

Fully relativistic calculations of NMR shielding tensors using restricted magnetically balanced basis and gauge including atomic orbitals^{a)}

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A recently developed relativistic four-component density functional method for calculation of nuclear magnetic resonance (NMR) shielding tensors using restricted magnetically balanced basis sets for the small component (mDKS-RMB) was extended to incorporate the gauge including atomic orbitals (GIAO) approach. The combined method eliminates a strong dependence of the results, calculated with a finite basis set, on the choice of the gauge origin for the magnetic potential of a uniform external magnetic field. Benchmark relativistic calculations have been carried out for xenon dimer and the HX series (X=F, Cl, Br, I), where spin-orbit effects are known to be very pronounced for hydrogen shieldings. Our results clearly demonstrate that shieldings calculated at the four-component level with a common gauge (i.e., without GIAO, IGLO, or similar methods to treat the gauge problem) depend dramatically on the choice of the common gauge. The GIAO approach solves the problem in fully relativistic calculations as it does in the nonrelativistic case. © 2010 American Institute of Physics. [doi:10.1063/1.3359849]

I. INTRODUCTION

Nowadays it is well known that calculations of nuclear magnetic shielding constants in compounds containing heavy elements require the proper inclusion of relativistic effects. In modern computational quantum chemistry there exists a variety of methods that take relativistic effects into consideration: the effective core potential (ECP) approach, a perturbational treatment of relativistic effects, quasirelativistic approaches, etc. While ECP or perturbational treatment of both spin-orbit and scalar relativistic effects are often computationally less expensive, their applicability is limited. On the other hand, two-component methods (which treat spin-orbit operators variationally) can be already computationally rather demanding while providing less accurate results than fully relativistic four-component approaches. In recent years, a number of two-component methods aimed to reach the same precision as four-component methods was developed (and some of them were also implemented).^{1–7} Unfortunately, these methods, if implemented without further approximations, lose their computational advantages and can become even more expensive than fully relativistic approaches. Therefore probably the best way to obtain the most accurate results for a reasonable computation cost is the use of four-component methods.

For calculations of nuclear magnetic resonance (NMR) shielding tensors (or another magnetic second-order property—indirect nuclear spin-spin coupling) a second-order perturbation theory has to be applied. In the nonrelativistic case, this will typically involve the expansion of the

first-order perturbed wave function in terms of excited states of the unperturbed system. That, in turn, requires the knowledge of the vacant molecular orbitals (MOs). At the four-component level of theory the vacant states also include the negative-energy states. This complicates the matters since these states are sensitive to the choice of the basis set for the small component. The arising computational difficulties are often associated with the diamagnetic term (as it is called in the nonrelativistic limit).⁸ One way to reduce the difficulty is to use unrestricted kinetically balanced basis sets.⁹ However this approach leads to other problems (described in Refs. 10 and 11 and cited therein) and thus it is worth considering alternative approaches. Since in the presence of a magnetic field the exact relation between the large and the small components involves field-dependent operators, one can choose, as one of the possible solutions, a basis for the small component dependent on the magnetic field. A concept of restricted magnetically balanced basis was first suggested by Aucar *et al.*⁹ and by Kutzelnigg.^{8,12} Recently we successfully used this concept of magnetic balance to develop a four-component method for calculations of NMR parameters—shielding tensor¹³ and indirect nuclear spin-spin coupling tensor.¹⁴ An alternative approach suggested by Kutzelnigg (so-called Kutzelnigg's transformation)⁸ was recently implemented by Visscher¹⁵ and by Xiao *et al.*¹⁶ The approaches based on Kutzelnigg's transformation of the Hamiltonian fix the problem associated with summation over negative states by reducing the contribution from negative energy states from $O(c^0)$ to $O(c^{-4})$. Thus methods based on this transformation can serve as efficient and accurate tools for shielding tensor calculations. From the other side, this transformation leads to operators which suffer from numerical instabilities in case of the magnetic field due to the magnetic moment of a nucleus that limits the applicability of the transformation

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for calculation of spin-spin couplings (for extensive discussion see).^{16–18} Another approach (orbital decomposition approach) to solve this problem was developed by Xiao and co-workers.^{16,19} All these methods have however one serious drawback—until recently²⁰ they were implemented using a common gauge [i.e., without special treatment of the gauge problem by employing GIAO,^{21,22} individual gauge for localized orbitals (IGLO),²³ or similar approaches]. What is “a must” in most nonrelativistic programs for NMR shielding tensor calculations still has not become a routine in four-component calculations.

It is widely accepted that the use of London atomic orbitals (LAOs) reduces the basis set requirements. However it will be a mistake to assign this desirable effect solely to the gauge invariance of the resulting equations. The fact that the use of LAO ensures the gauge independence of the calculated properties does not warrant meaningful results: one can choose very bad (from the computational point of view) schemes which would be still formally gauge independent (see corresponding discussion in Ref. 24). In the nonrelativistic treatment the use of GIAO approach is justified by the fact that for an atomic one-electron system LAOs provide the exact first-order response of the wave function on a uniform magnetic field. This is because the unperturbed wave function is an eigenfunction of the angular momentum operator that is also responsible for the interaction with a uniform external magnetic field.

In the fully relativistic framework the situation is more complicated because now different operators define spherical symmetry of the atomic system and interaction with a uniform external magnetic field. Therefore the first-order change in the wave function (in relativistic problem for a hydrogen-like atom) has along with leading four-component LAO term also additional terms. These terms are at least of order c^{-2} with respect to the leading LAO term. They all have purely relativistic origin and vanish in the nonrelativistic limit. That justifies the use of LAOs in fully relativistic approaches. Moreover, it is possible to show that in the fully relativistic case the use of LAO ensures proper symmetry of calculated shieldings (i.e., equal values on equivalent nuclei in a molecule) as well as first-order current and other magnetic properties as it does in the nonrelativistic case. The first consistent fully relativistic four-component calculations of the NMR shielding tensor (at Hartree–Fock level) using GIAO techniques were reported a short time ago.²⁵ This approach employs an unrestricted kinetically balanced basis set.

