# A fully relativistic method for calculation of nuclear magnetic shielding tensors with a restricted magnetically balanced basis in the framework of the matrix Dirac–Kohn–Sham equation[a)]

Stanislav Komorovský,[1] Michal Repiský,[1] Olga L. Malkina,[1] Vladimir G. Malkin,[1,b)]
Irina Malkin Ondík,[2] and Martin Kaupp[3]
[1]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-84536, Bratislava, Slovak Republic*
[2]*Laboratory of Physical Chemistry, ETH Zurich, Wolfgang-Pauli-Str. 10, CH-8093 Zurich, Switzerland*
[3]*Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany*

(Received 26 September 2007; accepted 2 January 2008; published online 10 March 2008)

A new relativistic four-component density functional approach for calculations of NMR shielding tensors has been developed and implemented. It is founded on the matrix formulation of the Dirac–Kohn–Sham (DKS) method. Initially, unperturbed equations are solved with the use of a restricted kinetically balanced basis set for the small component. The second-order coupled perturbed DKS method is then based on the use of restricted magnetically balanced basis sets for the small component. Benchmark relativistic calculations have been carried out for the $^{1}$H and heavy-atom nuclear shielding tensors of the H*X* series (*X*=F,Cl,Br,I), where spin-orbit effects are known to be very pronounced. The restricted magnetically balanced basis set allows us to avoid additional approximations and/or strong basis set dependence which arises in some related approaches. The method provides an attractive alternative to existing approximate two-component methods with transformed Hamiltonians for relativistic calculations of chemical shifts and spin-spin coupling constants of heavy-atom systems. In particular, no picture-change effects arise in property calculations. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2837472]

## I. INTRODUCTION

The calculation of NMR chemical shifts and spin-spin coupling constants by *ab initio* methods and, in particular, by density functional theory (DFT) approaches has become a routine tool in many fields of chemistry, biochemistry, and materials research (for overviews, see, e.g., Refs. 1 and 2). While the majority of the applications involves calculations of $^{1}$H, $^{13}$C, and $^{15/14}$N chemical shifts, e.g., in organic molecules, interest in theoretical prediction of the NMR parameters for compounds containing heavy elements has also grown. Adequate theoretical modeling of such systems is known to require the inclusion of relativistic effects[3–8] (spin-orbit effects may already be noticeable even in the presence of surprisingly light atoms such as chlorine substituents[9] or 3*d* transition-metal centers[10]). Methodologies reported to date range all the way from four- or two-component relativistic methods to perturbational treatments of spin-orbit coupling. While the latter types of methods are computationally less expensive, they cease to be applicable for systems with very heavy atoms. Fully relativistic methods in turn tend to be computationally more expensive and not applicable to very large systems. There is thus still substantial need for adequate relativistic methodology that may be applied to larger, chemically relevant systems.

Recently we showed that the four-component Dirac–Kohn–Sham (DKS) equations may be solved effectively in two-component fashion with explicit treatment of the small component using the matrix formulation of the DKS equations [which is equivalent to the use of resolution of identity (RI) techniques], based on a restricted kinetically balanced basis for the small component (RKB). The approach was termed DKS2-RI method.[11] Related approaches, based on the idea of Heully *et al.* of state-universal transformation,[12] were developed and implemented.[13–15] Since these methods account for the small component, they form an excellent basis for relativistic calculations of NMR and EPR parameters, as no problems arise with picture change. The DKS2-RI method has already been employed for relativistic calculations of EPR parameters (*g*- and hyperfine tensors) as first-order properties.[11]

For calculations of magnetic second-order properties (such as NMR shielding tensors or indirect nuclear spin-spin coupling tensors) 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. In DFT approaches, the vacant molecular orbitals (MOs) are thus required. In relativistic calculations the existence of negative-energy states complicates matters. These negative-energy states are essential for obtaining accurate results in four-component calculations, and they are often associated with the diamagnetic term (as it is called in the nonrelativistic limit, the Ramsey equations[16] in case of nuclear shield-

[a)]This work was initially presented on the *Relativistic Effects in Heavy Element Chemistry and Physics Conference* (REHE-2007), Domaine Saint-Jacques, Ottrott, France, 21–25 March 2007.
[b)]Author to whom correspondence should be addressed. Electronic mail: vladimir.malkin@savba.sk.

 

ings or spin-spin couplings)—cf. Ref. 17 for a thorough discussion. The negative-energy states are discarded in two-component approaches. Here we therefore reformulate the DKS2-RI approach in a four-component manner, henceforth termed matrix Dirac–Kohn–Sham method (mDKS-RKB; the extension RKB stresses use of restricted kinetic balance in the absence of magnetic fields). We find the elimination of the small component not to be essential, whereas the use of the resolution of identity (or matrix representation of the DKS equations) is more crucial for an efficient method. For calculations of ground-state properties, mDKS-RKB and DKS2-RI methods are essentially equivalent.

As mentioned above, the proper description of negative-energy states is important. This requires an adequate basis set for the small component. However, the choice of the basis for the small component for a system in the presence of a magnetic field is not trivial since exact relations between the large and small components involve now field-dependent operators. Among other solutions for this problem, the use of restricted or unrestricted kinetically balanced basis sets has been considered.[18–21] Use of the former is straightforward for calculations of NMR shieldings but leads to an error of the order $O(c^0)$. Normally, no explicit diamagnetic term appears then. Reasonable results can be obtained with very large basis sets (including orbitals with high angular momentum).[18] This problem can be reduced significantly by making clever use of resolution of identity which allows one to express the major part of the diamagnetic term as an expectation value over the occupied MOs.[19] This method gives an overall error of the order $O(c^{-2})$. The choice of an unrestricted kinetically balanced basis gives better flexibility in describing the response of the MOs but also leads to larger basis sets in molecular calculations, to problems with near-linear dependencies and other complications.[20]

As a possible solution, the basis for the small component may be made to depend on the magnetic field. For a system in the presence of a magnetic field it is common to use the principle of minimal coupling, that is, to replace $\vec{p}$ by $\vec{\pi}=\vec{p}+(1/c)\vec{A}$. Thus, the $\vec{\sigma}\cdot\vec{p}$ basis (the "restricted kinetically balanced basis set") for the small component should be replaced by a $\vec{\sigma}\cdot\vec{\pi}$ basis ("restricted magnetically balanced basis set"). Stanton and Havriliak[22] showed that in the absence of a magnetic field the use of restricted kinetic balance improves the variational stability to $O(c^{-4})$. By simple generalization of this proof for the case with magnetic field, one obtains the same result for a restricted magnetically balanced (RMB) basis set. A magnetically balanced basis was already suggested by Aucar *et al.*[19] and by Kutzelnigg,[17] and discussed in Ref. 21, but up to now there have been no rigorous implementations of the idea. Thus, it was the central line of our present work to develop and implement a method for calculation of second-order magnetic properties using a RMB basis set. A related development by Xiao *et al.*[23] is the orbital decomposition approach (ODA). Since this is the first such attempt, we will discuss carefully the ODA method and analyze its relation to the method proposed in this work. Another alternative approach to reduce the importance of the negative-energy states was suggested by Kutzelnigg[17] and implemented by Xiao *et al.* (termed "external field-dependent unitary transformation").[23]

We will first describe our approach for solving the four-component Dirac–Kohn–Sham equations using a RKB basis set (mDKS-RKB approach) for the system in the absence of magnetic fields (Sec. II). Then extension will be made to calculation of second-order magnetic properties, with emphasis on nuclear shieldings. In contrast to previous work, we will use RMB to tackle the problem. The basic equations and the corresponding discussion are presented in Sec. III–VI. Computational details are described in Sec. VII. Some pilot benchmark calculations of nuclear shieldings will be discussed in Sec. VIII, and conclusions in Sec. IX.

## II. MATRIX DIRAC–KOHN–SHAM METHOD USING A RESTRICTED KINETICALLY BALANCED BASIS

The idea of the modified Dirac equation was first proposed by Kutzelnigg[24] and examined in detail by Dyall.[25] The four-component Dirac–Kohn–Sham method using a RKB basis leads to the DFT analog of the modified Dirac equation, as first pointed out by Kutzelnigg and Liu.[26] Our implementation is based on the matrix representation of the DKS four-component method and use of the RKB basis for the small component. It further involves unrestricted noncollinear spin density functional methodology.

Throughout this paper we use the Hartree system of atomic units. Summation over repeated indices is assumed, and the following index notation is employed: $i,j$ denote occupied positive energy orbitals, $a$ unoccupied positive- and negative-energy orbitals, $p,q$ all positive- and negative-energy orbitals, and $\lambda,\tau$ are atomic orbital indices. We will use subscripts $2\times2$ and $4\times4$ to stress that the corresponding matrices are two- and four-component, respectively.

We shall start the description of our approach with a general formulation of the Dirac–Kohn–Sham equations for the case of a nonrelativistic local density approximation (LDA) or generalized gradient approximation (GGA) functional as follows:

$$(D_{\mathrm{kin}}+V_{4\times4})\varphi_i=\varepsilon_i\varphi_i,$$

$$D_{\mathrm{kin}}\equiv(\beta-1_{4\times4})c^2+c\vec{\alpha}\cdot\vec{p},\quad V_{4\times4}\equiv\begin{pmatrix}V_{2\times2} & 0_{2\times2}\\ 0_{2\times2} & V_{2\times2}\end{pmatrix}. \tag{1}$$

Here $\varepsilon_i$ is a one-electron energy, $\varphi_i^L$ and $\varphi_i^S$ are the large and the small components of the four-component $i$th molecular orbital $\varphi_i$, $c$ is the speed of light, $\vec{p}$ is the momentum operator $\vec{p}=-i\vec{\nabla}$, matrices $\vec{\alpha}$ and $\beta$ have the usual form

$$\alpha_l=\begin{pmatrix}0 & \sigma_l\\ \sigma_l & 0\end{pmatrix},\quad l=1,2,3,\quad \beta=\begin{pmatrix}1_{2\times2} & 0\\ 0 & -1_{2\times2}\end{pmatrix},$$

and $\vec{\sigma}$ and $1_{2\times2}$ are the vector composed of Pauli matrices and the identity matrix, respectively,

$$\sigma_1=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad \sigma_2=\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},$$

$$\sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad 1_{2\times 2} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

The potential $V_{2\times 2}$ has the form $V_{2\times 2} \equiv V_{\mathrm{nuc}} + V_{\mathrm{ee}} + V_{\mathrm{xc}}$ (the nuclear Coulomb potential $V_{\mathrm{nuc}}$, the Coulomb electron-electron repulsion potential $V_{\mathrm{ee}}$, and the exchange-correlation potential $V_{\mathrm{xc}}$),

$$V_{2\times 2} \equiv -\sum_M \frac{Z_M}{r_M} 1_{2\times 2} + \int \frac{\rho_0(\vec{r}')}{|\vec{r}-\vec{r}'|} dV' 1_{2\times 2} + \frac{\delta E_{\mathrm{xc}}[\rho_k]}{\delta \rho_k(\vec{r})} \sigma_k, \quad k = 0,x,y,z, \tag{2}$$

where $\vec{r}$ is the position vector, $\vec{r}_M = \vec{r} - \vec{R}_M$, $\vec{R}_M$ and $Z_M$ are position and charge of the $M$th nucleus, $E_{\mathrm{xc}}$ is the Kohn–Sham exchange-correlation energy, and $\rho_k$ represents the relativistic electron density ($k=0$) and three spin densities ($k=x,y,z$)

$$\rho_k \equiv \varphi_i^\dagger \Sigma_k \varphi_i, \quad \Sigma_0 \equiv 1_{4\times 4}, \quad \Sigma_l \equiv \begin{pmatrix} \sigma_l & 0_{2\times 2} \\ 0_{2\times 2} & \sigma_l \end{pmatrix}, \quad l = x,y,z. \tag{3}$$

It should be noted that the exchange-correlation part $V_{\mathrm{xc}}$ of the potential $V_{2\times 2}$ is implemented in "noncollinear" fashion,[27,28] resulting in nonzero contributions from $V_{\mathrm{xc}}$ to all $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ blocks of the two-component $V_{2\times 2}$ matrices for the large-large and the small-small blocks of the DKS operator in Eq. (1) (in contrast to the "collinear" potential widely used in many relativistic programs, which contributes to the $\alpha\alpha$ and $\beta\beta$ blocks only). On the other hand, we do not employ relativistic current-dependent exchange-correlation functionals, and the nonrelativistic electron-electron and electron-nucleus Coulomb interaction is assumed.

