calculations, the picture-change effects have been taken into account, i.e., the Douglas–Kroll transformation up to the second order has been applied to the hyperfine-structure operator (see Ref. 12, for more details). Here we would like to note that no picture-change problems appear at the four-component level.

The calculated hyperfine coupling constants are known to be very sensitive to the choice of the basis set. Since the four-component calculation of HFCCs is still *terra incognita* we have tried several available relativistic basis sets. In particular, we employed basis sets by Hirao. We decided to test them in our four-component calculations because they are convenient for comparison of the results obtained with PN and FN models: there exists one set of basis functions optimized for use with a point nucleus model²⁶ (Hirao-PN basis), and one for a finite-size nucleus model²⁷ (Hirao-FN). We also tried basis sets of Faegri²⁸ and double-, triple-, and quadruple-zeta bases of Dyal (Dyall-DZ, Dyall-TZ, and Dyall-QZ) (optimized for FN model).²⁹ All bases were employed in a fully uncontracted fashion. On heavy atoms (Zn, Ag, Cd, and Hg) Hirao and Faegri basis sets were augmented by a set of s-, p-, d-, and f- diffuse functions (obtained by dividing the smallest exponents of a given basis set by a factor of 2.35 for s and p, and by 3.0 for d and f). For light nuclei (H, C, N, and F), we used Hirao's basis sets with polarization functions taken from the IGLO-III basis set.³⁰

In our first benchmark calculations we suffered some difficulties doing calculations of HFCC with those original basis sets. By analyzing the problem we found out that it is related to the fact that many bases (such as Faegri, Hirao, IGLO³⁰ etc. basis sets) contain one or several “holes” (usually at the border between valence and diffuse functions), i.e., the ratio between two subsequent exponents can differ significantly from the average ratio. To fix the problem, we modified the original basis sets. The modifications concerned only s- and p-functions and were based on the analysis of the ratio between neighboring exponents. For each element we kept first (tight) s- and p- exponents intact until the change in the ratio stopped to be monotonic. The remaining exponents were obtained in an even-tempered manner in such a way that the smallest exponent was kept the same as in the original basis and the ratio was kept as close as possible to the original one. If we denote n_s and n_p —the number of the first intact s- and p- exponents, correspondingly; q_s and q_p —the factors employed for the even-tempered part of the basis, respectively, then the employed parameters (n_s , q_s ; n_p , q_p) can be summarized as follows:

Hg: Faegri – (10, 1.949; 9, 1.955), Dyal-DZ – (11, 1.939; 12, 1.980);
 Dyal-TZ – (14, 1.769; 14, 1.923), Dyal-QZ – (17, 1.590; 18, 1.752);
 Hirao-FN – (12, 1.944; 14, 1.824), Hirao-PN – (16, 1.984; 15, 1.853);
 Ag: Faegri – (10, 2.058; 7, 1.980), Dyal-DZ – (11, 2.068; 6, 2.194);
 Dyal-TZ – (15, 1.881; 13, 1.908), Dyal-QZ – (19, 1.584; 16, 1.752);
 Hirao-FN – (14, 2.016; 11, 1.938), Hirao-PN – (13, 2.098; 10, 1.960);
 Cd: Hirao-FN – (11, 2.079; 10, 1.957), Hirao-PN – (13, 2.067; 10, 1.980);
 Zn: Hirao-FN – (14, 2.166; 12, 1.767), Hirao-PN – (11, 2.171; 12, 1.759);
 Cs: Hirao-FN – (13, 2.038; 13, 1.930), Hirao-PN – (16, 1.974; 13, 1.909);³¹
 Fr: Hirao-FN – (7, 1.704; 12, 1.931), Hirao-PN – (7, 1.781; 14, 1.902);
 Dyal-TZ – (20, 1.692; 16, 1.834);
 C: Hirao-FN – (8, 2.225; 5, 2.446), Hirao-PN – (8, 2.232; 5, 2.450);
 N: Hirao-FN – (8, 2.226; 5, 2.459), Hirao-PN – (8, 2.221; 5, 2.664);
 F: Hirao-FN – (8, 2.259; 4, 2.578), Hirao-PN – (8, 2.283; 4, 2.621).