Here we report on the extension of the magnetic balance concept to include GIAO.²⁶ In this work we show that the restricted magnetic balance (RMB) condition and the GIAO approach are compatible. The mDKS-RMB method that employs the GIAO was developed and implemented into the MAG module of the ReSpect package. Our benchmark calculations on a few small molecules demonstrate the vulnerability of the relativistic calculations with a common gauge and effectiveness of the GIAO approach to solve the problem in fully relativistic calculations as it does in the nonrelativistic case.

II. CALCULATION OF NMR SHIELDING TENSOR USING GAUGE INCLUDING ATOMIC ORBITALS

Below we keep the following conventions. The Hartree system of atomic units is used. 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.

Let us start with the expression for the total energy in the presence of magnetic fields (the uniform external magnetic field and the magnetic field due to the nuclear magnetic moment) within the framework of the four-component Dirac–Kohn–Sham equations:

$$E(\vec{B}, \vec{\mu}^M) = \langle \varphi_i^{(\vec{B}, \vec{\mu}^M)} | D_{\text{kin}}^{00} + D^{10} + D^{01} | \varphi_i^{(\vec{B}, \vec{\mu}^M)} \rangle + E_{\text{pot}}^{(\vec{B}, \vec{\mu}^M)}, \quad (1a)$$

$$D_{\text{kin}}^{00} \equiv (\beta - 1_{4 \times 4})c^2 + c\vec{\alpha} \cdot \vec{p}, \quad (1b)$$

$$D^{10} \equiv \vec{\alpha} \cdot \vec{A}_{\vec{B}0}, \quad (1c)$$

$$D^{01} \equiv \vec{\alpha} \cdot \vec{A}_{\vec{\mu}^M}, \quad (1d)$$

$$E_{\text{pot}}^{(\vec{B}, \vec{\mu}^M)} \equiv E_{\text{nuc}}^{(\vec{B}, \vec{\mu}^M)} + E_{\text{ee}}^{(\vec{B}, \vec{\mu}^M)} + E_{\text{xc}}^{(\vec{B}, \vec{\mu}^M)}, \quad (1e)$$

where c is the speed of light, \vec{p} is the momentum operator $\vec{p} = -i\vec{\nabla}$, Dirac matrices $\vec{\alpha}$ and β have the usual form

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1_{2 \times 2} & 0 \\ 0 & -1_{2 \times 2} \end{pmatrix}, \quad (2a)$$

and vector $\vec{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ is composed of three Pauli matrices,

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2b)$$

The superscript $(\vec{B}, \vec{\mu}^M)$ denotes the dependence on a uniform external magnetic field \vec{B} and nuclear magnetic moment $\vec{\mu}^M$ of the M th nucleus. The corresponding vector potentials have the following form:

$$\vec{A}_{\vec{B}0} = \frac{1}{2}(\vec{B} \times \vec{r}_G), \quad (3a)$$

$$\vec{A}_{\vec{\mu}^M} = \frac{\vec{\mu}^M \times \vec{r}_M}{r_M^3}, \quad (3b)$$

where $\vec{r}_G \equiv \vec{r} - \vec{r}_0$ (\vec{r}_0 is the gauge origin) and $\vec{r}_M \equiv \vec{r} - \vec{R}_M$ (\vec{R}_M is the position of nucleus M). The potential energy $E_{\text{pot}}^{(\vec{B}, \vec{\mu}^M)}$ [Eq. (1e)] consists of the electron-nucleus Coulomb energy $E_{\text{nuc}}^{(\vec{B}, \vec{\mu}^M)}$, the electron-electron Coulomb energy $E_{\text{ee}}^{(\vec{B}, \vec{\mu}^M)}$, and the Kohn–Sham exchange-correlation energy $E_{\text{xc}}^{(\vec{B}, \vec{\mu}^M)}$ (we do not employ relativistic current-dependent exchange-correlation functionals),

$$E_{\text{nuc}}^{(\vec{B}, \vec{\mu}^M)} \equiv - \sum_M \int_{(V)} \frac{Z_M}{r_M} \rho_0^{(\vec{B}, \vec{\mu}^M)}(\vec{r}) dV, \quad (4a)$$

$$E_{\text{ce}}^{(\vec{B}, \vec{\mu}^M)} \equiv \frac{1}{2} \int \int_{(V, V')} \frac{\rho_0^{(\vec{B}, \vec{\mu}^M)}(\vec{r}) \rho_0^{(\vec{B}, \vec{\mu}^M)}(\vec{r}')}{|\vec{r} - \vec{r}'|} dV dV', \quad (4b)$$

$$E_{\text{xc}}^{(\vec{B}, \vec{\mu}^M)} \equiv \int_{(V)} \rho_0^{(\vec{B}, \vec{\mu}^M)}(\vec{r}) \varepsilon_{\text{xc}}^{(\vec{B}, \vec{\mu}^M)}[\{\rho_k^{(\vec{B}, \vec{\mu}^M)}(\vec{r})\}_{k=0}^3] dV. \quad (4c)$$

Here $\varepsilon_{\text{xc}}^{(\vec{B}, \vec{\mu}^M)}$ is the exchange-correlation energy density, where $k=0, 1, 2, 3$, \vec{r} is the position vector, Z_M is the charge of the M th nucleus, and $\rho_k^{(\vec{B}, \vec{\mu}^M)}$ represents the total relativistic electron density ($k=0$) and three spin densities ($k=1, 2, 3$),

$$\rho_k^{(\vec{B}, \vec{\mu}^M)} \equiv \varphi_i^{(\vec{B}, \vec{\mu}^M) \dagger} \Sigma_k \varphi_i^{(\vec{B}, \vec{\mu}^M)}, \quad \Sigma_0 \equiv 1_{4 \times 4},$$

$$\vec{\Sigma} \equiv \begin{pmatrix} \vec{\sigma} & 0 \\ 0 & \vec{\sigma} \end{pmatrix}. \quad (5)$$