We will use a RKB basis set[24] constructed from Gaussian atomic orbitals. Then the large and the small components are expressed as

$$\varphi_i^L = \mathbf{C}_{\lambda i}^L \chi_\lambda, \tag{4a}$$

$$\varphi_i^S = \mathbf{C}_{\lambda i}^S \frac{1}{2c} \vec{\sigma}\cdot\vec{p}\chi_\lambda, \tag{4b}$$

respectively, where $\chi_\lambda$ is $\lambda$th atomic orbital (AO). Importantly, the variational instability with a finite RKB basis set is only of order $O(c^{-4})$, while use of an arbitrary (i.e., kinetically unbalanced) basis set may result in errors of $O(c^0)$.[22] The frequently used and unrestricted kinetically balanced basis set leads to additional complications such as large size of the matrices and possible near linear dependence of the basis (see Refs. 20 and 29 for more details).

In the following, we will keep subscript $(p)$ in order to stress that $\mathbf{C}_{(p)}$ are coefficients for the $p$th MO (together with the assumption of the summation over the repeated indices, thus simplifying the expressions for the scalar products). Using restricted kinetic balance [Eqs. (4a) and (4b)] and switching to matrix formulation, we can write Eq. (1) as

$$\begin{pmatrix} \mathbf{V} & \mathbf{T} \\ \mathbf{T} & (1/4c^2)\mathbf{W} - \mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix} = \varepsilon_i \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & (1/2c^2)\mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix}, \tag{5}$$

where

$$\mathbf{V}_{\lambda\tau} \equiv \langle \chi_\lambda | V_{2\times 2} | \chi_\tau \rangle, \quad \mathbf{W}_{\lambda\tau} \equiv \langle \vec{\sigma}\cdot\vec{p}\chi_\lambda | V_{2\times 2} | \vec{\sigma}\cdot\vec{p}\chi_\tau \rangle, \tag{6a}$$

$$\mathbf{S}_{\lambda\tau} \equiv \langle \chi_\lambda | 1_{2\times 2} | \chi_\tau \rangle, \quad \mathbf{T}_{\lambda\tau} \equiv \tfrac{1}{2}\langle \chi_\lambda | p^2 1_{2\times 2} | \chi_\tau \rangle. \tag{6b}$$

The Dirac–Kohn–Sham total energy can be written as

$$E = \langle \varphi_i | D_{\mathrm{kin}} | \varphi_i \rangle + E_{\mathrm{pot}}, \tag{7a}$$

$$E_{\mathrm{pot}} \equiv \langle \varphi_i^L | E_{2\times 2} | \varphi_i^L \rangle + \langle \varphi_i^S | E_{2\times 2} | \varphi_i^S \rangle, \tag{7b}$$

$$E_{2\times 2} \equiv -\sum_M \frac{Z_M}{r_M} 1_{2\times 2} + \frac{1}{2}\int \frac{\rho_0(\vec{r}')}{|\vec{r}-\vec{r}'|} dV' 1_{2\times 2} + (\varepsilon_{\mathrm{xc}}[\rho_k])_{2\times 2}, \quad k = 0,x,y,z, \tag{7c}$$

where $E_{2\times 2}$ is the energy operator and $(\varepsilon_{\mathrm{xc}}[\rho_k])_{2\times 2}$ is the exchange-correlation energy density. Now we use again restricted kinetic balance [Eqs. (4a) and (4b)] to obtain an expression for the total energy in terms of the MO coefficients,

$$E = (\mathbf{C}_{(i)}^{L\dagger}\ \mathbf{C}_{(i)}^{S\dagger}) \begin{pmatrix} \mathbf{E} & \mathbf{T} \\ \mathbf{T} & (1/4c^2)\bar{\mathbf{E}} - \mathbf{T} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix}, \tag{8}$$

where

$$\mathbf{E}_{\lambda\tau} \equiv \langle \chi_\lambda | E_{2\times 2} | \chi_\tau \rangle, \quad \bar{\mathbf{E}}_{\lambda\tau} \equiv \langle \vec{\sigma}\cdot\vec{p}\chi_\lambda | E_{2\times 2} | \vec{\sigma}\cdot\vec{p}\chi_\tau \rangle. \tag{9}$$

Equations (5), (6a), (6b), (7a)–(7c), (8), and (9) provide the basis for the mDKS-RKB approach. No new types of integrals appear in comparison with the previous two-component DKS2-RI approach.[11] That is, no extra efforts arise in the evaluation of the Fock matrix. In DKS2-RI, the two-component Fock matrix has to be diagonalized separately for every occupied orbital, whereas in mDKS-RKB, the four-component Fock matrix has to be diagonalized, but only once. This has actually computational advantages for large systems. Note that mDKS-RKB is fully equivalent to the original Dirac–Kohn–Sham method in the limit of a complete basis set, and thus it is gauge invariant with respect to the electrostatic potential [in contrast to methods such as zeroth order regular approximation (ZORA)].

## III. CALCULATION OF NUCLEAR MAGNETIC SHIELDINGS USING A RESTRICTED MAGNETICALLY BALANCED BASIS (mDKS-RMB)

Calculations of shielding tensors (or of other second-order magnetic properties) require adequate inclusion of a magnetic field. Several crucial points have already been discussed previously.[8,17,19,20,23] However, we decided to explore a new route connected with the introduction of the RMB basis set. We consider this a natural extension of the restricted kinetic balance for systems in the presence of a magnetic field. In the following, all the entities carrying (0,0) or

00 superscripts are identical with the corresponding counterparts without the superscripts in the previous section.

We start with the expression for the total energy in the presence of magnetic fields (an external uniform magnetic field and the magnetic field due to the magnetic moment of a nucleus) within the framework of the four-component Dirac–Kohn–Sham approach. Using the principle of minimal coupling, the total energy can be written as

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

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

$$D^{10} \equiv \vec{\alpha}\cdot\vec{A}_{\vec{B}}, \tag{10b}$$

$$D^{01} \equiv \vec{\alpha}\cdot\vec{A}_{\vec{\mu}^M},$$

$$E_{\mathrm{pot}}^{(\vec{B},\vec{\mu}^M)} \equiv \langle \varphi_i^{L(\vec{B},\vec{\mu}^M)} | E_{2\times 2}^{(\vec{B},\vec{\mu}^M)} | \varphi_i^{L(\vec{B},\vec{\mu}^M)} \rangle + \langle \varphi_i^{S(\vec{B},\vec{\mu}^M)} | E_{2\times 2}^{(\vec{B},\vec{\mu}^M)} | \varphi_i^{S(\vec{B},\vec{\mu}^M)} \rangle, \tag{10c}$$

where $\varphi_i^{(\vec{B},\vec{\mu}^M)}$ is the four-component occupied $i$th MO in the presence of external uniform magnetic field $\vec{B}$ and nuclear magnetic moment $\vec{\mu}^M$ of the $M$th nucleus. We choose the corresponding vector potentials as

$$\vec{A}_{\vec{B}} = \tfrac{1}{2}(\vec{B}\times\vec{r}_G), \quad \vec{r}_G = \vec{r} - \vec{r}_0, \tag{11a}$$

$$\vec{A}_{\vec{\mu}^M} = \frac{\vec{\mu}^M \times \vec{r}_M}{r_M^3}, \quad \vec{r}_M = \vec{r} - \vec{R}_M. \tag{11b}$$

Here $\vec{r}_0$ is an arbitrary fixed gauge origin and $\vec{R}_M$ is the position of the $M$th nucleus.

The key point in the calculation of second-order properties is to obtain the linear response of the molecular orbitals due to a perturbation. We start with the Taylor expansion of the $i$th four-component MO

$$\varphi_i^{(\vec{B},\vec{\mu}^M)} = \varphi_i^{(0,0)} + \varphi_i^{(1,0)_u} B_u + \varphi_i^{(0,1)_v^M} \mu_v^M + \cdots, \tag{12}$$

where

$$\varphi_i^{(1,0)_u} \equiv \partial_{B_u}(\varphi_i^{(\vec{B},\vec{\mu}^M)})\big|_{\vec{B},\vec{\mu}^M=0},$$

$$\varphi_i^{(0,1)_v^M} \equiv \partial_{\mu_v^M}(\varphi_i^{(\vec{B},\vec{\mu}^M)})\big|_{\vec{B},\vec{\mu}^M=0}.$$

From now on, superscripts (0,0), $(1,0)_u$, and $(0,1)_v^M$ indicate the dependences of the MOs, MO coefficients, operators, and so on, on the external magnetic field $B_u$ and nuclear magnetic moment $\mu_v^M$, respectively. For example, $(1,0)_u$ means a term which is linear with respect to the "$u$th" component of the external magnetic field and independent of the field due to the magnetic moment of nucleus $M$.

To evaluate the above mentioned derivatives, one has to specify the dependence of the four-component MOs on the magnetic fields. Following Kutzelnigg[17] and Aucar *et al.*[19] we will introduce an explicit dependence of our basis on the magnetic fields. However, we will use here (learning from the arguments of Stanton and Havriliak[22]) the restricted magnetic balance defined as a fixed sum of RKB and magnetic field dependent term as

$$\varphi_i^{L(\vec{B},\vec{\mu}^M)} = \mathbf{C}_{\lambda i}^{L(\vec{B},\vec{\mu}^M)} \chi_\lambda, \tag{13a}$$

$$\varphi_i^{S(\vec{B},\vec{\mu}^M)} = \mathbf{C}_{\lambda i}^{S(\vec{B},\vec{\mu}^M)} \chi_\lambda^{S(\vec{B},\vec{\mu}^M)}. \tag{13b}$$

Here the basis function for the small component $\chi_\lambda^{S(\vec{B},\vec{\mu}^M)}$ depends explicitly on the magnetic fields

$$\chi_\lambda^{S(\vec{B},\vec{\mu}^M)} \equiv \frac{1}{2c}\left(\vec{\sigma}\cdot\vec{p} + \frac{1}{c}\vec{\sigma}\cdot\vec{A}_{\vec{B}} + \frac{1}{c}\vec{\sigma}\cdot\vec{A}_{\vec{\mu}^M}\right)\chi_\lambda, \tag{14}$$

whereas the basis function for the large component $\chi_\lambda$ remains independent of both perturbations. Thus the four-component molecular orbital depends on the magnetic fields via both MO coefficients and basis functions

$$\varphi_i^{(\vec{B},\vec{\mu}^M)} = \mathbf{C}_{\lambda i}^{(\vec{B},\vec{\mu}^M)} \chi_\lambda^{(\vec{B},\vec{\mu}^M)}. \tag{15}$$

Since we are looking for a second-order property (nuclear shielding) the use of Dalgarno's exchange theorem[30] allows us to choose with respect to which magnetic field the linear response of MOs is expressed. Visscher *et al.*[31] used the magnetic moment of a nucleus as the primary perturbation parameter since the nuclear shielding of that nucleus and the spin-spin coupling constants (of this nucleus with all others) may then be calculated in one shot. In nonrelativistic calculations, it is customary to choose the external uniform magnetic field as the primary perturbation, as then all shielding tensors are obtained at once. We will use this latter option and will search for the linear response of the MOs to the external magnetic field $\varphi_i^{(1,0)_u}$ [for $\varphi_i^{(0,1)_v^M}$ analogous expressions can be obtained].