No modification of s-exponents for hydrogen in Hirao-FN and Hirao-PN bases was required. For readers' convenience, the exponents of the modified basis sets are given in Supplementary Material.³¹ Except for a few benchmark calculations with the original basis sets, in all calculations we have used the modified basis sets. To test the convergence with respect to the tight s-functions in the basis set, in some calculations the modified basis sets were augmented by one tight s-exponent. This exponent was chosen to keep the smooth monotonic character of the ratio between the adjacent exponents. This extension is marked as (+1S).

For fitting of the total electron density and the components of spin density, in most calculations we have used uncontracted auxiliary basis sets with s- and p- exponents twice larger than the corresponding exponents in the modified orbital bases. The auxiliary d- (f-) functions are constructed in the even-tempered manner covering the space of orbital p- (d-) functions multiplied by 2. The number of d- and f- exponents is equal to the number of p- and d- functions in the orbital basis, correspondingly. These auxiliary basis sets will be referred to as **A-mod**. For illustrating purposes, in a few calculations we have also used other auxiliary basis sets (denoted as **A-orig**) built using the exponents in the original orbital basis sets. In **A-orig** bases, s-exponents are twice larger than the s-exponents in the original orbital basis; p- and d-exponents evenly cover the space of orbital p- functions multiplied by two whereas f-functions cover the corresponding space for orbital d-functions (i.e., d-functions multiplied by two). The number of p-, d-, and f- exponents is kept the same as the number of p-, p-, and d-functions, correspondingly, in the original orbital basis. Additional tests indicated that, for

systems considered in the paper, addition of auxiliary functions with higher angular momentum than in the orbital basis set was not necessary.

Throughout this work, an A+B notation is used, where A stands for the Hamiltonian used in the calculation of the wavefunction (with point-nucleus model (PN) or finite-size nucleus model (FN)), and B stands for the HFC operator employed (again either PN or FN). The HFC computations were done for the following isotopes: ⁶⁷Zn, ¹⁰⁷Ag, ¹¹¹Cd, ¹³³Cs, ¹⁹⁹Hg, and ²²³Fr.³²

IV. BENCHMARK CALCULATIONS AND DISCUSSION

We will start our discussion with study of the dependence of the calculated HFCC on the quality of the orbital and auxiliary basis sets. It is well known that HFCC are extremely sensitive to the quality of the basis sets (especially at the core area). However, our first benchmark calculations indicated an additional trouble connected with how the basis sets were constructed (see below). The problem is that many basis sets (such as Faegri,²⁸ Hirao,^{26,27} IGLO,³⁰ etc. basis sets) contain one or several holes (usually at the border between valence and diffuse functions), i.e., the ratio between two subsequent exponents can differ significantly from the average ratio. Since these basis sets are commonly used, it is instructive to check how such irregularities can affect the calculated HFCC. To do so, we will compare the results obtained with the original and modified basis sets. The detailed description of the modification procedure is given in the previous section. The important point is that the modified basis set spans the same range of exponents as the original one and it has approximately the same ratio between the consequent exponents as in the original basis set. When we had used the original basis and only patched the "holes" we got similar improvement of the results, but we decided to use the modified basis sets for consistency—this is especially important in cases when it is difficult to decide whether the "hole" is big enough to add one exponent or not. However, even bigger effect on the calculated HFCC has the choice of the auxiliary basis set for fitting the total and spin- densities. We have used two types of auxiliary basis sets, **A-orig** and **A-mod**, described in Sec. III. The most important difference between them is in the s- exponents: in both cases the s-exponents are obtained from the s-exponents in an orbital basis set by multiplication by two, but for building **A-orig** we have taken the original orbital basis (**O-orig**) whereas for **A-mod** the modified orbital basis set (**O-mod**) have been used. We found that the use of **A-orig** basis sets with holes inherited from the original orbital set could affect the calculations in many different ways ranging from a bad SCF convergence (or no convergence at all) to poor results. In Table I, we collected results for HFCC calculated with FN+FN model (which is the most stable with respect to the basis set quality) for XH (X = Zn, Cd, Hg) series and Fr atom. From the presented data it is clear that the use of the auxiliary basis set **A-orig** can lead to poor results unless it is constructed on the basis of a very good orbital basis (i.e., orbital basis without big "holes"—as in the case of Dyal-TZ basis). The use of the original basis sets together with the

TABLE I. Dependence of the calculated HFCC for heavy nuclei on the modification of the orbital and auxiliary basis sets. mDKS-RKB, FN+FN model.