The common way to calculate the nuclear magnetic shielding tensor in the four-component framework is to expand the four-component MOs $\varphi_p^{(\vec{B}, \vec{\mu}^M)}$ in a finite set of basis functions. There are two major sources of a poor basis set convergence. The first one is due to the well-known gauge dependence of the vector potential $\vec{A}_{\vec{B}0}$ and the second one is related to the four-component nature of fully relativistic calculations. Among the solutions of the gauge dependence problem, the most popular one is to include the gauge dependence directly into atomic orbitals (thus obtaining the so-called London orbitals). This leads to the LAO method introduced first by London²¹ and developed later by Ditchfield²² (also known as GIAO approach—gauge invariant or gauge including atomic orbitals approach). The second problem, specific for the four-component case, is connected to the choice of the basis set for the small component. While the choice of the basis set for the large component is rather straightforward and in many aspects it resembles the choice of the basis in nonrelativistic calculations, the selection of a basis for the small component is more difficult and crucial for achievement of sensible results. The RMB concept is one of the most efficient ways to deal with this problem.¹³ The RMB concept provides a good balanced connection between basis sets for the large and the small components, for a system in the presence of magnetic fields, exactly in the same way, as RKB condition does in their absence.^{27,28} This was demonstrated in Ref. 13 for the case of a common gauge origin.

The next logical step to solve simultaneously the two problems discussed above would be to combine both approaches (GIAO and RMB) to obtain more stable results in fully relativistic calculations of NMR shielding tensors. This leads to a new mDKS-RMB GIAO method presented below.

Following the GIAO formalism, we will write the large component of the i th MO $\varphi_i^{L(\vec{B}, \vec{\mu}^M)}$ as a linear combination of LAOs $\chi_\lambda^{L(\vec{B})}$,

$$\varphi_i^{L(\vec{B}, \vec{\mu}^M)} = C_{\lambda i}^{L(\vec{B}, \vec{\mu}^M)} \chi_\lambda^{L(\vec{B})}, \quad \chi_\lambda^{L(\vec{B})} \equiv \omega_\lambda^{(\vec{B})} \chi_\lambda, \quad (6)$$

where $\omega_\lambda^{(\vec{B})}$ is the phase factor, which ensures the energy invariance with respect to a change of the gauge origin \vec{r}_0 ,

$$\omega_\lambda^{(\vec{B})} \equiv \exp \left\{ - \frac{i}{2c} [\vec{B} \times (\vec{R}_\lambda - \vec{r}_0)] \cdot \vec{r} \right\}, \quad (7)$$

$C_{\lambda i}^{L(\vec{B}, \vec{\mu}^M)}$ represents the expansion coefficients for the system in the presence of the external magnetic field \vec{B} and nuclear magnetic moment $\vec{\mu}^M$, and \vec{R}_λ is the position of the nucleus at which the atomic orbital χ_λ is centered. We have chosen χ_λ to be Gaussian-type orbitals, but other types of basis functions can be used as well. Note that the basis function χ_λ does not depend on the magnetic fields, whereas the basis function for the large component $\chi_\lambda^{L(\vec{B})}$ depends on the external magnetic field through the phase factor. It is worth to note that for even and odd λ indices χ_λ represent alpha ($\begin{smallmatrix} 1 \\ 0 \end{smallmatrix}$) and beta ($\begin{smallmatrix} 0 \\ 1 \end{smallmatrix}$) spinors, respectively.

In the RMB framework, the small component $\varphi_i^{S(\vec{B}, \vec{\mu}^M)}$ is expanded as (see Ref. 13 for more details)

$$\varphi_i^{S(\vec{B}, \vec{\mu}^M)} = C_{\lambda i}^{S(\vec{B}, \vec{\mu}^M)} \chi_\lambda^{S(\vec{B}, \vec{\mu}^M)}. \quad (8)$$

The basis functions for the small component $\chi_\lambda^{S(\vec{B}, \vec{\mu}^M)}$ depend on the magnetic fields via both RMB condition and the basis function for the large component $\chi_\lambda^{L(\vec{B})}$,

$$\chi_\lambda^{S(\vec{B}, \vec{\mu}^M)} \equiv \frac{1}{2c} \left(\vec{\sigma} \cdot \vec{p} + \frac{1}{c} \vec{\sigma} \cdot \vec{A}_{\vec{B}0} + \frac{1}{c} \vec{\sigma} \cdot \vec{A}_{\vec{\mu}^M} \right) \chi_\lambda^{L(\vec{B})}. \quad (9)$$

Due to identity

$$\left(\vec{p} + \frac{1}{c} \vec{A}_{\vec{B}0} \right) \omega_\lambda^{(\vec{B})} = \omega_\lambda^{(\vec{B})} \left(\vec{p} + \frac{1}{c} \vec{A}_{\vec{B}\lambda} \right), \quad (10a)$$

$$\vec{A}_{\vec{B}\lambda} = \frac{1}{2} (\vec{B} \times \vec{r}_\lambda), \quad \vec{r}_\lambda \equiv \vec{r} - \vec{R}_\lambda, \quad (10b)$$

the basis for the small component (9) can be rewritten in the following form:

$$\chi_\lambda^{S(\vec{B}, \vec{\mu}^M)} = \frac{1}{2c} \omega_\lambda^{(\vec{B})} \left(\vec{\sigma} \cdot \vec{p} + \frac{1}{c} \vec{\sigma} \cdot \vec{A}_{\vec{B}\lambda} + \frac{1}{c} \vec{\sigma} \cdot \vec{A}_{\vec{\mu}^M} \right) \chi_\lambda. \quad (11)$$

After defining the basis set expansion of the both large and the small components [Eqs. (6)–(9), (10a), (10b), and (11)], we can formulate the second order perturbation theory for the calculation of shielding tensors. NMR shielding tensor is defined as a bilinear derivative of the energy [Eq. (1a)], with respect to parameters B_u and μ_v^M ,

$$\sigma_{uv}^M = \left. \frac{d^2 E(\vec{B}, \vec{\mu}^M)}{dB_u d\mu_v^M} \right|_{\vec{B}, \vec{\mu}^M=0}. \quad (12)$$

Since we are looking for a second-order property—NMR shielding, Dalgarno's exchange theorem²⁹ allows us to choose the magnetic field, with respect to which the linear response of MOs is expressed. If the magnetic moment of a nucleus is chosen as the primary perturbation (as done by Visscher *et al.*)³⁰ then the nuclear shielding of the nucleus and the spin-spin coupling constants of this nucleus with all

others may be calculated in one shot. On the other hand in nonrelativistic calculations, the usual choice of the primary perturbation is the external uniform magnetic field as then all shielding tensors are obtained at once. We will use the latter option and we will search for the linear response of the MOs to the external magnetic field.