Due to the dependence of the four-component MOs on the external magnetic field via both MO coefficients and basis function [see Eq. (15)], their linear response reads

$$\varphi_i^{(1,0)_u} = \mathbf{C}_{\lambda i}^{(1,0)_u} \chi_\lambda^{(0,0)} + \mathbf{C}_{\lambda i}^{(0,0)} \chi_\lambda^{(1,0)_u} \equiv \varphi_i^{r(1,0)_u} + \varphi_i^{m(1,0)_u}, \tag{16}$$

where regular $\varphi_i^{r(1,0)_u}$ and magnetic $\varphi_i^{m(1,0)_u}$ parts in two-component notation are

$$\varphi_i^{r(1,0)_u} = \begin{pmatrix} \mathbf{C}_{\lambda i}^{L(1,0)_u}\chi_\lambda \\ \mathbf{C}_{\lambda i}^{S(1,0)_u}\chi_\lambda^{S(0,0)} \end{pmatrix}, \quad \varphi_i^{m(1,0)_u} = \begin{pmatrix} \mathbf{0} \\ \mathbf{C}_{\lambda i}^{S(0,0)}\chi_\lambda^{S(1,0)_u} \end{pmatrix} \tag{17a}$$

and

$$\chi_\lambda^{S(0,0)} \equiv \frac{1}{2c}\vec{\sigma}\cdot\vec{p}\chi_\lambda, \quad \chi_\lambda^{S(1,0)_u} \equiv \frac{1}{4c^2}(\vec{r}_G\times\vec{\sigma})_u\chi_\lambda. \tag{17b}$$

These expressions emphasize the fact that the linear response of MOs is composed of two parts: $\varphi_i^{r(1,0)_u}$ and $\varphi_i^{m(1,0)_u}$. The first one depends on the magnetic field only via the MO coefficients, whereas the second part contains unperturbed MO coefficients and the dependence on the magnetic field comes via explicit field-dependent basis functions for the small component. This is analogous to the use of the gauge including atomic orbitals[32] (GIAO) or individual

gauge for localized orbitals[33] (IGLO) approaches at the nonrelativistic level (due to the use of atomic or molecular orbitals with explicit field dependence). Let us emphasize here that this is only a formal similarity due to the use of field-dependent basis and that our approach at this stage does not provide invariance with respect to the choice of gauge origin for a finite basis.

Since the unperturbed (field-free) atomic orbital basis covers the same space as the unperturbed MOs, we can go further and express the first term in Eq. (17a) in the basis of the unperturbed molecular orbitals,

$$\varphi_i^{r(1,0)_u} = \mathbf{C}_{\lambda i}^{(1,0)_u} \chi_\lambda^{(0,0)} = \boldsymbol{\beta}_{pi}^{B_u} \varphi_p^{(0,0)}, \tag{18}$$

where index $p$ denotes occupied positive energy MOs as well as unoccupied positive- and all negative-energy MOs. Here $\boldsymbol{\beta}_{pi}^{B_u}$ are the usual linear-response expansion coefficients of the perturbed MOs in the basis of the unperturbed MOs. The second ("magnetic") term, $\varphi_i^{m(1,0)_u}$ in Eq. (17a), arises as a consequence of the magnetically balanced basis set used here and it does not contain unknown coefficients.

The bilinear derivatives of the energy, Eqs. (10a)–(10c), with respect to the parameters $B_u$ and $\mu_v^M$, may be expressed as [derivation of Eq. (19) is given in Appendix A]

$$\left.\frac{d^2E(\vec{B},\vec{\mu}^M)}{dB_u d\mu_v^M}\right|_{B_u,\mu_v^M=0} = \langle \varphi_i^{(1,0)_u} | D^{(0,1)_v^M} | \varphi_i^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | D^{(0,1)_v^M} | \varphi_i^{(1,0)_u} \rangle. \tag{19}$$

As expected, the nonrelativistic diamagnetic term in its standard form (an expectation value over the occupied positive-energy MOs of an operator bilinear with respect to parameters $B_u$ and $\mu_v^M$) is "missing." However, the use of restricted magnetic balance allows one to recover the term naturally as will be shown below. By substituting Eqs. (17a) and (18) into Eq. (19), we arrive at the final expression for the shielding tensor as follows:

$$\sigma_{uv} = \left.\frac{d^2E(\vec{B},\vec{\mu}^M)}{dB_u d\mu_v^M}\right|_{\vec{B},\vec{\mu}^M=0} \equiv \sigma_{uv}^D + \sigma_{uv}^{P0} + \sigma_{uv}^{P1}, \tag{20}$$

$$\sigma_{uv}^D = \langle \varphi_i^{m(1,0)_u} | D^{(0,1)_v^M} | \varphi_i^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | D^{(0,1)_v^M} | \varphi_i^{m(1,0)_u} \rangle, \tag{21a}$$

$$\sigma_{uv}^{P0} = (\boldsymbol{\beta}_{ji}^{B_u})^* \langle \varphi_j^{(0,0)} | D^{(0,1)_v^M} | \varphi_i^{(0,0)} \rangle + \boldsymbol{\beta}_{ji}^{B_u} \langle \varphi_i^{(0,0)} | D^{(0,1)_v^M} | \varphi_j^{(0,0)} \rangle, \tag{21b}$$

$$\sigma_{uv}^{P1} = (\boldsymbol{\beta}_{ai}^{B_u})^* \langle \varphi_a^{(0,0)} | D^{(0,1)_v^M} | \varphi_i^{(0,0)} \rangle + \boldsymbol{\beta}_{ai}^{B_u} \langle \varphi_i^{(0,0)} | D^{(0,1)_v^M} | \varphi_a^{(0,0)} \rangle. \tag{21c}$$

In the nonrelativistic limit, $\sigma_{uv}^D$ turns into the classical diamagnetic term, $\sigma_{uv}^{P0}$ vanishes, and $\sigma_{uv}^{P1}$ becomes the standard paramagnetic contribution with summation only over unoccupied positive-energy MOs. The separation and notation of the terms is done by analogy with the nonrelativistic GIAO approach: The $P0$ term sums only over occupied positive-energy MOs $j$ and arises due to the explicit dependence of the basis set on the magnetic field. $P1$ is a (paramagnetic) term typical for second-order perturbation theory. It involves summation over virtual positive- and negative-energy MOs $a$.

By substituting Eqs. (4a) and (4b) and the second equation in Eq. (17a) into the above equations for the shielding tensor we obtain the final expressions via the unperturbed MO coefficients and the linear-response coefficients $\boldsymbol{\beta}_{pi}^{B_u}$ [below we will use the shorthand notations $\mathbf{C}_{(i)}^{L(0,0)} = \mathbf{C}_{(i)}^L$ and $\mathbf{C}_{(i)}^{S(0,0)} = \mathbf{C}_{(i)}^S$ for simplicity]

$$\sigma_{uv}^D = \frac{1}{4c^2} (\mathbf{C}_{(i)}^{L\dagger}\ \mathbf{C}_{(i)}^{S\dagger}) \begin{pmatrix} \mathbf{0} & \boldsymbol{\Lambda}_{B_u\mu_v^M}^{D\dagger} \\ \boldsymbol{\Lambda}_{B_u\mu_v^M}^{D} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^L \\ \mathbf{C}_{(i)}^S \end{pmatrix}, \tag{22a}$$

$$\sigma_{uv}^{P0} = \frac{1}{2c} [(\boldsymbol{\beta}_{ij}^{B_u})^* + \boldsymbol{\beta}_{ji}^{B_u}] (\mathbf{C}_{(i)}^{L\dagger}\ \mathbf{C}_{(i)}^{S\dagger}) \begin{pmatrix} \mathbf{0} & \boldsymbol{\Lambda}_{\mu_v^M}^{P\dagger} \\ \boldsymbol{\Lambda}_{\mu_v^M}^{P} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(j)}^L \\ \mathbf{C}_{(j)}^S \end{pmatrix}, \tag{22b}$$

$$\sigma_{uv}^{P1} = \frac{1}{c} \mathrm{Re} \left[ \boldsymbol{\beta}_{ai}^{B_u} (\mathbf{C}_{(i)}^{L\dagger}\ \mathbf{C}_{(i)}^{S\dagger}) \begin{pmatrix} \mathbf{0} & \boldsymbol{\Lambda}_{\mu_v^M}^{P\dagger} \\ \boldsymbol{\Lambda}_{\mu_v^M}^{P} & \mathbf{0} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(a)}^L \\ \mathbf{C}_{(a)}^S \end{pmatrix} \right], \tag{22c}$$

where

$$(\boldsymbol{\Lambda}_{B_u\mu_v^M}^D)_{\lambda\tau} \equiv \left\langle \chi_\lambda \left| \delta_{uv} \frac{\vec{r}_G \cdot \vec{r}_M}{r_M^3} - \frac{(\vec{r}_G)_v (\vec{r}_M)_u}{r_M^3} + i\sigma_v \frac{(\vec{r}_G \times \vec{r}_M)_u}{r_M^3} - i\varepsilon_{vuk} (\vec{r}_G)_k \frac{\vec{\sigma} \cdot \vec{r}_M}{r_M^3} \right| \chi_\tau \right\rangle, \tag{23a}$$

$$(\boldsymbol{\Lambda}_{\mu_v^M}^P)_{\lambda\tau} \equiv \left\langle \chi_\lambda \left| \vec{\sigma} \cdot \vec{p} \left( \frac{\vec{r}_M \times \vec{\sigma}}{r_M^3} \right)_v \right| \chi_\tau \right\rangle. \tag{23b}$$

Here we should note a few points: First, the unperturbed MO coefficients $\mathbf{C}_{(i)}^L$ and $\mathbf{C}_{(i)}^S$ can be obtained [Eq. (5)] during one self-consistent-field (SCF) procedure. Second, in the nonrelativistic limit the first two terms in Eq. (23a) recover the classical diamagnetic term. Third, the term in Eq. (23b) has to be treated with special care: its direct evaluation leads to an expression which contains terms such as the nonrelativistic Fermi contact or spin-dipolar operators. It is well known that use of such operators in relativistic calculations may give rise to numerical problems. However, a well-known way to avoid computational difficulties with similar operators is to use the turnover rule.[11,34,35]

Let us now come to the equations for evaluation of the $\boldsymbol{\beta}_{pi}^{B_u}$ coefficients. The expression for the coefficients of the occupied molecular orbitals can be derived from the normalization condition as shown in Appendix B. The $\boldsymbol{\beta}_{pi}^{B_u}$ coefficients for the unoccupied molecular orbitals (both positive and negative-energy MOs) can be obtained by perturbation theory (see Appendix C for more details). The final expression for the $\boldsymbol{\beta}_{pi}^{B_u}$ coefficients is

$$(\boldsymbol{\beta}_{ij}^{B_u})^* + \boldsymbol{\beta}_{ji}^{B_u} = \frac{1}{2c}(\mathbf{C}_{(j)}^{L\dagger}\ \mathbf{C}_{(j)}^{S\dagger})\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & -(1/2c^2)\tilde{\mathbf{\Lambda}}_{B_u}^{P}\end{pmatrix}\begin{pmatrix}\mathbf{C}_{(i)}^{L}\\ \mathbf{C}_{(i)}^{S}\end{pmatrix}, \tag{24}$$

$$\boldsymbol{\beta}_{ai}^{B_u} = \frac{1}{2c}\frac{1}{\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)}}(\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\begin{pmatrix}2c\mathbf{V}' & \tilde{\mathbf{\Lambda}}_{B_u}^{P}\\ \tilde{\mathbf{\Lambda}}_{B_u}^{P} & (1/4c^2)\mathbf{W}_{B_u} - \tilde{\mathbf{\Lambda}}_{B_u}^{P} - (\varepsilon_i^{(0,0)}/2c^2)\tilde{\mathbf{\Lambda}}_{B_u}^{P} + (1/2c)\mathbf{W}'\end{pmatrix}\begin{pmatrix}\mathbf{C}_{(i)}^{L}\\ \mathbf{C}_{(i)}^{S}\end{pmatrix}, \tag{25}$$

where $\boldsymbol{\beta}_{ji}^{B_u}$ and $\boldsymbol{\beta}_{ai}^{B_u}$ are the linear-response coefficients for the occupied MOs $j$ and vacant MOs $a$; $\varepsilon_p^{(0,0)}$ are unperturbed one-electron energies,

$$(\tilde{\mathbf{\Lambda}}_{B_u}^{P})_{\lambda\tau} \equiv \langle\chi_\lambda|(\vec{r}_G \times \vec{p})_u + \sigma_u|\chi_\tau\rangle \tag{26}$$

is the matrix representation of the sum of the orbital and spin Zeeman operators, and

$$(\mathbf{W}_{B_u})_{\lambda\tau} \equiv \langle(\vec{r}_G \times \vec{\sigma})_u\chi_\lambda|V_{2\times2}^{(0,0)}|\vec{\sigma}\cdot\vec{p}\chi_\tau\rangle + \langle\vec{\sigma}\cdot\vec{p}\chi_\lambda|V_{2\times2}^{(0,0)}|(\vec{r}_G \times \vec{\sigma})_u\chi_\tau\rangle \tag{27}$$

is a pure relativistic contribution which depends on the unperturbed MO coefficients via the unperturbed potential $V_{2\times2}^{(0,0)}$. The terms $\mathbf{V}'$ and $\mathbf{W}'$

$$\mathbf{V}'_{\lambda\tau} \equiv \langle\chi_\lambda|O_{2\times2}^{(1,0)_u}|\chi_\tau\rangle, \quad \mathbf{W}'_{\lambda\tau} \equiv \langle\vec{\sigma}\cdot\vec{p}\chi_\lambda|O_{2\times2}^{(1,0)_u}|\vec{\sigma}\cdot\vec{p}\chi_\tau\rangle, \tag{28}$$

with

$$O_{2\times2}^{(1,0)_u} \equiv \int \frac{\delta(V_{\mathrm{ee}}^{(0,0)}(\vec{r}) + V_{\mathrm{xc}}^{(0,0)}(\vec{r}))}{\delta\rho_k^{(0,0)}(\vec{r}')}\rho_k^{(1,0)_u}(\vec{r}')dV', \tag{29a}$$

$$\rho_k^{(1,0)_u} = \varphi_i^{(1,0)_u\dagger}\Sigma_k\varphi_i^{(0,0)} + \varphi_i^{(0,0)\dagger}\Sigma_k\varphi_i^{(1,0)_u}, \tag{29b}$$