Molecule	Basis	O-orig	O-orig	O-mod
		A-orig	A-mod	A-mod
ZnH	Hirao-FN	1301	563	564
CdH	Hirao-FN	-2647	-3504	-3431
HgH	Hirao-FN	12253	6143	6244
Fr	Hirao-FN	6978	6478	7593
Fr	Dyall-TZ	7600	7602	7605

modified auxiliary basis provided quite reasonable results for ZnH, CdH, and HgH molecules but failed for Fr. For Fr atom, the HFCC calculated with the original Hirao-FN basis are significantly underestimated whereas the results obtained with the modified Hirao-FN basis are in good mutual agreement with those with Dyall-TZ basis (either original or modified). We also found that the use of original basis sets might lead to a worsening SCF convergence in comparison with the calculations performed with modified basis sets. Since the list of the systems studied in this work is rather short, we can expect that there exist more examples where the use of an original basis set with holes would lead to irregular results. The same phenomenon was also observed in DKH-2 calculations of HFCC without fitting the electron density. Clearly, the basis set problem in the relativistic HFCC calculations requires a more thorough investigation which is beyond the scope of the present work. We plan to perform such a study in future. However even now we can state that the use of holes-free basis sets as a reliable option.

The use of the FN model should reduce the overall high sensitivity of calculated HFCC on the quality of the employed basis set. However *a priori* it is unclear to which extent such expectations are correct. Thus before discussing the FN effect on a wider set of nuclei and systems, we analyze further a basis set dependence of ^{199}Hg HFCC, calculated with mDKS-RKB method for a series of small molecules (HgH, HgF, HgCN, and HgAg). Our results are summarized in Table II. The Faegri, Hirao-FN, and Dyall's DZ, TZ, and QZ basis sets (all modified) have been used together with FN+FN model. While these basis sets are of rather different quality, only slight deviation of the results was found. The agreement becomes even more remarkable if we would leave out the data obtained with Faegri basis set which is the smallest one among used here bases. We can conclude that it is safe to use

TABLE II. Dependence of the calculated ^{199}Hg HFCC on the basis set. mDKS-RKB, finite-size nucleus model for the charge and magnetic moment distributions (FN+FN) has been employed.

Basis	HgH	HgF	HgCN	HgAg
Faegri	6214	16989	13862	3366
Hirao-FN	6244	16895	13967	3285
Dyall-DZ	6241	16846	13988	3306
Dyall-TZ	6234	16833	13945	3325
Dyall-QZ	6226	16839	13935	3313

TABLE III. The effect of the finite size nucleus model on the hyperfine coupling constant for Cs and Fr.^a Ratio = $\text{HFCC}^{\text{FN+FN}}/\text{HFCC}^{\text{PN+PN}}$.

Atom	Model	O-mod/A-mod
Cs	PN+PN	2273
	FN+FN	2235
	ratio	0.983
Fr	PN+PN	9165
	FN+FN	8096
	ratio	0.883

^amDKS-RKB, Hirao-PN basis set.

the modified Hirao and Dyall's basis sets employing FN+FN model in HFCC calculations.