The bilinear derivative of energy (1a) can be expressed as

$$\sigma_{uv}^M = \langle \varphi_i^{(1,0)u} | D^{(0,1)v} | \varphi_i^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | D^{(0,1)v} | \varphi_i^{(1,0)u} \rangle, \quad (13a)$$

where

$$\varphi_i^{(1,0)u} \equiv \left. \frac{d\varphi_i^{(\vec{B}, \vec{\mu}^M)}}{dB_u} \right|_{\vec{B}, \vec{\mu}^M=0}, \quad D^{(0,1)v} \equiv \left. \frac{\partial D^{01}}{\partial \mu_v^M} \right|_{\vec{B}, \vec{\mu}^M=0}. \quad (13b)$$

Derivation of Eq. (13) is described in Ref. 13. Note that in contrast with the nonrelativistic case, in the expression for NMR shielding tensor, we have no bilinear (with respect to the \vec{B} and $\vec{\mu}^M$) operators in the Hamiltonian. From now on, the superscript (0,0) means the independence of MOs, MO coefficients, operators on both perturbations B_u , μ_v^M , whereas $(1,0)_u$ and $(0,1)_v^M$ represent derivation with respect to B_u and μ_v^M , respectively.

In calculations of the NMR shielding tensor the first step is to obtain the linear response of MOs [Eq. (13b)]. Since we use now both RMB and GIAO ansatz, the four-component spinors [the large component (6) and the small component (8)] depend on the magnetic fields via MO coefficients, RMB condition and phase factor $\omega_\lambda^{(\vec{B})}$. Thus the perturbed MOs can be decomposed in three parts: the first two terms resemble those in the mDKS-RMB CGO (common gauge origin) approach [Eq. (16) in Ref. 13], i.e., regular $\varphi_i^{r(1,0)u}$ and magnetic term $\varphi_i^{m(1,0)u}$, and an additional term that comes from the phase factor $\omega_\lambda^{(\vec{B})}$,

$$\varphi_i^{(1,0)u} \equiv \varphi_i^{r(1,0)u} + \varphi_i^{m(1,0)u} + \varphi_i^{\omega(1,0)u}. \quad (14)$$

The regular and the magnetic parts have the following form:

$$\varphi_i^{r(1,0)u} = \begin{pmatrix} \mathbf{C}_{\lambda i}^{L(1,0)u} \chi_\lambda \\ \mathbf{C}_{\lambda i}^{S(1,0)u} \chi_\lambda^{S(0,0)} \end{pmatrix}, \quad (15a)$$

$$\varphi_i^{m(1,0)u} = \begin{pmatrix} \mathbf{0} \\ \mathbf{C}_{\lambda i}^{S(0,0)} \chi_\lambda^{Sm(1,0)u} \end{pmatrix},$$

where

$$\chi_\lambda^{S(0,0)} \equiv \frac{1}{2c} \vec{\sigma} \cdot \vec{p} \chi_\lambda, \quad \chi_\lambda^{Sm(1,0)u} \equiv \frac{1}{4c^2} (\vec{r}_\lambda \times \vec{\sigma})_u \chi_\lambda. \quad (15b)$$

The phase-related part $\varphi_i^{\omega(1,0)u}$ can be written in the following two-component form:

$$\varphi_i^{\omega(1,0)u} = \begin{pmatrix} \mathbf{C}_{\lambda i}^{L(0,0)} \chi_\lambda^{L\omega(1,0)u} \\ \mathbf{C}_{\lambda i}^{S(0,0)} \chi_\lambda^{S\omega(1,0)u} \end{pmatrix}, \quad (16a)$$

where

$$\chi_\lambda^{L\omega(1,0)u} \equiv \frac{i}{2c} [(\vec{r}_0 - \vec{R}_\lambda) \times \vec{r}]_u 1_{2 \times 2} \chi_\lambda, \quad (16b)$$

$$\chi_\lambda^{S\omega(1,0)u} \equiv \frac{i}{4c^2} [(\vec{r}_0 - \vec{R}_\lambda) \times \vec{r}]_u \vec{\sigma} \cdot \vec{p} \chi_\lambda. \quad (16c)$$

Since the unperturbed (field-free) atomic orbital basis covers the same space as the unperturbed MOs, we can express the first term in Eq. (14) in the basis of the unperturbed MOs,

$$\varphi_i^{r(1,0)u} = \beta_{pi}^{B_u} \varphi_p^{(0,0)}, \quad (17)$$

where index p denotes occupied positive energy MOs as well as unoccupied positive and all negative energy MOs. We note that for calculation of phase related part $\varphi_i^{\omega(1,0)u}$ (likewise for the magnetic part $\varphi_i^{m(1,0)u}$) only the unperturbed MO coefficients are necessary.