$(k=0,x,y,z)$, represent new coupling terms which are not present in nonrelativistic pure DFT equations (that is, when using local and multiplicative potentials as those arising from LDA or GGA functionals). In the present paper we consider only nonrelativistic exchange-correlation functionals dependent on $\rho_k$ and its derivatives. Our theory is easily extendable for a functional dependent also on current. In Eq. (29b) the symbol $\Sigma_k$ is the four-component matrix composed of Pauli matrices, as explained in Eq. (3).

The linear response of the density and spin density to the external magnetic field must be real (because density and spin density are measurable properties). On the other hand, in the nonrelativistic case the operator responsible for the interaction with an external magnetic field in a closed-shell electronic system only the orbital interaction with the external magnetic field remains and thus the corresponding operator is purely imaginary. The unperturbed wave function can always be chosen real. Therefore, the linear response of the density and spin density to the external magnetic field in the nonrelativistic case vanishes, and (for a closed-shell system) no coupling terms arise in linear-response theory in the absence of nonlocal operators (such as the nonlocal Hartree–Fock exchange potential), e.g., for LDA or GGA functionals. It is essential to note here that this does not hold anymore in the relativistic case, as the operators linear with respect to the magnetic field are now complex and the unperturbed wave function is also complex, due to the presence of spin-orbit interactions. The main contribution to the coupling terms comes from the exchange-correlation potential. Here we disagree with the following statement in Ref. 36: "…in the Kohn–Sham scheme with a pure density functional even $V_{\mathrm{resp}}^{01}$ vanishes because of no first-order response in the (closed-shell) density to the magnetic field." As will be discussed in Secs. V and VIII below, the coupling terms have an appreciable influence on the resulting shielding tensors.

The terms $\tilde{\mathbf{\Lambda}}_{B_u}^{P}$ and $\mathbf{W}_{B_u}$ together with the linear-response terms $\mathbf{V}'$ and $\mathbf{W}'$, account for the nonvanishing responses of the density and spin density. For example, looking at the contribution from the nuclear (leading) part of $V_{2\times2}^{(0,0)}$ to $\mathbf{W}_{B_u}$ in more detail, we obtain

$$(\mathbf{W}_{B_u}^{\mathrm{nuc}})_{\lambda\tau} \equiv -\sum_M Z_M\left\langle\chi_\lambda\left|\frac{2}{r_M}[(\vec{r}_G \times \vec{p})_u + \sigma_u] + \frac{(\vec{r}_G\cdot\vec{\sigma})}{r_M^3}(\vec{r}_M)_u - \frac{\vec{r}_G\cdot\vec{r}_M}{r_M^3}\sigma_u + i\frac{(\vec{r}_G \times \vec{r}_M)_u}{r_M^3}\right|\chi_\tau\right\rangle. \tag{30}$$

The expression for $\mathbf{W}_{B_u}^{\mathrm{nuc}}$ contains imaginary as well as real operators. Combined with the nonzero spin density arising from the spin-orbit effects, $\mathbf{W}_{B_u}^{\mathrm{nuc}}$ contributes to the linear response of MOs on the external magnetic field.

It is well known from experience with perturbational spin-orbit corrections to NMR chemical shifts[37] that one should not judge the relative importance of different operators by their formal order with respect to $c^{-1}$ alone: Sometimes terms of higher order may play important roles. That is, operators $\langle\chi_\lambda|2|r_M|^{-1}\sigma_u|\chi_\tau\rangle$ in Eq. (30) may not be neglected, even though they enter Eq. (25) for the coefficients $\boldsymbol{\beta}_{ai}^{B_u}$ with a prefactor of $c^{-2}$: The main contribution to this operator comes from the core region due to the dependence on $|r_M|^{-1}$. Moreover, the spin density is largest in the core region.

The approach presented above may be extended naturally to include a finite-size nuclear model, as should anyway be done for heavy atoms.[38] This would involve the use of finite nuclear charge and magnetic moment distributions. The model distribution function can be chosen in many different ways.[39] Recently we used a finite-size nuclear model in Douglas–Kroll–Hess[40] calculations of hyperfine structure.[41]

The finite distribution model for the nuclear magnetic moment operator was found to have a noticeable effect even when a finite nuclear-charge model had already been included in the ground-state calculation of the spin density[41] (note that charge and nuclear magnetic dipole moment distributions for a nucleus are not necessary the same function). While we did not use these finite distribution models in the present work, the extension is straightforward and currently in progress in our laboratory.

During presentation of the present work on a recent conference[42] we experienced a criticism concerning to the symmetry properties of the Hamiltonian: use of restricted magnetic balance in the form of Eq. (14) does not retain the symmetry of the unperturbed solution. It can be shown that $\vec{\sigma}\cdot\vec{p}$ and $\vec{\sigma}\cdot\vec{A}_{\vec{B}}$ generate states with different rotation symmetries. However, this is physically correct, as the magnetic perturbation lowers the symmetry of the system. Again, the analogy with the lowering of the symmetry by the use of London orbitals[32] in the GIAO approach may be invoked.

## IV. COMPARISON OF mDKS-RMB WITH METHODS BASED ON KINETICALLY BALANCED BASIS SETS

Until recently, only kinetically balanced basis sets (restricted or unrestricted) were used for calculations of second-order magnetic properties.[8,20] In this case, $\varphi_i^{(1,0)_u}$ does not contain the magnetic part $\varphi_i^{m(1,0)_u}$, and therefore the equations for the $\beta$ coefficients can be written (for RKB case) as

$$(\boldsymbol{\beta}_{ai}^{B_u})^{\mathrm{RKB}} = \frac{1}{2c}\frac{1}{\varepsilon_i^{(0,0)}-\varepsilon_a^{(0,0)}}(\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\begin{pmatrix}\mathbf{0} & \boldsymbol{\Lambda}_{B_u}^{P\dagger}\\ \boldsymbol{\Lambda}_{B_u}^{P} & \mathbf{0}\end{pmatrix}\times\begin{pmatrix}\mathbf{C}_{(i)}^{L}\\ \mathbf{C}_{(i)}^{S}\end{pmatrix} + \frac{1}{\varepsilon_i^{(0,0)}-\varepsilon_a^{(0,0)}}(\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\times\begin{pmatrix}\mathbf{V}' & \mathbf{0}\\ \mathbf{0} & (1/4c^2)\mathbf{W}'\end{pmatrix}\begin{pmatrix}\mathbf{C}_{(i)}^{L}\\ \mathbf{C}_{(i)}^{S}\end{pmatrix}, \tag{31}$$

where we use the notation defined above and

$$(\boldsymbol{\Lambda}_{B_u}^{P})_{\lambda\tau} \equiv \tfrac{1}{2}\langle\chi_\lambda|\vec{\sigma}\cdot\vec{p}(\vec{r}_G\times\vec{\sigma})_u|\chi_\tau\rangle. \tag{32}$$

The resulting expression for shielding

$$\sigma_{uv} = \sigma_{uv}^{P} = \frac{1}{c}\,\mathrm{Re}\left[(\boldsymbol{\beta}_{ai}^{B_u})^{\mathrm{RKB}}(\mathbf{C}_{(i)}^{L\dagger}\ \mathbf{C}_{(i)}^{S\dagger})\begin{pmatrix}\mathbf{0} & \boldsymbol{\Lambda}_{\mu_v^M}^{P\dagger}\\ \boldsymbol{\Lambda}_{\mu_v^M}^{P} & \mathbf{0}\end{pmatrix}\times\begin{pmatrix}\mathbf{C}_{(a)}^{L}\\ \mathbf{C}_{(a)}^{S}\end{pmatrix}\right] \tag{33}$$

consists of a paramagnetic contribution [similar to Eq. (22c)] only, i.e., the shielding tensor has no paramagnetic $\sigma_{uv}^{P0}$ and diamagnetic $\sigma_{uv}^{D}$ contributions [the summation over the negative-energy MOs in Eq. (33) in the nonrelativistic limit provides the classical diamagnetic contribution]. In practical applications straightforward use of Eqs. (31)–(33) is problematic: While the summation over the unoccupied positive-energy MOs in Eq. (33) converges rapidly with the size of the basis set, the summation over the negative-energy MOs yields poor results which can be improved only by using very large basis sets.[18]

The use of restricted magnetic balance allows us to avoid this problem. Technically, the RMB basis results in different expressions for the beta coefficients. To emphasize this, we rewrite Eq. (25) for the coefficients $\boldsymbol{\beta}_{ai}^{B_u}$, obtained in the previous section, in a different form (for the derivation see Appendix C) as follows:

$$(\boldsymbol{\beta}_{ai}^{B_u})^{\mathrm{RMB}} = (\boldsymbol{\beta}_{ai}^{B_u})^{\mathrm{RKB}} + \frac{1}{2c}(\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & -(1/2c^2)\boldsymbol{\Lambda}_{B_u}^{P}\end{pmatrix}\times\begin{pmatrix}\mathbf{C}_{(i)}^{L}\\ \mathbf{C}_{(i)}^{S}\end{pmatrix}. \tag{34}$$

That is, a new term appears due to the use of a RMB basis. As a result, the paramagnetic contribution is affected via the change in $(\boldsymbol{\beta}_{ai}^{B_u})^{\mathrm{RMB}}$ coefficients [see the expression for $\sigma^{P1}$ in Eq. (22c) and the equivalent expression for $\sigma^{P}$ in Eq. (33)]. Moreover, the use of RMB leads to new contributions to shieldings [see expressions for $\sigma^{D}$ and $\sigma^{P0}$ in Eqs. (22a) and (22b)]. Our numerical tests show that the $\sigma^{P0}$ contribution is relatively small in comparison with the other terms. The major advantage of the use of RMB is actually similar to that of distributed gauge origin approaches (GIAO or IGLO) in a nonrelativistic framework: the use of RMB reduces the contribution to shielding coming from the summation over the negative-energy MOs [because the contributions from negative-energy MOs to the first term in Eq. (31) and to the second term in Eq. (34) almost cancel each other[43]]. Thereby the use of RMB reduces the overall sensitivity of the results to the basis set. The remaining part ($\sigma^{D}$) is calculated via summation over occupied MOs. This is much less basis-set dependent. Similar advantages over kinetically balanced basis set were also found in the ODA approach.[23]

Note also that we do not use Eq. (34) in our implementation: The use of expression (25) for $\boldsymbol{\beta}_{ai}^{B_u}$ provides a more stable computational procedure than Eq. (34), allowing us to avoid the calculation of some odd terms that are large but almost cancel each other.

## V. COMPARISON OF mDKS-RMB WITH THE ODA APPROACH

Recently another approach for relativistic DKS calculations of nuclear shielding tensors was proposed by Liu and co-workers, the ODA method.[23,36] Since the mDKS-RMB and ODA approaches exhibit a number of close similarities, it is worthwhile to compare them in more detail.