While the accurate calculation of HFCC is the ultimate goal and it is extremely important in practical applications, in our paper devoted to method development we will discuss the FN/PN ratio that is crucial for estimation of the finite nucleus effect. In Table III, we present the calculated HFCC values for Cs and Fr—they have been selected because some earlier results for these atoms are available.^{6,33,34} The calculations were done with Hirao-PN basis sets. Let us look first at the results for Cs atom. The obtained previously FN/PN ratios (i.e., HFCC with FN+FN divided by HFCC with PN+PN in percents) for Cs atom were 0.97 (Ref. 6) and 0.976 (Ref. 34). Taking into account that these were basis-free calculations (at the Dirac–Hartree–Fock level for the atomic core with correlation effects treated at the second order perturbation theory as in Ref. 6 or using the nonrelativistic configuration interaction method for lithium-like ions where relativistic corrections were calculated up to first order in $1/Z$ employing a perturbation theory),³⁴ the agreement with our Dirac–Kohn–Sham FN/PN value (0.983) is rather good. It is even more interesting to compare the effect of the FN model found in the present work with available data for a heavier atom, Fr. Again, our result for the FN/PN ratio (0.883) is in good agreement with available data [0.846 using fully relativistic Dirac–Hartree–Fock method,³³ 0.84 (Ref. 6)].

Now we will compare the finite size model effect on HFCCs calculated with mDKS-RKB and scalar DKH-2 methods on ^{199}Hg for some small molecules.³⁵ We have chosen these systems because they were studied previously at DKH-2 level and it was shown that finite-size effects for ^{199}Hg HFCC play an important role.¹² The results of our calculations (with both DKH-2 and mDKS-RKB methods) are presented in Table IV in comparison with experimental data. The finite size nucleus effects are given in parentheses (defined as $(\text{HFCC}_{\text{PN+PN}} - \text{HFCC}_{\text{FN+FN}})/\text{HFCC}_{\text{PN+PN}}$ in percents). The basis sets of Hirao (optimized for PN model) were used in the calculations to allow the direct comparison of PN and FN models.

We see that DKH-2 results obtained with PN model are about 20–24% larger in the absolute values than those of mDKS-RKB method. Interestingly, the impact of the finite size model for mDKS-RKB method (numbers in the parentheses) for the considered here molecules is slightly more uniform in the considered series (10.89–14.67%) than at the DKH-2 level (11.62–17.48%). Consequently, mDKS-RKB

TABLE IV. Finite size nucleus effect on ^{199}Hg HFCC calculated at the one- (scalar DKH-2) and four-component (mDKS-RKB) levels. Hirao-PN basis set. Values in parentheses are the finite size nucleus effect defined as $(\text{HFCC}_{\text{PN+PN}} - \text{HFCC}_{\text{FN+FN}})/\text{HFCC}_{\text{PN+PN}}$ in percents.

Method	Model	HgH	HgF	HgCN	HgAg
DKH-2	PN+PN	8586	23463	19285	4459
DKH-2	FN+FN	7471 (12.99)	19362 (17.48)	16183 (16.09)	3941 (11.62)
mDKS-RKB	PN+PN	6921	18927	15599	3690
mDKS-RKB	FN+FN	5906 (14.67)	16810 (11.19)	13875 (11.05)	3288 (10.89)
Exp. ^a		7002	22127	15850	2723

^aExperimental data from Ref. 37.

and DKH-2 methods give rather different HFCC values with FN model. There can be several possible reasons for this discrepancy. First of all, the DKH-2 description of the deep core area has a limited accuracy. Certainly, one has to go beyond the second level of DKH method to get the accuracy of calculated HFCCs close to that in mDKS-RKB. A heavy use of the resolution of identity in DKH-2 is another potential source of loosing the accuracy. From the other side, DKH-2 calculations were performed without fitting the Coulomb and exchange-correlation potentials whereas in the present implementation of mDKS-RKB the fit of the electron density is unavoidable. Although we have paid great attention to the choice of auxiliary basis sets the final answer about the influence of the density fit on the calculated HFCCs should wait till the implementation of the four-index integrals for evaluation of electron–electron Coulomb repulsion without fitting in the mDKS-RKB framework. This work is currently in progress.

Unfortunately, comparison with experimental data could not allow one to judge undeniably about the accuracy of a method: since it is well known, that the HFCC possesses a pronounced sensitivity to the exchange-correlation functionals employed, the overall better agreement of DKH-2 (in comparison with mDKS-RKB) results with experimental data are likely due to fortunate error cancellations. And, of course, for a careful comparison with experimental results the environmental and ro-vibrational effects have to be considered in the calculations.