Since the derivation of the equation for mDKS-RMB-GIAO is analogous to that of the original mDKS-RMB method,¹³ below we will summarize only the final equations. For the sake of simplicity, in the following we employ the matrix notation $\mathbf{C}_{\lambda i}^{(0,0)} = \mathbf{C}_{(i)}^{(0,0)}$ and the shorthand notations $\mathbf{C}_{(i)}^{L(0,0)} = \mathbf{C}_{(i)}^L$ and $\mathbf{C}_{(i)}^{S(0,0)} = \mathbf{C}_{(i)}^S$. We keep subscript (p) in order to stress that $\mathbf{C}_{(p)}$ are coefficients for the p th MO. Substituting the partitioning (14) of the linear response of four-component MO, together with the expressions for regular, magnetic and phase-related part [Eqs. (15a), (16a), and (17)], into the expression for chemical shielding [Eq. (13a)] we obtain (after some technical manipulations)

$$\sigma_{uv}^M \equiv (\sigma^D)_{uv}^M + (\sigma^{P0})_{uv}^M + (\sigma^{P1})_{uv}^M, \quad (18a)$$

$$(\sigma^D)_{uv}^M = \frac{1}{4c^2} \begin{pmatrix} \mathbf{C}_{(i)}^{L\dagger} & \mathbf{C}_{(i)}^{S\dagger} \end{pmatrix} \begin{pmatrix} \mathbf{0} & \Lambda_{B_u \mu_v^M}^{D\omega^\dagger} \\ \Lambda_{B_u \mu_v^M}^{D\omega} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix}, \quad (18b)$$

$$(\sigma^{P0})_{uv}^M = \frac{1}{2c} [(\beta_{ij}^{B_u})^* + \beta_{ji}^{B_u}] \begin{pmatrix} \mathbf{C}_{(i)}^{L\dagger} & \mathbf{C}_{(i)}^{S\dagger} \end{pmatrix} \begin{pmatrix} \mathbf{0} & \Lambda_{\mu_v^M}^{P\dagger} \\ \Lambda_{\mu_v^M}^P & \mathbf{0} \end{pmatrix} \times \begin{pmatrix} \mathbf{C}_{(j)}^L \\ \mathbf{C}_{(j)}^S \end{pmatrix}, \quad (18c)$$

$$(\sigma^{P1})_{uv}^M = \frac{1}{c} \text{Re} \left[\beta_{ai}^{B_u} \begin{pmatrix} \mathbf{C}_{(i)}^{L\dagger} & \mathbf{C}_{(i)}^{S\dagger} \end{pmatrix} \begin{pmatrix} \mathbf{0} & \Lambda_{\mu_v^M}^{P\dagger} \\ \Lambda_{\mu_v^M}^P & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(a)}^L \\ \mathbf{C}_{(a)}^S \end{pmatrix} \right], \quad (18d)$$

where

$$(\Lambda_{\mu_v^M}^P)_{\lambda\tau} \equiv \langle \chi_\lambda | \vec{\sigma} \cdot \vec{p} \left(\frac{\vec{r}_M \times \vec{\sigma}}{r_M^3} \right)_v | \chi_\tau \rangle, \quad (19a)$$

$$(\Lambda_{B_u \mu_v^M}^{D\omega})_{\lambda\tau} \equiv \langle \chi_\lambda | [\vec{\sigma} \cdot \vec{p} i (\vec{R}_{\lambda\tau}^- \times \vec{r})_u + (\vec{r}_\lambda \times \vec{\sigma})_u] \times \frac{(\vec{r}_M \times \vec{\sigma})_v}{r_M^3} | \chi_\tau \rangle, \quad (19b)$$

$$\vec{R}_{\lambda\tau}^- = \vec{R}_{\lambda}^- - \vec{R}_{\tau}^- \quad (19c)$$

The evident difference between the corresponding equations for CGO approach [Eqs. (20) and (22a)–(22c) in Ref. 13] is only in Eq. (18b), where an additional diamagnetic operator appears. Yet, more pronounced changes will be in linear response coefficients $\beta_{pi}^{B_u}$. It is clear from the following expressions for these coefficients for occupied MOs

$$\begin{aligned} (\beta_{ij}^{B_u})^* + \beta_{ji}^{B_u} = & -\frac{1}{2c} (\mathbf{C}_{(j)}^{L\dagger} \quad \mathbf{C}_{(j)}^{S\dagger}) \begin{pmatrix} \mathbf{S}^{L(1,0)u} & \mathbf{0} \\ \mathbf{0} & \mathbf{S}^{S(1,0)u} \end{pmatrix} \\ & \times \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix}, \end{aligned} \quad (20a)$$

where

$$\mathbf{S}_{\lambda\tau}^{L(1,0)u} \equiv \langle \chi_{\lambda} | i(\vec{R}_{\lambda\tau}^- \times \vec{r})_u | \chi_{\tau} \rangle, \quad \mathbf{S}^{S(1,0)u} \equiv \frac{1}{2c^2} \tilde{\Lambda}_{B_u}^{P\omega}, \quad (20b)$$

$$\begin{aligned} (\tilde{\Lambda}_{B_u}^{P\omega})_{\lambda\tau} \equiv & \frac{1}{2} \langle \chi_{\lambda} | 2\sigma_u + [(2\vec{r} - \vec{R}_{\lambda\tau}^+) \times \vec{p}]_u \\ & + i \left[\frac{p^2}{2}, (\vec{R}_{\lambda\tau}^- \times \vec{r})_u \right]_+ | \chi_{\tau} \rangle, \end{aligned} \quad (20c)$$

$$\vec{R}_{\lambda\tau}^+ = \vec{R}_{\lambda}^+ + \vec{R}_{\tau}^+, \quad (20d)$$

and for the linear response coefficients for vacant MOs,

$$\begin{aligned} \beta_{ai}^{B_u} = & \frac{1}{2c} \frac{1}{\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)}} (\mathbf{C}_{(a)}^{L\dagger} \quad \mathbf{C}_{(a)}^{S\dagger}) \\ & \times \begin{pmatrix} \mathbf{V}_{B_u}^{L\omega} - \varepsilon_i^{(0,0)} \mathbf{S}^{L(1,0)u} & \tilde{\Lambda}_{B_u}^{P\omega} \\ \tilde{\Lambda}_{B_u}^{P\omega} & \mathbf{V}_{B_u}^{S\omega} - \left(1 + \frac{\varepsilon_i^{(0,0)}}{2c^2}\right) \tilde{\Lambda}_{B_u}^{P\omega} \end{pmatrix} \\ & \times \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix} + \frac{1}{\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)}} (\mathbf{C}_{(a)}^{L\dagger} \quad \mathbf{C}_{(a)}^{S\dagger}) \\ & \times \begin{pmatrix} \mathbf{V}' & \mathbf{0} \\ \mathbf{0} & \frac{1}{4c^2} \mathbf{W}' \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix}, \end{aligned} \quad (21a)$$