The two approaches relate in that they both go beyond kinetic balance, and both take special care, albeit in different ways, of the magnetic part of the response of the small component. While in the present mDKS-RMB approach restricted magnetic balance is applied straightforwardly from the very beginning (by formulating the DKS equations in matrix form using the RMB basis), in the derivation of ODA the authors started from the operator form of the DKS equa-

tions. Introduction of a basis set was postponed until the response equations were written via the basis for the large component only.

This results in more complicated equations due to the occurrence of a nontrivial operator with a denominator depending on the potential and on one-electron energies [see the central ODA equations (14)–(18) in Ref. 36]. The ODA method is thus based on the expression of the small component via the large component (i.e., elimination of the small component) in the presence of an external magnetic field. An advantage of this approach is that now one can use the basis for the large component only. However, the problems arising resemble those of the approach by van Lenthe *et al.*[44] (see also the related recent discussion in Ref. 11). The resulting complicated response equations would be very time consuming. This is a consequence of not using a matrix formulation and the definition of a basis for both large and small components right from the start. Probably for this reason, an approximation was introduced by removing the denominator in the magnetic part of the response of the small component (i.e., the denominator was replaced by the factor $2c^{-2}$). This corresponds to the nonrelativistic approximation for the magnetic part of the response of the small component.

Let us look at this difference between the mDKS-RMB and ODA approaches in more detail. It can be shown easily that in case of a RKB basis [Eqs. (4a) and (4b)] in the nonrelativistic limit the MO coefficients for the small and large components coincide (see Appendix D),

$$\lim_{c\to\infty} \mathbf{C}_{(i)}^{S} = \mathbf{C}_{(i)}^{L}. \tag{35}$$

The use of this approximation for $\varphi_i^{m(1,0)_u}$ [the magnetic part of $\varphi_i^{(1,0)_u}$—see Eq. (17a) in the present work] gives

$$\varphi_i^{m(1,0)_u} \equiv \begin{pmatrix} \mathbf{0} \\ \mathbf{C}_{\lambda i}^{L(0,0)} \chi_\lambda^{S(1,0)_u} \end{pmatrix}. \tag{36}$$

In our experience (see discussion in Sec. VIII) this is not a very serious approximation (at least, for relatively light elements).

After using this approximate expression for $\varphi_i^{m(1,0)_u}$ in the derivation of the second-order properties [Eqs. (22a)–(22c), (24), and (34)], one arrives at the ODA working equations. In the ODA approach the shielding arising from $\varphi_i^{m(1,0)_u}$ ("magnetic part") is of order $O(c^{-2})$ (as was mentioned in Ref. 36) but contains also terms of higher order. In that initial paper, the summation over the negative-energy MOs in terms $E_p^{11}$ and $E_x^{11}$ was removed [since the approximation (36) and the neglect of the summation over the negative-energy MOs are of the same order of $O(c^{-2})$] to keep the final expression consistent to order $O(c^{-2})$.[36] This approximation is not necessary and was reconsidered in a second paper.[23] In practice, the two approximations discussed above are of different quality (see Sec. VIII). As is well known for relativistic calculations of magnetic properties, arguments based on the consistent inclusion of operators to order $O(c^{-2})$ are not always safe, as neglected higher-order terms may nevertheless be important. One example are spin-orbit corrections to shielding.[37] Our present mDKS-RMB approach does not exhibit such problems, as it is consistent to the higher-order $O(c^{-4})$.

While it is likely that the suggested approximation [Eq. (35)] for $\varphi_i^{m(1,0)_u}$ gives reasonable results for not too heavy elements, it remains to be seen how accurate it is for a wider variety of systems. A ZORA-like approximation[45] for this term could probably also be used and should be more accurate. Overall, however, we find here that neither approximation is necessary if one uses the RMB basis from the start, as is done in the present work (the additional computational effort is negligible).

A more crucial approximation made in the implementation of the ODA approach is the neglect of coupling terms [the second term in Eq. (31)]. As will be shown below (Sec. VIII), these coupling terms may become very important in case of strong spin-orbit interactions, and their neglect may lead to large errors already in calculations of compounds containing relatively light elements.

## VI. FINITE-PERTURBATION IMPLEMENTATION OF THE mDKS-RMB APPROACH

Rigorous analytical implementation of the coupled-perturbed scheme for the mDKS-RMB approach requires the nontrivial programming of the kernel for a given exchange-correlation functional. To have a benchmark method to compare to our coupled scheme, we decided to implement the mDKS-RMB method first using finite-perturbation theory (FPT) with the external magnetic field as a primary perturbation. Apart from its benchmark character, such an implementation has its own advantages. For example, it allows us to study the field dependence of the shielding, which may become interesting due to the increase of experimentally accessible field strengths.[46]

Again, we choose the external magnetic field $\vec{A}_{\vec{B}}$ as initial perturbation. Applying the principle of minimal coupling $[\vec{\pi}=\vec{p}+(1/c)\vec{A}_{\vec{B}}]$ to the DKS equation (1) and using the RMB basis, we obtain

$$(D_{\mathrm{kin}}^{00} + D^{10} + V_{4\times4}^{(\vec{B},0)})\varphi_i^{(\vec{B},0)} = \varepsilon_i \varphi_i^{(\vec{B},0)}, \tag{37}$$

or in matrix form (neglecting an explicit quadratic dependence of the operators on the external magnetic field)

$$\begin{pmatrix} \mathbf{V} & \hat{\mathbf{T}} \\ \hat{\mathbf{T}} & (1/4c^2)\hat{\mathbf{W}} - \hat{\mathbf{T}} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^{L(\vec{B},0)} \\ \mathbf{C}_{(i)}^{S(\vec{B},0)} \end{pmatrix} = \varepsilon_i^{(\vec{B},0)} \begin{pmatrix} \mathbf{S} & \mathbf{0} \\ \mathbf{0} & (1/2c^2)\hat{\mathbf{T}} \end{pmatrix} \begin{pmatrix} \mathbf{C}_{(i)}^{L(\vec{B},0)} \\ \mathbf{C}_{(i)}^{S(\vec{B},0)} \end{pmatrix}, \tag{38}$$

where

$$\hat{\mathbf{T}}_{\lambda\tau} \equiv \mathbf{T}_{\lambda\tau} + \frac{1}{2c}(\tilde{\mathbf{\Gamma}}_{\vec{B}}^{P})_{\lambda\tau}, \tag{39a}$$

$$(\tilde{\mathbf{\Gamma}}_{\vec{B}}^{P})_{\lambda\tau} \equiv \langle \chi_\lambda | (\vec{r}_G \times \vec{p}) \cdot \vec{B} + \vec{\sigma} \cdot \vec{B} | \chi_\tau \rangle, \tag{39b}$$

$$\hat{\mathbf{W}}_{\lambda\tau} \equiv \mathbf{W}_{\lambda\tau}^{(0,0)} + \frac{1}{c}\langle \vec{\sigma}\cdot\vec{p}\chi_\lambda | V_{2\times 2}^{(\vec{B},0)} | \vec{\sigma}\cdot\vec{A}_{\vec{B}}\chi_\tau\rangle + \frac{1}{c}\langle \vec{\sigma}\cdot\vec{A}_{\vec{B}}\chi_\lambda | V_{2\times 2}^{(\vec{B},0)} | \vec{\sigma}\cdot\vec{p}\chi_\tau\rangle. \tag{39c}$$

Equation (38) is the basic working equation for the present FPT approach. The numerical derivative of the density matrix with respect to the perturbation parameter was calculated by symmetric derivation,

$$\mathbf{P}' \equiv \frac{\mathbf{P}^{(\vec{B},0)} - \mathbf{P}^{(-\vec{B},0)}}{2|\vec{B}|}, \tag{40}$$

where

$$(\mathbf{P}^{(\vec{B},0)})_{\lambda\tau} \equiv \begin{pmatrix} \mathbf{C}_{\lambda i}^{L(\vec{B},0)}\mathbf{C}_{i\tau}^{L(\vec{B},0)\dagger} & \mathbf{C}_{\lambda i}^{L(\vec{B},0)}\mathbf{C}_{i\tau}^{S(\vec{B},0)\dagger} \\ \mathbf{C}_{\lambda i}^{S(\vec{B},0)}\mathbf{C}_{i\tau}^{L(\vec{B},0)\dagger} & \mathbf{C}_{\lambda i}^{S(\vec{B},0)}\mathbf{C}_{i\tau}^{S(\vec{B},0)\dagger} \end{pmatrix}. \tag{41}$$

The nuclear shielding tensor may then be expressed as

$$\sigma_{uv} = \mathrm{Tr}\left[\mathbf{P}'\begin{pmatrix} \mathbf{0} & \mathbf{\Lambda}_{\mu_v^M}^{P\dagger} \\ \mathbf{\Lambda}_{\mu_v^M}^{P} & \mathbf{0} \end{pmatrix}\right] = 2\,\mathrm{Re}\{\mathrm{Tr}[(\mathbf{P}')^{LS}\mathbf{\Lambda}_{\mu_v^M}^{P}]\}. \tag{42}$$

where the nondiagonal part of the derivative of the density matrix is

$$(\mathbf{P}')_{\lambda\tau}^{LS} \equiv \frac{\mathbf{C}_{\lambda i}^{L(\vec{B},0)}\mathbf{C}_{i\tau}^{S(\vec{B},0)\dagger} - \mathbf{C}_{\lambda i}^{L(-\vec{B},0)}\mathbf{C}_{i\tau}^{S(-\vec{B},0)\dagger}}{2|\vec{B}|}. \tag{43}$$

Disadvantages of the FPT implementation are a larger computational effort, since six perturbed SCF calculations have to be performed (this could be reduced to four calculations for nonsymmetrical derivation), and possible sensitivity to the value of the finite-perturbation parameter (albeit we have not encountered such problems in our benchmark calculations).

Note that double finite-perturbation theory can be of interest in some applications (for example, when trying to mimic more directly the NMR experiment). Then a more general dependence of the AOs on external magnetic field and magnetic field due to the magnetic moment of a nucleus [see Eq. (14)], might also be considered.

## VII. COMPUTATIONAL DETAILS

Structures of the HF, HCl, HBr, and HI molecules have been taken from Ref. 47. All calculations were performed at DFT level, using the ReSpect (Ref. 48) program (including the property module MAG-ReSpect). Here we will use either the local density approximation (Slater exchange and VWN correlation, termed SVWN),[49] or the Perdew and Wang GGA functional for exchange[50] with the Perdew GGA correlation functional[51] (this combination is known to provide reasonable hyperfine parameters[52] and will be referred to as PP86 below). Since the analytical evaluation of all the 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 heavy elements Br and I were those of Faegri,[53] 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 the Huzinaga–Kutzelnigg IGLO-III basis sets.[54] 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). For fitting the total electron density and the components of the spin density, uncontracted auxiliary basis sets were used ($6s2p2d$ for H; $11s7p7d$ for F; $13s8p8d$ for Cl; $18s13p13d$ for Br; $22s17p17d$ for I; *s*-exponents were chosen as twice the *s*-exponents in the corresponding orbital basis set; *p*- and *d*-sets were composed of shared exponents covering the space of *p*-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. For the angular part, we used 86 points for compounds containing light elements (HF and HCl) and 110 points otherwise (HBr and HI). FPT results were obtained with perturbation parameter $B=0.001$ a.u.).

For comparison purposes, a few calculations of $^1$H shieldings and spin-orbit corrections to the shieldings were done at the one-component Douglas–Kroll–Hess (DKH) level.[40] In those calculations, scalar relativistic effects were included during the SCF step (at the second-order transformed DKH level of the one-electron operators). Then the shielding tensors were obtained using uncoupled second-order perturbation theory[55] (without energy denominator correction). To evaluate spin-orbit corrections, a third-order perturbation approach (PT3) was applied[56] based on the one-component second-order DKH wave function. While the picture change requires the DKH transformation to be applied to all perturbation operators, it is known[28] that the use of the untransformed orbital-Zeeman operator (responsible for the interaction with an external magnetic field) has an insignificant effect on the results. Also, we have found[35] that transformation of the Fermi-contact operator on a light element such as hydrogen has a negligible effect (the same is expected for other operators responsible for interaction with magnetic moment of hydrogen). Therefore, only the spin-orbit operator was used in first-order transformed DKH fashion, within the atomic mean-field (AMFI) approximation.[57] In the tables, the calculations at this level will be denoted DKH+SO, whereas the abbreviation NR will be used for nonrelativistic calculations without SO corrections and NR +SO for nonrelativistic calculations with SO corrections (at Breit–Pauli level). Since scalar DKH results of hydrogen shifts differ by less than 0.1 ppm from their nonrelativistic counterparts they are not included in the tables.