The mDKS-RKB results for HFCC calculated for a number of metals in two- and three-atomic molecules are presented in Table V in comparison with available experimental data. As it was expected, the FN effect is minimal for light metals such as Zn and increases sturdily with the atomic number. The consequence of extra tight exponent added to the basis set has been very minor in all FN+FN, FN+PN, and PN+FN calculations. In the PN+PN calculations, this effect has been also small except for the calculations of the ^{107}Ag HFCC. Therefore, we included these data in Table V. The calculated HFCC on Ag show a rather strong dependence on the adding a tight exponent. It is interesting to note that for the ^{107}Ag HFCC we found that the effect of the FN model for the magnetic moment of the nuclei (PN+FN data) has an “inverse” character in comparison with other data: the use of the FN model here increases the absolute value of HFCC while normally the FN model decreases it. However this phenomenon is basis set dependent: adding one tight exponent

to the Hirao-PN basis leads to the normal effect of the FN model (i.e., PN+FN HFCC is smaller in the absolute value than the PN+PN result). This observation can be rationalized by analyzing different contributions to the HFCC. We separated them into four terms: Fermi-contact (FC), paramagnetic spin-orbit (PSO) spin-dipolar (SD) and a new relativistic term that vanishes in the nonrelativistic limit (the dominating part of this term can be called as counter-Fermi-contact term or CFC because its sign is opposite to the sign of the FC term and CFC has a similar dependence on the basis set as FC does). The resulting HFCC on heavy nuclei in molecules consists basically of two contributions: standard Fermi-contact and this purely relativistic CFC term with the opposite sign. Thus, the resulting HFCC is practically a difference between two big numbers (see the values of the FC and CFC terms in Supplementary Material³¹). The change of the basis set in core area and the nucleus model affect these two terms in a slightly different way and it is difficult to predict *a priori* whether their sum will be increasing or decreasing. We are planning to pay special attention to this issue in future work. All in all, we can conclude, that the Hirao-PN basis set for calculations of ^{107}Ag HFCC using the PN model (for both charge and magnetic moment distributions) is not sufficient.

Despite the discussed above limited accuracy of DFT method in calculations of hyperfine structure, the overall agreement with experimental data is noticeable. Only the results for HgF molecule are clearly deviate from the general picture. It would be interesting to see to which extend this discrepancy is related to poor simulation of real experimental conditions by consideration of a single molecule as it has been done in this study.

V. CONCLUSIONS

This work is a continuation of our previous study¹² performed at the Douglas–Kroll–Hess level of theory, on the use of a finite size nucleus model (in particular for the nuclear magnetic moment distribution) in relativistic calculations of EPR hyperfine structure. The relativistic four-component density functional approach based on the use of restricted kinetically balanced basis (mDKS-RKB) for calculations of EPR hyperfine structure was extended to include the finite size Gaussian-type model for the magnetic moment distribution. The method was applied for calculations of EPR hyperfine constants for a series of small molecules

TABLE V. HFCC on heavy nuclei (marked bold) in a series of small compounds, calculated with mDKS-RKB method and different basis sets. Data for PN and FN models for charge and magnetic moment distributions are presented.