where

$$(\mathbf{V}_{B_u}^{L\omega})_{\lambda\tau} \equiv \langle \chi_{\lambda} | i(\vec{R}_{\lambda\tau}^- \times \vec{r})_u V_{2 \times 2}^{(0,0)} | \chi_{\tau} \rangle, \quad (21b)$$

$$\begin{aligned} (\mathbf{V}_{B_u}^{S\omega})_{\lambda\tau} \equiv & \frac{1}{4c^2} \{ \langle \vec{\sigma} \cdot \vec{p} \chi_{\lambda} | V_{2 \times 2}^{(0,0)} | (\vec{r}_{\tau} \times \vec{\sigma})_u \chi_{\tau} \rangle \\ & + \langle (\vec{r}_{\lambda} \times \vec{\sigma})_u \chi_{\lambda} | V_{2 \times 2}^{(0,0)} | \vec{\sigma} \cdot \vec{p} \chi_{\tau} \rangle \\ & + \langle \vec{\sigma} \cdot \vec{p} \chi_{\lambda} | i(\vec{R}_{\lambda\tau}^- \times \vec{r})_u V_{2 \times 2}^{(0,0)} | \vec{\sigma} \cdot \vec{p} \chi_{\tau} \rangle \}. \end{aligned} \quad (21c)$$

$$\mathbf{V}_{2 \times 2}^{(0,0)} \equiv \frac{\delta E_{\text{pot}}^{(0,0)}}{\delta \rho_k^{(0,0)}(\vec{r})} \sigma_k, \quad k = 0, 1, 2, 3. \quad (21d)$$

In the nonrelativistic case the Eq. (20c) is often shown in literature in a shorter form (see for example Ref. 31). We,

however, prefer a slightly different expression, because here matrix $\tilde{\Lambda}_{B_u}^{P\omega}$ is obviously Hermitian (whereas in the usually published form it is not). The coupling terms \mathbf{V}' and \mathbf{W}' have the same form as in the CGO case:

$$\mathbf{V}'_{\lambda\tau} \equiv \langle \chi_{\lambda} | O_{2 \times 2}^{(1,0)u} | \chi_{\tau} \rangle, \quad \mathbf{W}'_{\lambda\tau} \equiv \langle \vec{\sigma} \cdot \vec{p} \chi_{\lambda} | O_{2 \times 2}^{(1,0)u} | \vec{\sigma} \cdot \vec{p} \chi_{\tau} \rangle, \quad (22a)$$

with

$$\begin{aligned} O_{2 \times 2}^{(1,0)u} \equiv & \int \frac{\delta(V_{\text{ee}}^{(0,0)}(\vec{r}) + V_{\text{xc}}^{(0,0)}(\vec{r}))}{\delta \rho_k^{(0,0)}(\vec{r}')} \rho_k^{(1,0)u}(\vec{r}') dV', \quad (22b) \\ \rho_k^{(1,0)u} = & \varphi_i^{(1,0)u\dagger} \sum_k \varphi_i^{(0,0)} + \varphi_i^{(0,0)\dagger} \sum_k \varphi_i^{(1,0)u}, \quad k = 0, 1, 2, 3, \end{aligned} \quad (22c)$$

where $V_{\text{ee}}^{(0,0)}$ and $V_{\text{xc}}^{(0,0)}$ are the Coulomb electron-electron repulsion potential and the exchange-correlation potential, respectively. The linear response density $\rho_k^{(1,0)u}$ has now three parts [regular, magnetic, and phase-related, Eq. (14)] in contrast with the case of CGO where it consists of only two parts: regular and magnetic. It is instructive to note that since all the equations are meant to be valid for both open- and close-shell systems one has to keep linear response of density in the equations (i.e., this response is nonzero for open-shell systems).

III. COMPUTATIONAL DETAILS

Structures of the HF, HCl, HBr, and HI molecules have been taken from Ref. 32 and of C₂H₄ molecule from Ref. 33. The internuclear distance in the Xe dimer was chosen as 20 Å. All calculations were performed at the density functional theory (DFT) level, using the ReSpect (Ref. 34) program (including the property module MAG-ReSpect). Relativistic calculations were done with a new four-component module of ReSpect developed in Bratislava.^{26,35} We used the Becke GGA functional for exchange³⁶ with the Perdew GGA correlation functional.³⁷ Since the analytical evaluation of the GGA kernels requires nontrivial programming, at present we use a numerical scheme for calculation of the kernels (i.e., the derivatives of the corresponding potentials were taken numerically).

Orbital basis sets for the elements Br and I were those of Faegri,³⁸ used in a fully uncontracted fashion augmented by a set of additional diffuse s-, p-, and d-functions, obtained by dividing the smallest exponent of a given angular momentum by a factor of 3. For light atoms (H, F, and Cl) we fully uncontracted IGLO-III basis sets.³⁹ To fill up “holes” in the set of exponents (for better SCF convergence), an extra s-exponent was added to the basis sets for the heavier halogen atoms (1.165 448 49 for Cl, 0.907 029 776 for Br, and 0.606 110 391 for I). In calculations of shieldings in C₂H₄ molecule, we employed the uncontracted polarization-consistent triple-zeta basis sets of Jensen (termed upcJ-2) (Ref. 40) which were primarily designed for calculation of spin-spin coupling. For Xe dimer calculations we used uncontracted triple-zeta basis of Dyll.⁴¹ Fitting of the total electron density and the components of the spin density was done with uncontracted auxiliary basis sets (6s2p2d for H in

TABLE I. ^1H and ^{13}C isotropic shieldings (in ppm) in C_2H_4 molecule calculated with common gauge origin (CGO) and GIAO methods. (NR: nonrelativistic calculations. REL: relativistic mDKS-RMB calculations. The data in columns are given for H1, H4, H5, H6, C2, and C3 (from left to right). See text for description.)