We also paid special attention to the comparison of our method with the ODA method. To have a better insight into the approximations made in ODA (see discussion above), we implemented ODA in our code as well. In our implementa-

tion we are able to separate effects of different approximations used in ODA. This allows us to judge their relative importance.

## VIII. BENCHMARK CALCULATIONS AND DISCUSSION

The major goal here is to study different aspects of the new method and to perform some benchmark calculations on well-studied molecules before going to systems with very heavy elements in future work. In particular, the effects of spin polarization, the interplay of spin-orbit and field-dependent operators, as well as the response from exchange-correlation and Coulomb potentials are of interest. With this in mind we chose the well-established series of chemical shifts in the halogen halides H*X* (*X*=F,Cl,Br,I), with emphasis on the hydrogen shieldings for which spin-orbit effects are known to be large.[56]

We start with $^1$H shieldings using the local SVWN functional (Table I). As is well known, for the heaviest molecules in this series, HBr and HI, nonrelativistic (NR) calculations give much too low shieldings compared to experiment. Interestingly, our well-studied earlier third-order perturbation scheme[56] (PT3) for the calculation of spin-orbit corrections to shieldings based on a nonrelativistic DFT calculation performs very well (cf. NR+SO row in Table I). These results may be improved somewhat further by including scalar relativistic effects partially (both in the PT3 calculation of SO corrections and in the underlying one-component second-order calculation of the shieldings) at second-order DKH level (see Sec. VII). The noticeable difference between NR+SO and DKH+SO results for HI shows that even scalar relativistic effects may play a visible role for compounds including relatively light elements such as iodine (via interplay of scalar and spin-orbit effects).

Turning to the mDKS-RMB data, we note that the FPT results and those obtained with the coupled scheme agree perfectly (within 0.01 ppm or better for hydrogen and within 0.1 ppm for iodine). While all FPT results in Tables I–IV were obtained with perturbation parameter 0.001, we found that variation of the parameter by an order of magnitude had negligible effects on the results. We may therefore concentrate on the coupled results in the following. In contrast, the uncoupled results are too low, increasingly so for the heavier members of the series. This confirms that the coupling terms, arising from the interplay between spin-orbit and field-dependent operators (see discussion above), are essential. Neglect of coupling terms reduces the $^1$H shielding by ~3 ppm for HI, clearly a non-negligible error. The situation differs thus fundamentally from a nonrelativistic framework where no coupling terms arise for LDA or GGA functionals (or for other local and multiplicative potentials). Note that the coupling terms arise from relativistic field-dependent operators rather than from relativistic exchange-correlation functionals. The influence of the coupling terms and the performance of the different approaches are shown graphically in Fig. 1(a). The influence of the coupling terms is even larger with the gradient-corrected PP86 functional [e.g., 4.5 ppm for HI; Table II, Fig. 1(b)]. Unfortunately, in Ref. 36 only heavy-atom shieldings were provided (see below), so that we cannot directly compare with ODA calculations (which were in the uncoupled approximation only).

Since the coding of the analytical evaluation of the kernel of an exchange-correlation functional (beyond LDA) is demanding, it is common to use a LDA kernel in calculations of second-order properties (or in time-dependent DFT calcu-

TABLE I. $^1$H NMR isotropic shieldings (in ppm) in the hydrogen halides, using the local SVWN functional.

| Method | HF | HCl | HBr | HI |
|---|---|---|---|---|
| NR[a] | 28.41 | 30.31 | 29.87 | 30.16 |
| NR+SO[b] | 28.51 | 30.87 | 33.18 | 39.85 |
| DKH+SO[c] | 28.52 | 30.91 | 33.37 | 40.99 |
| | | mDKS-RMB | | |
| Uncoupled[d] | 28.45 | 30.77 | 32.44 | 37.81 |
| Coupled[e] | 28.47 | 30.94 | 33.42 | 40.88 |
| FPT[f] | 28.47 | 30.94 | 33.42 | 40.88 |
| Expt.[g] | 28.50 | 31.06 | 34.96 | 43.86 |

[a]Nonrelativistic Kohn–Sham calculation.
[b]Spin-orbit corrections by third-order perturbation theory with nonrelativistic unperturbed wave function were added to NR shifts (see Sec. VII).
[c]Spin-orbit corrections by third-order perturbation theory with DKH relativistic unperturbed wave function were added to DKH shifts (see Sec. VII).
[d]Uncoupled approximation.
[e]Coupled-perturbed mDKS-RMB scheme.
[f]Finite-perturbation implementation.
[g]Experimental data from Ref. 60.

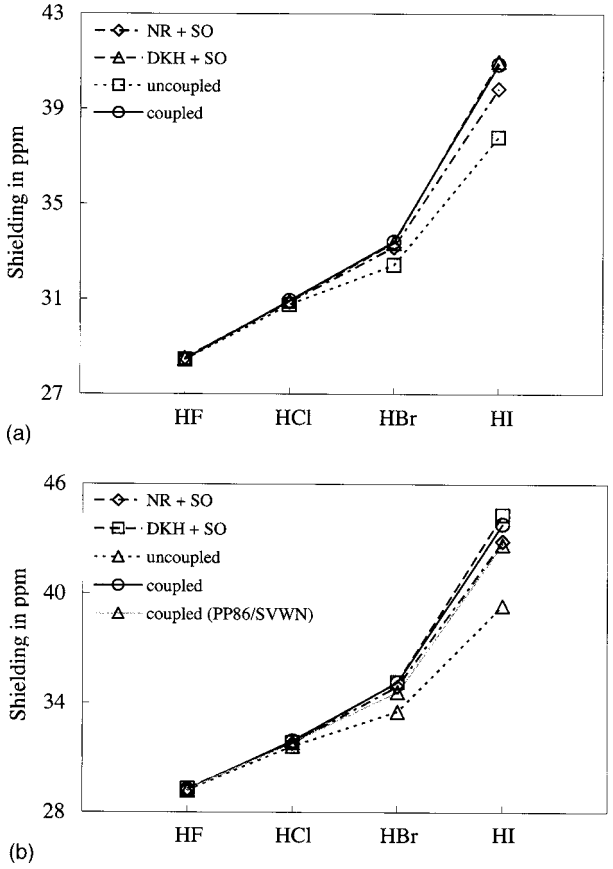


FIG. 1. Comparison of $^1$H NMR shieldings in the hydrogen halides (a) with SVWN and (b) with PP86 functionals, respectively, calculated with different approaches. See footnotes of Tables I and II for notations.

TABLE II. $^1$H NMR isotropic shieldings (in ppm) in the hydrogen halides, using the gradient-corrected PP86 functional (unless noted otherwise).

| Method | HF | HCl | HBr | HI |
|---|---|---|---|---|
| NR[a] | 29.16 | 31.10 | 30.86 | 31.25 |
| NR+SO[b] | 29.28 | 31.79 | 34.90 | 42.88 |
| DKH+SO[c] | 29.30 | 31.83 | 35.14 | 44.32 |
| | | mDKS-RMB | | |
| Uncoupled[d] | 29.20 | 31.63 | 33.52 | 39.34 |
| Coupled[e] | 29.24 | 31.92 | 35.13 | 43.82 |
| FPT[f] | 29.25 | 31.92 | 35.12 | 43.83 |
| Coupled (PP86/SVWN)[g] | 29.22 | 31.82 | 34.60 | 42.69 |
| Expt.[h] | 28.50 | 31.06 | 34.96 | 43.86 |

[a]Nonrelativistic Kohn–Sham calculation.
[b]Spin-orbit corrections by third-order perturbation theory with nonrelativistic unperturbed wave function were added to NR shifts (see Sec. VII).
[c]Spin-orbit corrections by third-order perturbation theory with DKH relativistic unperturbed wave function were added to DKH shifts (see Sec. VII).
[d]Uncoupled approximation.
[e]Coupled-perturbed mDKS-RMB scheme.
[f]Finite-perturbation implementation.
[g]Coupled-perturbed mDKS-RMB scheme with PP86 functional used in unperturbed calculations and SVWN kernel used in coupled equations.
[h]Experimental data from Ref. 60.

lations), while the unperturbed MOs may have been obtained from calculations with a more sophisticated functional and potential. A LDA kernel is also computationally somewhat more efficient. The influence of the kernel is evaluated in Table II where PP86 calculations are used either with the PP86 kernel or with the local SVWN kernel. Obviously, use of the LDA kernel introduces non-negligible errors: The computed $^1$H shielding is lower than the full PP86 results by 0.5 ppm for HBr and by 1.1 ppm for HI. Figure 1(b) compares graphically results obtained with different methods, using the PP86 functional.

Differences between the different approximations are most pronounced for the perpendicular component of the $^1$H shielding tensors (Table III), much less so for the parallel one. This is consistent with the large importance of spin-orbit coupling for $\sigma_\perp$. Notably, use of a LDA kernel in a PP86 calculation reduces $\sigma_\perp$ less than going all the way from a full PP86 to a full SVWN LDA calculation. Effects of the coupling terms are also particularly striking for $\sigma_\perp$. Notably, while the third-order perturbation treatment of SO corrections captures nicely the enhancement of $\sigma_\perp$ by SO effects, it fails to reproduce the lowered $\sigma_\parallel$ obtained at the mDKS-RMB level for HBr and HI. This may point to relativistic terms neglected in the PT3 approach which are present in a fully relativistic treatment.

A different picture emerges when turning to the isotropic shieldings of the heavy nuclei (Table IV; we do not include PT3 results here, which will be inadequate for the heavy-atom shieldings[37]): Now the use of a LDA kernel in the coupled-perturbed calculations influences the results negligibly, and even the switch from PP86 to SVWN has a much smaller overall effect than for the $^1$H shieldings (cf. above). Notably, also the importance of the coupling terms is much less pronounced in this case. This may be rationalized by the different dominant terms identified in perturbation theoretical analyses of the relativistic corrections to the shielding of the neighboring atom ["heavy-atom effect on the shielding of the light atom"[58] (HALA)] compared to the heavy-atom effect on the heavy-atom shielding[59] (HAHA).[58] The HALA effect is known to be dominated by spin-orbit effects and is thus affected substantially by the coupling terms, due to the interplay between field-dependent operators and spin-orbit coupling (see above). On the other hand, other shielding mechanisms become important for the HAHA effects,[58] with a conceivably smaller influence of coupling terms.

Table IV collects mDKS-RMB results for the heavy element shieldings in the H*X* series together with published ODA data.[36] Additionally we included results obtained with

TABLE III. $^1$H NMR shieldings tensor components (in ppm) in the hydrogen halides at PP86 level (unless noted otherwise).

| | HF | | HCl | | HBr | | HI | |
|---|---|---|---|---|---|---|---|---|
| Method | $\sigma_\parallel$ | $\sigma_\perp$ | $\sigma_\parallel$ | $\sigma_\perp$ | $\sigma_\parallel$ | $\sigma_\perp$ | $\sigma_\parallel$ | $\sigma_\perp$ |
| NR[a] | 44.50 | 21.48 | 45.75 | 23.77 | 49.19 | 21.69 | 52.28 | 20.73 |
| NR+SO[b] | 44.51 | 21.66 | 45.76 | 24.80 | 49.20 | 27.74 | 52.30 | 38.17 |
| DKH+SO[c] | 44.50 | 21.70 | 45.72 | 24.88 | 48.97 | 28.23 | 51.72 | 40.60 |
| | | | | mDKS-RMB | | | | |
| Uncoupled[d] | 44.50 | 21.55 | 45.65 | 24.63 | 48.62 | 25.97 | 50.08 | 33.97 |
| Coupled[e] | 44.50 | 21.62 | 45.65 | 25.05 | 48.50 | 28.45 | 48.98 | 41.24 |
| FPT[f] | 44.50 | 21.62 | 45.65 | 25.05 | 48.48 | 28.44 | 48.98 | 41.25 |
| Coupled (SVWN/SVWN)[g] | 44.24 | 20.58 | 45.18 | 23.81 | 47.97 | 26.13 | 48.68 | 36.98 |
| Coupled (PP86/SVWN)[h] | 44.50 | 21.58 | 45.65 | 24.90 | 48.53 | 27.63 | 49.33 | 39.37 |

[a]Nonrelativistic Kohn–Sham calculation.
[b]Spin-orbit corrections by third-order perturbation theory with nonrelativistic unperturbed wave function were added to NR shifts (see Sec. VII).
[c]Spin-orbit corrections by third-order perturbation theory with DKH relativistic unperturbed wave function were added to DKH shifts (see Sec. VII).
[d]Uncoupled approximation.
[e]Coupled-perturbed mDKS-RMB scheme.
[f]Finite-perturbation implementation.
[g]Coupled-perturbed mDKS-RMB scheme with SVWN functional used in unperturbed calculations and SVWN kernel used in coupled equations.
[h]Coupled-perturbed mDKS-RMB scheme with PP86 functional used in unperturbed calculations and SVWN kernel used in coupled equations.