Molecule	Basis	PN+PN	PN+FN	FN+PN	FN+FN	Exp. ^a
ZnH	Hirao-PN	562	559	567	565	-
	Hirao-FN			564	564	
CdH	Hirao-PN	-3477	-3430	-3437	-3418	+/- 4097
	Hirao-FN			-3449	-3431	
HgH	Hirao-PN	6921	6335	6034	5906	7002
	Hirao-FN			6386	6244	
ZnF	Hirao-PN	1249	1243	1255	1250	-
	Hirao-FN			1254	1252	
CdF	Hirao-PN	-7792	-7688	-7697	-7655	-
	Hirao-FN			-7727	-7687	
HgF	Hirao-PN	18927	17376	17173	16810	22127
	Hirao-FN			17265	16895	
ZnCN	Hirao-PN	1075	1070	1078	1074	-
	Hirao-FN			1075	1073	
CdCN	Hirao-PN	-6822	-6731	-6739	-6702	-7669
	Hirao-FN			-6756	-6720	
HgCN	Hirao-PN	15599	14313	14176	13875	15850
	Hirao-FN			14275	13967	
ZnAg	Hirao-PN	355	353	359	358	-
	Hirao-FN			359	359	
CdAg	Hirao-PN	-2244	-2214	-2215	-2203	-2053
	Hirao-FN			-2225	-2213	
HgAg	Hirao-PN	3690	3382	3360	3288	2723
	Hirao-FN			3359	3285	
ZnAg	Hirao-PN	-1170	-1213	-1298	-1292	-1324
	Hirao-PN+1S	-1318	-1300	-1301	-1294	
	Hirao-FN			-1337	-1324	
CdAg	Hirao-PN	-1141	-1188	-1280	-1274	-1327
	Hirao-PN+1S	-1300	-1281	-1283	-1276	
	Hirao-FN			-1291	-1284	
HgAg	Hirao-PN	-1331	-1390	-1502	-1495	-1562
	Hirao-PN+1S	-1526	-1505	-1506	-1498	
	Hirao-FN			-1541	-1527	
	Dyall-QZ				-1506	

^aExperimental data from Ref. 37.

containing heavy metals up to Hg. The effects of the orbital and auxiliary basis sets were studied. We found that the use of an orbital and especially an auxiliary basis that contains “holes” (i.e., large irregularity in consequent exponents of the Gaussian functions) might lead to significant loss of accuracy.

Our results for the finite size nucleus effect on HFCC are in a good quantitative agreement with older atomic calculations. Since the computational efficiency of our four-component mDKS-RKB code allows one to study systems of real chemical interest, as it was demonstrated recently in calculation of electronic g-tensors³⁶ the ability of the presented

method lies far beyond of being a pure theoretical tool for obtaining accurate benchmark data. Rather it provides a strong alternative to the existing approximate two-component methods with transformed Hamiltonians (such as the Douglas–Kroll–Hess method, zero-order regular approximation or related approaches) in calculations of EPR parameters.

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- ¹O. L. Malkina, D. R. Salahub, and V. G. Malkin, *J. Chem. Phys.* **105**, 8793 (1996).
- ²D. Andrae, *Phys. Rep.* **336**, 413 (2000).
- ³R. G. Woolley, *Mol. Phys.* **30**, 649 (1975).
- ⁴E. A. Moore and R. E. Moss, *Mol. Phys.* **30**, 1315 (1975).
- ⁵M. J. Gregson, G. G. Hall, and D. Rees, *J. Phys. B* **3**, 1195 (1970).
- ⁶V. A. Dzuba, V. V. Flambaum, and O. P. Sushkov, *J. Phys. B: At. Mol. Phys.* **17**, 1953 (1984).
- ⁷V. A. Dzuba, V. V. Flambaum, P. G. Silvestrov, and O. P. Sushkov, *J. Phys. B: At. Mol. Phys.* **20**, 1399 (1987).
- ⁸V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **62**, 052101 (2000).
- ⁹Z. C. Zhang and N. C. Pyper, *Mol. Phys.* **64**, 963 (1988).
- ¹⁰R. Fukuda, M. Hada, H. Nakatsuji, *J. Chem. Phys.* **118**, 1015 (2003).
- ¹¹J. Autschbach, *ChemPhysChem* **10**, 2274 (2009); J. Autschbach, *J. Chem. Theor. Comp.* **6**, 223 (2010).
- ¹²I. Malkin, O.L. Malkina, V.G. Malkin, M. Kaupp, *Chem. Phys. Lett.* **396**, 268 (2004); E. Malkin, I. Malkin, O. L. Malkina, V. G. Malkin, and M. Kaupp, *Phys. Chem. Chem. Phys.* **8**, 4079 (2006).
- ¹³L. Visscher and K. G. Dyall, *Atom. Data Nucl. Tables* **67**, 207 (1997).
- ¹⁴I. Malkin, O. L. Malkina, V. G. Malkin, and M. Kaupp, *J. Chem. Phys.* **123**, 244103 (2005).
- ¹⁵A. C. Hennum, W. Klopper, and T. Helgaker, *J. Chem. Phys.* **115**, 7356 (2001).
- ¹⁶C. van Wüllen, *J. Comput. Chem.* **23**, 779 (2002).