Method	^1H	^1H	^1H	^1H	^{13}C	^{13}C
NR-CGO	27.8	26.3	24.7	23.2	47.2	44.4
REL-CGO	27.8	26.3	24.7	23.2	48.8	46.3
NR-GIAO	25.6	25.6	25.6	25.6	45.1	45.1
REL-GIAO	25.5	25.5	25.5	25.5	46.9	46.8

calculations for HX series and 8s3p3d for C_2H_4 , 15s11p11d3f3g for C, 11s7p7d for F, 13s8p8d for Cl, 18s13p13d for Br, 22s17p17d for I, 28s21p21d for Xe, s-exponents were chosen as twice the s-exponents in the corresponding orbital basis set, and p- and d-sets (f- and g-sets) were composed of shared exponents covering the space of p-functions (d-functions) in the orbital basis sets multiplied by 2 in an even-tempered manner). Special attention was paid to the accuracy of numerical integration. In particular, the grid for numerical evaluation of integrals was denser in the core area. The grid for numerical integration contained 256 points of radial quadrature and in the angular part we used 110 points. All relativistic calculations were done with a finite nucleus model employing the Gaussian charge distribution.⁴²

IV. BENCHMARK CALCULATIONS AND DISCUSSION

To demonstrate the importance of the GIAO treatment and the correctness of the mDKS-RMB method and its implementation when approaching the nonrelativistic limit, we start our discussion with benchmark calculations of ^1H and ^{13}C shieldings in C_2H_4 molecule where relativistic effects are expected to be very small. This molecule has been placed nonsymmetrically: one of the hydrogens (H1) was placed at (0,0,0) and the C2–H1 bond was directed along the Z-axis. The common gauge origin was chosen at the coordinate center (0,0,0). Hydrogens H5 and H6 were bound to C3, H5 being in *cis*-position with respect to H1. It allowed us to judge about the gauge-dependence of the results by comparison of the calculated shieldings on different hydrogen and carbon nuclei; due to the symmetry of the molecule all ^1H shieldings should be equivalent (the same holds for ^{13}C shieldings on both carbons). In Table I, the obtained fully relativistic mDKS-RMB and nonrelativistic CGO and GIAO results for ^1H and ^{13}C shieldings are presented. Despite the fact that in CGO calculations we have chosen a relatively large basis set of Jensen (upcJ-2) the difference between shieldings calculated on different hydrogen nuclei is dramatic: up to 4.6 ppm! Keeping in mind that the whole scale of ^1H shifts in organic compounds is about 12 ppm, this is an evidence for strong gauge dependence. Obviously one cannot use such approach (even with this basis set) in real applications. From the other side, the GIAO calculations performed with the same basis set and for the same orientation of the molecule are completely free from this drawback and all the hydrogen shieldings are equal. The same conclusions could be drawn also for shieldings calculated on carbon nuclei (here an insignificant difference of about 0.1 ppm occurs

which reflects the accuracy of numerical integration; the use of a larger grid makes results more symmetric). Comparison of relativistic and nonrelativistic GIAO results shows that they differ by about 1.8 ppm for ^{13}C . While similar findings were already reported (see for example Ref. 43 where such corrections were calculated using a perturbation theory; for ^{13}C in CH_3F the calculated value was 2.52 ppm) it is remarkable to see such large effects in molecules containing only light elements. A detailed analysis of our results shows that while diamagnetic and usual paramagnetic contributions differ only marginally (345.86 and -298.63 ppm in the nonrelativistic case versus 345.89 and -298.23 ppm in relativistic calculations), the major difference (2.0 ppm) is due to a purely relativistic contribution (sometimes called as FC/SZ-KE in Breit–Pauli Hamiltonian—see Ref. 44 and cited therein). We believe that the remaining difference in diamagnetic and paramagnetic contributions is due to numerical reasons (the use of fitting for calculation of two-electron Coulomb integrals in fully relativistic code as well as different grid point distributions in our relativistic and nonrelativistic codes).

Let us consider another test example—xenon dimer. The results are presented in the Table II. Two Xe atoms have been well separated (20 Å) to ensure that they are not interacting. The gauge origin was chosen at the position of the first Xe atom (for comparison, an additional calculation with the gauge in the center of symmetry was also performed). The CGO results indicate only a slight gauge-dependence, probably due to high symmetry of well-separated Xe atoms. While one would expect that the shielding for the first atom (at which the gauge-origin was placed) would be closer to the result for an isolated atom, the opposite was found: the shielding for the second atom is closer to the value for the isolated Xe. This observation goes in parallel with nonrelativistic results for shieldings in rare-gas dimers with long interatomic distances. The rationalization of the phenomenon

TABLE II. ^{129}Xe isotropic shieldings (in ppm) in xenon dimer calculated with CGO and GIAO methods. mDKS-RMB calculations.

Method	^{129}Xe	^{129}Xe
CGO-center ^a	7044.4	7044.4
CGO-Xe ^b	7046.7	7037.9
GIAO ^c	7033.3	7033.3

^aCommon gauge was placed in the center of symmetry.

^bCommon gauge was placed on the first atom. The data for this atom are given in the left column.

^cGIAO value corresponds exactly to the value calculated on isolated atom ^{129}Xe .

TABLE III. Isotropic shieldings (in ppm) in HX (X=F, Cl, Br, I) series calculated with CGO and GIAO methods. mDKS-RMB calculations.