TABLE IV. Heavy-atom isotropic shieldings (in ppm) in the hydrogen halides at PP86 level (unless noted otherwise).

| Method | HF | HCl | HBr | HI |
|---|---|---|---|---|
| NR[a] | 405.6 | 908.6 | 2547.8 | 4394.0 |
| ODA[b] | ··· | ··· | 2965.0 | 5881.0 |
| ODA-1[c] | 412.9 | 946.5 | 2959.9 | 5892.5 |
| ODA-2[d] | 411.2 | 935.6 | 2881.0 | 5677.1 |
| | mDKS-RMB | | | |
| Uncoupled[e] | 411.1 | 935.0 | 2876.0 | 5661.6 |
| Coupled[f] | 411.4 | 936.3 | 2887.9 | 5705.1 |
| Coupled (SVWN/SWVN)[g] | 416.4 | 950.9 | 2912.5 | 5749.1 |
| Coupled (PP86/SVWN)[h] | 411.3 | 935.9 | 2884.1 | 5698.1 |
| FPT[i] | 411.4 | 936.3 | 2887.9 | 5705.1 |

[a]Nonrelativistic Kohn–Sham calculation.
[b]Reference 36.
[c]Present ODA implementation without summation over negative-energy MOs (see Sec. VIII).
[d]Present ODA implementation with summation over negative-energy MOs (see Sec. VIII).
[e]The uncoupled approximation was used in mDKS-RMB.
[f]Coupled-perturbed mDKS-RMB scheme.
[g]Coupled-perturbed mDKS-RMB scheme with SVWN functional used in unperturbed calculations and SVWN kernel used in coupled equations.
[h]Coupled-perturbed mDKS-RMB scheme with PP86 functional used in unperturbed calculations and SVWN kernel used in coupled equations.
[i]Finite-perturbation implementation.

our implementation of the ODA approach. Our implementation allows us to go, step by step, from mDKS-RMB to ODA by involving one approximation at a time. In particular, we made the nonrelativistic approximation according to Eq. (35) ($\lim_{c\to\infty} \mathbf{C}^S_{(i)} = \mathbf{C}^L_{(i)}$). The corresponding results are marked as ODA-2 in Table IV. Then, we also neglected the contribution from the negative-energy MOs [see Eq. (32) in the original paper of Xiao *et al.*[36]], which we named ODA-1. In both cases we followed the original ODA formulation, and therefore no coupling terms were included. By going from coupled to uncoupled mDKS-RMB to ODA-2 and finally to ODA-1, we can judge the relative importance of these approximations. Moreover, all comparison are made with the same exchange-correlation functionals and basis sets. Since ODA-1 is equivalent to the original ODA formulation, the corresponding results are very close to each other (Table IV). The remaining difference is probably due to different basis sets used for the large component, difference exchange-correlation functionals, and different nucleus models used in the calculations.

Beyond the already mentioned larger importance of coupling terms for HALA compared to HAHA effects, two major conclusions may be drawn: First, the comparison of uncoupled results with the ODA-2 results reveals that the use of the nonrelativistic limit for the unperturbed MO coefficients of the small component [$\lim_{c\to\infty} \mathbf{C}^S_{(i)} = \mathbf{C}^L_{(i)}$ in Eq. (35)] is relatively unimportant for the series studied. However, the importance of the missing contribution increases as $O(c^{-2})$. This difference is about 0.09 ppm for fluorine and about 15.5 ppm for iodine. One may expect larger effects for heavier elements.

The neglect of the summation over negative-energy MOs (ODA-1 results in Table IV) is a more serious approximation: it accounts for about 215 ppm for the iodine shielding in HI (difference between ODA-1 and ODA-2 results in Table IV). Again, the effect will be more pronounced for heavier elements. While neglect of the summation over negative-energy MOs and of coupling terms are not crucial for the ODA method, we believe that the use of the nonrelativistic limit for the unperturbed MO coefficients of the small component ($\lim_{c\to\infty} \mathbf{C}^S_{(i)} = \mathbf{C}^L_{(i)}$) is essential for an efficient implementation of ODA. This discussion is based on very limited data, and a more detailed study on a wider class of examples will be desirable in the future.

## IX. CONCLUSIONS

A new relativistic four-component DFT approach (mDKS-RMB) for the calculation of nuclear shieldings has been reported. It is based on the matrix formulation of the Dirac–Kohn–Sham method. While restricted kinetic balance has been employed for the unperturbed system, a core feature of the present second-order coupled-perturbation approach for magnetic properties is the use of a restricted magnetically balanced basis set for the small component. This has allowed us to avoid additional approximations and/or the strong basis set dependence that arises in related approaches. Benchmark relativistic calculations of nuclear shieldings for the hydrogen halides, H$X$ ($X$=F,Cl,Br,I), indicate perfect agreement between the full coupled-perturbed approach and a finite-perturbation approach, and good agreement with available experimental data.

Coupling terms arise in a correct relativistic framework even when local or gradient-corrected functionals are used. The coupling terms, which were missing in a recent, related implementation,[23,36] were found to be essential for the $^1$H shieldings (in particular, for the $\sigma_\perp$ component) but less pronounced for the heavy-atom shieldings. The mDKS-RMB approach provides a basis for a very efficient implementation of full four-component Dirac–Kohn–Sham calculations of nuclear shieldings and spin-spin couplings. It offers an attractive alternative to existing approximate two-component methods with transformed Hamiltonians (such as the Douglas–Kroll–Hess method, zero-order regular approximation, or related approaches). In particular, no picture-change effects arise in property calculations.

## ACKNOWLEDGMENTS

The support for the present work by the European Commission through the EURATOM FP6 Integrated Project "Fundamental Processes of Radionuclide Migration" (FUNMIG, cf. www.funmig.com) is acknowledged. Work in Bratislava has also been supported by the Slovak Grant Agencies APVV (No. 0625-06) and VEGA (No. 2/6182/26). Work in

Würzburg has been supported by Deutsche Forschungsgemeinschaft (Project No. KA1187/5-2) and graduate college *Modern Methods of Magnetic Resonance* at Universität Stuttgart (scholarship to I. M. O.). The authors appreciate very helpful and stimulating discussions with W. Liu, W. Kutzelnigg, and G. A. Aucar during the REHE-2007 conference.

## APPENDIX A: DERIVATION OF THE EXPRESSION FOR BILINEAR DERIVATIVE OF THE TOTAL ENERGY

Notations defined in Secs. II–IV will be used in the Appendices. The second derivative of the total energy with respect to an external magnetic field and the nuclear magnetic moment may be written (up to the bilinear terms) as

$$\frac{d^2E(\vec{B},\vec{\mu}^M)}{dB_u d\mu_v^M} = \left.\frac{\partial^2 E(\vec{B},\vec{\mu}^M)}{\partial B_u \partial \mu_v^M}\right|_{\vec{B},\vec{\mu}^M=0} + \sum_i \left( \int \frac{\delta}{\delta \varphi_i^{(\vec{B},\vec{\mu}^M)}} \left( \frac{\partial E(\vec{B},\vec{\mu}^M)}{\partial \mu_v^M} \right)\Bigg|_{\vec{B},\vec{\mu}^M=0} \left.\frac{\partial \varphi_i^{(\vec{B},\vec{\mu}^M)}}{\partial B_u}\right|_{\vec{B},\vec{\mu}^M=0} dV \right) + \text{c.c.} \tag{A1}$$

Here, for the sake of transparency, we use index $i$ to denote the $i$th four-component occupied molecular orbital. All partial derivatives in the above equation mean differentiation only with respect to the explicit dependence on the given parameters. After substituting the expression for the total energy from Eqs. (10a)–(10c), one obtains the relation

$$\left.\frac{d^2E(\vec{B},\vec{\mu}^M)}{dB_u d\mu_v^M}\right|_{B_u,\mu_v^M=0} = \langle \varphi_i^{(1,0)_u} | D^{(0,1)_v^M} | \varphi_i^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | D^{(0,1)_v^M} | \varphi_i^{(1,0)_u} \rangle. \tag{A2}$$

## APPENDIX B: DERIVATION OF EQUATION (24) FOR $(\boldsymbol{\beta}_{ij}^{B_u})^* + \boldsymbol{\beta}_{ij}^{B_u}$ (WHERE *i* AND *j* DENOTE OCCUPIED MOs)

The normalization condition is the natural requirement for a four-component molecular orbital as follows:

$$\langle \varphi_i^{(\vec{B},\vec{\mu}^M)} | \varphi_j^{(\vec{B},\vec{\mu}^M)} \rangle \overset{!}{=} \delta_{ij}. \tag{B1}$$

If we expand both sides of this expression up to first order with respect to the external magnetic field we obtain

$$\langle \varphi_i^{(0,0)} | \varphi_j^{(0,0)} \rangle + [\langle \varphi_i^{(1,0)_u} | \varphi_j^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | \varphi_j^{(1,0)_u} \rangle] B_u + \cdots \overset{!}{=} \delta_{ij} + 0.B_u + \cdots . \tag{B2}$$

Therefore

$$\langle \varphi_i^{(0,0)} | \varphi_j^{(0,0)} \rangle \overset{!}{=} \delta_{ij}, \tag{B3}$$

$$\langle \varphi_i^{(1,0)_u} | \varphi_j^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | \varphi_j^{(1,0)_u} \rangle \overset{!}{=} 0. \tag{B4}$$

Equation (B3) is already satisfied by construction of the unperturbed MOs. By substitution of Eqs. (16) and (17a) (for $\varphi_i^{(1,0)_u}$ and its magnetic part $\varphi_i^{m(1,0)_u}$), (18) (for beta coefficients), and (B3) in Eq. (B4) one obtains

$$\langle \varphi_i^{r(1,0)_u} | \varphi_j^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | \varphi_j^{r(1,0)_u} \rangle + \langle \varphi_i^{m(1,0)_u} | \varphi_j^{(0,0)} \rangle + \langle \varphi_i^{(0,0)} | \varphi_j^{m(1,0)_u} \rangle = 0$$

$$(\boldsymbol{\beta}_{ji}^{B_u})^* + \boldsymbol{\beta}_{ij}^{B_u} = -\mathbf{C}_{i\lambda}^{S\dagger} \langle \chi_\lambda^{S(1,0)_u} | \chi_\tau^{S(0,0)} \rangle \mathbf{C}_{\tau j}^S - \mathbf{C}_{i\lambda}^{S\dagger} \langle \chi_\lambda^{S(0,0)} | \chi_\tau^{S(1,0)_u} \rangle \mathbf{C}_{\tau j}^S$$

$$(\boldsymbol{\beta}_{ji}^{B_u})^* + \boldsymbol{\beta}_{ij}^{B_u} = -\frac{1}{4c^3} \mathbf{C}_{i\lambda}^{S\dagger} (\tilde{\boldsymbol{\Lambda}}_{B_u}^P)_{\lambda\tau} \mathbf{C}_{\tau j}^S. \tag{B5}$$

In Sec. III, we have seen that $\varphi_i^{m(1,0)_u}$ is not zero, exclusively due to the dependence of the basis on the magnetic field. In the absence of such dependence we would get $(\boldsymbol{\beta}_{ji}^{B_u})^* + \boldsymbol{\beta}_{ij}^{B_u} = 0$. It is worth noting that the situation is analogous to the GIAO approach in nonrelativistic calculations: one obtains also a nonzero result because of the dependence of the basis on the magnetic field.