- ¹⁷Note, that Gaussian functions for the finite magnetic moment distribution [Eq. (6)] and for the nuclear charge distribution [Eq. (14)], are not necessarily the same functions.
- ¹⁸R. E. Stanton and S. Havriliak, *J. Chem. Phys.* **81**, 1910 (1984).
- ¹⁹W. Kutzelnigg and W. Liu, *J. Chem. Phys.* **131**, 044129 (2009).
- ²⁰V. G. Malkin, O. L. Malkina, R. Reviakine, A. V. Arbuznikov, M. Kaupp, B. Schimmelpfennig, I. Malkin, M. Repiský, S. Komorovský, P. Hrobárik, E. Malkin, T. Helgaker, and K. Ruud, ReSpect program, version 3.1, 2007.
- ²¹M. Repiský, Development and implementation of efficient relativistic methods for calculations of NMR and EPR parameters, PhD. thesis (Slovak Academy of Sciences, Bratislava 2009).
- ²²S. Komorovský, Development and implementation of relativistic four-component methods using the concept of restricted magnetically balanced basis set, PhD. thesis (Comenius University, Bratislava 2009).
- ²³E. Malkin, Effects of finite size nuclei in relativistic two- and four-component calculations of NMR and EPR parameters, PhD. thesis (Comenius University, Bratislava, 2010).
- ²⁴A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- ²⁵J. P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986).
- ²⁶T. Tsuchiya, M. Abe, T. Nakajima, and K. Hirao, *J. Chem. Phys.* **115**, 4463 (2001).
- ²⁷T. Nakajima and K. Hirao, *J. Chem. Phys.* **116**, 8270 (2002).
- ²⁸K. Faegri and J. Almlöf, *J. Comput. Chem.* **7**, 396 (1986).
- ²⁹K. G. Dyall, *Theor. Chem. Acc.* **108**, 335 (2002); Erratum, *ibid. Theor. Chem. Acc.* **109**, 284 (2003); Revision *Theor. Chem. Acc.* **115**, 441 (2006). Basis sets available from the Dirac web site, <http://dirac.chem.sdu.dk>.
- ³⁰W. Kutzelnigg, U. Fleischer, and M. Schindler, in *NMR-Basic Principles and Progress*, edited by P. Diehl, E. Fluck, H. Günther, R. Kosfeld, and J. Seelig (Springer Verlag, Heidelberg, 1990), Vol. 23, p. 165.
- ³¹See supplementary material at <http://dx.doi.org/10.1063/1.3526263> for the basis sets used and the values of the FC and CFC contributions to the ¹⁰⁷Ag HFCC. In the Hirao-PN basis set for Cs fixed a “hole” in the region of tight exponents as well. See the modified basis set for Cs in supplementary material.
- ³²N. E. Holden, “Table of the Isotopes”, in *CRC Handbook of Chemistry and Physics*, 90th ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 2009).
- ³³P. Pyykkö, private communication (March 16, 2010).
- ³⁴V. M. Shabaev, *J. Phys. B: At. Mol. Opt. Phys.* **27**, 5825 (1984).
- ³⁵For s-type systems considered here, the spin-orbit effects are usually very small, especially on HFCC on a heavy nucleus. This has been confirmed by our unpublished results at the two-component DKH-2 level.
- ³⁶M. Repiský, S. Komorovský, E. Malkin, O. L. Malkina, and V. G. Malkin, *Chem. Phys. Lett.* **488**, 94 (2010).
- ³⁷P. Belanzoni, E. van Lenthe, and E. J. Baerends, *J. Chem. Phys.* **114**, 4421 (2001).