Method	HF		HCl		HBr		HI	
	¹⁹ F	¹ H	³⁵ Cl	¹ H	⁸¹ Br	¹ H	¹²⁷ I	¹ H
CGO-X	412.4	29.1	945.6	31.7	2889.1	35.0	5707.1	44.7
CGO-H	420.8	35.2	1007.6	57.5	2924.1	130.4	5758.7	209.8
GIAO	416.2	30.5	973.9	32.6	2899.4	36.4	5716.3	46.3
Exp. ^a	...	28.5	...	31.1	...	35.0	...	43.9

^aReference 46.

involves the fact that shielding of a spherical atom is gauge independent⁴⁵ and thus the contribution from MOs of the second atom is decisive. In such case it is crucial to have a good gauge for another atom rather than for the atom of interest itself.⁴⁵

The GIAO calculations were performed for the system placed nonsymmetrically with respect to the coordinate frame. This provided us an additional test for the mDKS-RMB GIAO approach. From general considerations, NMR shieldings on well-separated Xe nuclei in xenon dimer should be equal to the NMR shielding for the isolated Xe atom. This fact can be also derived from the mDKS-RMB GIAO equations. Since in our test calculations (see Table II) isotropic shieldings on both Xe nuclei are symmetric and equal to the value calculated for the isolated Xe atom (7033.3 ppm) we can conclude that this test supports the correctness of our definition of relativistic LAO basis.

Table III illustrates the importance of the proper treatment of the gauge-origin problem in shielding calculations in the HX series (X=F, Cl, Br, I), where relativistic spin-orbit effects are known to be very pronounced.⁴⁷ With this in mind, the fully relativistic calculations with CGO were performed using two different origins: either on H or on X (X=F, Cl, Br, I) nuclei. The difference between ¹H shieldings calculated in the same molecule but with such different gauge origins dramatically increases along this series: 6.1 ppm for HF, 25.8 ppm for HCl, 95.4 ppm for HBr, and 165.1 ppm for HI molecules. Since this trend goes in parallel with the nonrelativistic results (7.2, 27.3, 96.9, and 167.0 ppm; calculated with the same exchange-correlation functional and basis set) we can conclude that spin-orbit effects have minimal gauge dependences (at least for this type of systems).

Again, taking into account the typical value of ¹H shielding (about 30 ppm) and the overall range of ¹H shifts (about 12 ppm in usual organic compounds) one has to admit that calculations of such accuracy are useless. On the other hand, the shifts on the heavier nuclei are much less affected by this gauge-origin problem: the corresponding differences are 8.4 ppm for HF, 62.0 ppm for HCl, 35.0 ppm for HBr, and 51.6 ppm for HI molecules. While these changes are also significant in absolute values, they are much less dramatic taking into account the values of the shielding in those molecules. For example, the ¹²⁷I “gauge shift” in HI molecule is only about 1% of the total shielding (5716.3 ppm; calculated with GIAO). Obviously, the importance of coupling terms (which have purely relativistic nature)¹³ also increases along this series for both hydrogen and heavy-elements nuclei. It is

interesting to note that the major part of the difference between the results with different common gauge origins (first on iodine and then on hydrogen) comes from the diamagnetic contribution to the perpendicular component of ¹H shielding tensor (increase by about 460 ppm) whereas the change in the corresponding paramagnetic contribution is much smaller (decrease of about 175 ppm). Thus paramagnetic contribution, being much more sensitive to the quality of the basis set, fails to compensate the changes in the diamagnetic one. We found that addition of higher angular momentum functions on iodine increases (in absolute values) the paramagnetic part and, as the result, decreases the gauge dependence.

The comparison of the GIAO results with experimental data reveals that the theoretical values overshoot the experimental counterparts by a significant amount (up to 2.4 ppm for ¹H in HI molecule). From our experience we know that such overestimation usually has a rather systematic behavior and therefore slightly affects the calculated shifts. Yet, the fact that the biggest deviation was found for HI molecule can indicate that we might slightly overestimate spin-orbit effects due to the neglect of spin-other-orbit (Gaunt) terms in our treatment of the spin-orbit operator. As it follows from our experience with calculations of spin-orbit corrections to chemical shifts and calculations of g-tensor (see Ref. 48), for light elements the contribution of the spin-other-orbit term might be of about 25%–30% of the total value of the two-electron spin-orbit terms and thus accounts for about 5%–10% of overall spin-orbit effect (see extended discussion of related questions in Refs. 48–50 and cited therein). Certainly, many other aspects, such as neglect of rovibration corrections and the limited accuracy of the used exchange-correlation DFT functionals, play a significant role too. However, their study lies outside of the scope of the present paper.

The simple tests considered above demonstrate the seriousness of the gauge-dependence problem in relativistic calculations: the use of special approaches (like GIAO, IGLO, and similar) to overcome the problem is, at least, as compulsory as it is in nonrelativistic calculations. Of course, employment of special approaches makes computational methods more complicated for realization. In particular, the use of GIAO in the framework of the mDKS-RMB method requires implementation of new integrals as it can be clearly seen, for example, from comparison Eq. (27) in Ref. 13 with Eq. (21c). While at present, most of those integrals we calculate

using a numerical integration (as it is typical in DFT) we are working on a new implementation that would include analytical evaluation of GIAO integrals.

In examples considered above the effect of adding basis and/or fitting functions with higher angular momentum was studied. Such increase in the basis had a negligible effect on the GIAO results. This demonstrates that the use of RMB approach in combination with LAO basis significantly reduces the basis set dependence of shielding tensors in fully relativistic calculations in contrast with methods employing unrestricted kinetic balance.²⁵

V. CONCLUSIONS

In this work we developed a new method for fully relativistic calculation of NMR shielding tensor using the concept of RMB and GIAO formalism. We demonstrated that the RMB condition and the GIAO approach are compatible. The mDKS-RMB method that employs the GIAO was developed and implemented into the MAG module of the ReSpect package. The mDKS-RMB GIAO method was successfully applied for calculations of the NMR shielding tensors in hydrogen halides and xenon dimer. This work demonstrates the importance of a proper treatment of gauge-origin problem in the relativistic calculations of the NMR shielding.

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