## APPENDIX C: DERIVATION OF EQUATIONS (25) and (34) FOR $\boldsymbol{\beta}_{ai}^{B_u}$ (WHERE INDEX *i* DENOTES OCCUPIED MOs AND *a* UNOCCUPIED MOs, CORRESPONDING TO EITHER POSITIVE- OR NEGATIVE-ENERGY MOs)

Our general goal is to find a stationary point of the energy functional (10) subject to normalization constraint (B1). Let us find the stationary point of the Lagrange functional $L$

$$\frac{\delta L(\vec{B},\vec{\mu}^M)}{\delta \varphi_i^{(\vec{B},\vec{\mu}^M)*}} \overset{!}{=} 0,$$

$$L(\vec{B},\vec{\mu}^M) \equiv E(\vec{B},\vec{\mu}^M) + \varepsilon_i^{(\vec{B},\vec{\mu}^M)} (\langle \varphi_i^{(\vec{B},\vec{\mu}^M)} | \varphi_i^{(\vec{B},\vec{\mu}^M)} \rangle - 1). \tag{C1}$$

where the variation $\delta / \delta \varphi_i^{(\vec{B},\vec{\mu}^M)*}$ is a simplified notation for the four variations with respect to all four components of $\varphi_i^{(\vec{B},\vec{\mu}^M)*}$. $E(\vec{B},\vec{\mu}^M)$ is the energy functional (10), and $\varepsilon_i^{(\vec{B},\vec{\mu}^M)}$ are Lagrange multipliers.

Let us expand expression (C1) into a Taylor series. Since we are interested only in the response on the external magnetic field, we can terminate the expansion after the linear term with respect to $\vec{B}$ as follows:

$$\frac{\delta L(\vec{B},\vec{\mu}^M)}{\delta\varphi_i^{(\vec{B},\vec{\mu}^M)*}} = \left.\frac{\delta L(\vec{B},\vec{\mu}^M)}{\delta\varphi_i^{(\vec{B},\vec{\mu}^M)*}}\right|_{\vec{B},\vec{\mu}^M=0} + \left.\frac{d}{dB_u}\left(\frac{\delta L(\vec{B},\vec{\mu}^M)}{\delta\varphi_i^{(\vec{B},\vec{\mu}^M)*}}\right)\right|_{\vec{B},\vec{\mu}^M=0} B_u + \cdots \overset{!}{=} 0. \tag{C2}$$

From Eq. (C2), we can obtain two conditions:

$$\left.\frac{\delta L(\vec{B},\vec{\mu}^M)}{\delta\varphi_i^{(\vec{B},\vec{\mu}^M)*}}\right|_{\vec{B},\vec{\mu}^M=0} \overset{!}{=} 0, \tag{C3}$$

$$\frac{d}{dB_u}\left(\frac{\delta L(\vec{B},\vec{\mu}^M)}{\delta\varphi_i^{(\vec{B},\vec{\mu}^M)*}}\right)\Bigg|_{\vec{B},\vec{\mu}^M=0} \overset{!}{=} 0. \tag{C4}$$

Condition (C3) leads to the working equation of the unperturbed SCF procedure as follows:

$$(D_{\mathrm{kin}}^{00} + V_{4\times4}^{(0,0)})\varphi_i^{(0,0)} = \varepsilon_i^{(0,0)}\varphi_i^{(0,0)}, \tag{C5}$$

from which the unperturbed MOs $\varphi_i^{(0,0)}$ are obtained.

After some technical manipulation with condition (C4) we acquire the response of MOs with respect to the external magnetic field $\varphi_i^{(1,0)_u}$

$$D^{(1,0)_u}\varphi_i^{(0,0)} + (D_{\mathrm{kin}}^{00} + V_{4\times4}^{(0,0)})\varphi_i^{(1,0)_u} - \varepsilon_i^{(1,0)_u}\varphi_i^{(0,0)} - \varepsilon_i^{(0,0)}\varphi_i^{(1,0)_u} + O_{4\times4}^{(1,0)_u}\varphi_i^{(0,0)} = 0, \tag{C6}$$

where

$$O_{4\times4}^{(1,0)_u} \equiv \begin{pmatrix} O_{2\times2}^{(1,0)_u} & 0_{2\times2} \\ 0_{2\times2} & O_{2\times2}^{(1,0)_u} \end{pmatrix}. \tag{C7}$$

The last term in Eq. (C6) is responsible for the coupled character of the equations. Here it is timely to recall that Eqs. (B1) and (C5) also hold for unoccupied MOs. Using this fact we can rewrite Eq. (C6) in a more suitable form by multiplying it by an unoccupied molecular orbital $\varphi_a^{(0,0)\dagger}$ and integrating over all variables as follows:

$$(\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)})\boldsymbol{\beta}_{ai}^{B_u} = \langle\varphi_a^{(0,0)}|D^{(1,0)_u}|\varphi_i^{(0,0)}\rangle + \langle\varphi_a^{(0,0)}|D_{\mathrm{kin}}^{00} + V_{4\times4}^{(0,0)}|\varphi_i^{m(1,0)_u}\rangle - \varepsilon_i^{(0,0)}\langle\varphi_a^{(0,0)}|\varphi_i^{m(1,0)_u}\rangle + \langle\varphi_a^{(0,0)}|O_{4\times4}^{(1,0)_u}|\varphi_i^{(0,0)}\rangle. \tag{C8}$$

We see two principle routes to proceed further: The first way is analogous to the approach used by Liu and coworkers in ODA.[23,36] It is based on substitution of expression (C5) (valid also for unoccupied MOs) into the second term of the right hand side of Eq. (C8). Then one can easily obtain

$$\boldsymbol{\beta}_{ai}^{B_u} = \frac{1}{\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)}}(\langle\varphi_a^{(0,0)}|D^{(1,0)_u}|\varphi_i^{(0,0)}\rangle + \langle\varphi_a^{(0,0)}|O_{4\times4}^{(1,0)_u}|\varphi_i^{(0,0)}\rangle) - \langle\varphi_a^{(0,0)}|\varphi_i^{m(1,0)_u}\rangle. \tag{C9}$$

After substituting expressions (4a) and (4b) for unperturbed MOs and the magnetic part of the linear response of MOs (17a) we arrive at the following equation for beta coefficients

$$\boldsymbol{\beta}_{ai}^{B_u} = \frac{1}{2c}\left[\frac{1}{\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)}}(\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\begin{pmatrix} 2c\mathbf{V}' & \boldsymbol{\Lambda}_{B_u}^{P\dagger} \\ \boldsymbol{\Lambda}_{B_u}^{P} & (1/2c)\mathbf{W}' \end{pmatrix}\begin{pmatrix} \mathbf{C}_{(i)}^{L} \\ \mathbf{C}_{(i)}^{S} \end{pmatrix} + (\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & -(1/2c^2)\boldsymbol{\Lambda}_{B_u}^{P} \end{pmatrix}\begin{pmatrix} \mathbf{C}_{(i)}^{L} \\ \mathbf{C}_{(i)}^{S} \end{pmatrix}\right], \tag{C10}$$

which is, in fact, Eq. (34) in Sec. IV.

The second way is inspired by the derivation of the GIAO approach. From Eq. (C5), it follows that

$$\langle\varphi_a^{m(1,0)_u}|D_{\mathrm{kin}}^{00} + V_{4\times4}^{(0,0)}|\varphi_i^{(0,0)}\rangle = \varepsilon_i^{(0,0)}\langle\varphi_a^{m(1,0)_u}|\varphi_i^{(0,0)}\rangle, \tag{C11}$$

where

$$\varphi_a^{m(1,0)_u} \equiv \begin{pmatrix} \mathbf{0} \\ \mathbf{C}_{\lambda a}^{S(0,0)}\chi_\lambda^{S(1,0)_u} \end{pmatrix}. \tag{C12}$$

Combining Eqs. (C11) and (C8) we obtain

$$(\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)})\boldsymbol{\beta}_{ai}^{B_u} = \langle\varphi_a^{(0,0)}|D^{(1,0)_u}|\varphi_i^{(0,0)}\rangle + \langle\varphi_a^{(0,0)}|D_{\mathrm{kin}}^{00} + V_{4\times4}^{(0,0)}|\varphi_i^{m(1,0)_u}\rangle + \langle\varphi_a^{m(1,0)_u}|D_{\mathrm{kin}}^{00} + V_{4\times4}^{(0,0)}|\varphi_i^{(0,0)}\rangle - \varepsilon_i^{(0,0)}\langle\varphi_a^{(0,0)}|\varphi_i^{m(1,0)_u}\rangle - \varepsilon_i^{(0,0)}\langle\varphi_a^{m(1,0)_u}|\varphi_i^{(0,0)}\rangle + \langle\varphi_a^{(0,0)}|O_{4\times4}^{(1,0)_u}|\varphi_i^{(0,0)}\rangle. \tag{C13}$$

We substitute the expressions for $\varphi_i^{m(1,0)_u}$ and $\varphi_a^{m(1,0)_u}$ [second equation in Eqs. (17a) and (C12), respectively] and expressions (4a) and (4b) for the unperturbed MOs and finally arrive at expression (25) in Sec. III for the coefficients $\boldsymbol{\beta}_{ai}^{B_u}$

$$\boldsymbol{\beta}_{ai}^{B_u} = \frac{1}{2c}\frac{1}{\varepsilon_i^{(0,0)} - \varepsilon_a^{(0,0)}}(\mathbf{C}_{(a)}^{L\dagger}\ \mathbf{C}_{(a)}^{S\dagger})\begin{pmatrix} 2c\mathbf{V}' & \tilde{\boldsymbol{\Lambda}}_{B_u}^{P} \\ \tilde{\boldsymbol{\Lambda}}_{B_u}^{P} & (1/4c^2)\mathbf{W}_{B_u} - \tilde{\boldsymbol{\Lambda}}_{B_u}^{P} - (\varepsilon_i^{(0,0)}/2c^2)\tilde{\boldsymbol{\Lambda}}_{B_u}^{P} + (1/2c)\mathbf{W}' \end{pmatrix}\begin{pmatrix} \mathbf{C}_{(i)}^{L} \\ \mathbf{C}_{(i)}^{S} \end{pmatrix}. \tag{C14}$$

## APPENDIX D: DERIVATION OF THE RELATION BETWEEN THE COEFFICIENTS FOR THE LARGE AND SMALL COMPONENT FOR THE RKB BASIS IN THE NONRELATIVISTIC LIMIT ($\lim_{c\to\infty} \mathbf{C}^S_{(i)} = \mathbf{C}^L_{(i)}$)

First we rewrite expression (5) into two equations:

$$\mathbf{V}\mathbf{C}^L_{(i)} + \mathbf{T}\mathbf{C}^S_{(i)} = \varepsilon_i \mathbf{S}\mathbf{C}^L_{(i)}, \tag{D1}$$

$$\mathbf{T}\mathbf{C}^L_{(i)} + \left(\frac{1}{4c^2}\mathbf{W} - \mathbf{T}\right)\mathbf{C}^S_{(i)} = \varepsilon_i \frac{1}{2c^2}\mathbf{T}\mathbf{C}^S_{(i)}. \tag{D2}$$

In the nonrelativistic limit $c\to\infty$, from Eq. (D2) we immediately obtain

$$\mathbf{T}\mathbf{C}^L_{(i)} = \mathbf{T}\mathbf{C}^S_{(i)}. \tag{D3}$$

If the kinetic-energy matrix is nonsingular, we can finally write

$$\lim_{c\to\infty} \mathbf{C}^S_{(i)} = \mathbf{C}^L_{(i)}. \tag{D4}$$

This "unusual" result is the consequence of the RKB choice of the basis for the small component $\chi^S_\lambda = (1/2c)\vec{\sigma}\cdot\vec{p}\chi_\lambda$. For this basis $\lim_{c\to\infty} \chi^S_\lambda = 0$ holds, and therefore $\lim_{c\to\infty} \varphi^S_i = 0$, and this is the already well-known relation.


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