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Relativistic effects on nuclear magnetic shielding constants in HX and CH₃X (X=Br,I) based on the linear response within the elimination of small component approach

J. I. Melo,^{a)} M. C. Ruiz de Azua,^{b),c)} and C. G. Giribet^{b)}

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Cdad. Universitaria, Pab. 1, 1428 Buenos Aires, Argentina

G. A. Aucar^{b)} and P. F. Provasi

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad Nacional del Nordeste, Avenida Libertad 5300, 3400 Corrientes, Argentina

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Numerical calculations of relativistic effects on nuclear magnetic shielding constants σ corresponding to all one-body operators obtained within a formalism developed in previous work [J. I. Melo *et al.*, *J. Chem. Phys.* **118**, 471 (2003)] were carried out. In this formalism, the elimination of small component scheme is applied to evaluate all quantities entering a four-component RSPT(2) expression of magnetic molecular properties. HX and CH₃X (X=Br,I) were taken as model compounds. Calculations were carried out at the Hartree-Fock level for first-order quantities, and at the random-phase approximation (RPA) level for second- and third-order ones. It was found that values of $\sigma(X)$ are largely affected by several relativistic corrections not previously considered in the bibliography. σ values of the H nucleus are in close agreement with four-component RPA ones. Overall relativistic effects on the shift of $\sigma(X)$ from HX to CH₃X are smaller than the nonrelativistic shifts. © 2004 American Institute of Physics. [DOI: 10.1063/1.1787495]

I. INTRODUCTION

NMR spectral parameters in heavy atom containing compounds are very sensitive to relativistic effects. From a theoretical point of view, in the last years four-component formalisms for the calculation of the magnetic shielding tensor and indirect spin-spin coupling tensor based on the Dirac-Hartree-Fock approach were developed.¹⁻⁶ In parallel, different decoupling schemes aiming to reduce the calculation to one based in two-component spinors and to avoid explicit calculation of negative energy states (“positronic” states) were considered. In particular, for the calculation of the nuclear magnetic shielding tensor, different theoretical methods were presented based on the Breit Pauli Hamiltonian,⁷⁻⁹ zeroth order regular approximation (ZORA),^{10,11} and Douglas-Kroll-Hess (DKH)¹²⁻¹⁴ approaches. It was shown that in addition to relativistic effects on the unperturbed molecular states, there are other field-dependent operators that must be considered in order to take account of relativistic effects consistently. In fact, some of these newly found operators yield very important values to the magnetic shielding constants of the heavy nuclei.⁵ However, numerical results of different methods are very different in some instances. Early four-component results were obtained within the “diamagnetic approximation,” in which the diamagnetic contribution to magnetic properties is evalu-

ated with the relativistically corrected molecular ground state but with the nonrelativistic diamagnetic operator. It was recently shown that this procedure may largely underestimate the effect of “electron-positron rotations” in the calculation of the nuclear magnetic shielding tensor.⁶

Recently, we have presented a new approach based on the elimination of small component (ESC) scheme.¹⁵ In it, the relativistic four-component second-order (Rayleigh-Schrodinger perturbation theory) RSPT-like expression of magnetic properties which are bilinear in the magnetic potential were considered. The ESC procedure was applied to reduce the evaluation of all the required quantities in terms of two-component spinors which are solutions of the molecular Breit-Pauli Hamiltonian. As a consequence, the lowest order (in $1/c$) relativistic effects are consistently obtained. They are expressed as one- and two-body operators entering RSPT corrections of order 1, 2, and 3 to the Schrödinger molecular state energy. For clarity, we will identify our scheme as the linear response (LR) ESC formalism, since the four-component RSPT(2) expression reflects the linear response of the system to a magnetic field. Manninen *et al.* have also extended previous work within the Breit Pauli Hamiltonian.⁹ The LR-ESC and Manninen *et al.* approaches are closely related. However, different expressions for closely related operators are found. The existence of a sum rule connecting both approaches was proven in Ref. 15. In preliminary calculations based on the LR-ESC approach, numerical results for some newly found operators were presented.¹⁶

In the present work, numerical calculations of all one-

^{a)}With a fellowship from Universidad de Buenos Aires.

^{b)}Member of “Carrera del Investigador,” CONICET.

^{c)}Author to whom correspondence should be addressed. Electronic mail: azua@df.uba.ar

body relativistic corrections to the magnetic shielding constant found within the LR-ESC approach are presented. In order to compare the obtained results with benchmark four-component results obtained within the Dirac-Fock approach,⁵ all calculations are carried out within the Hartree-Fock approximation for first-order quantities, and within the random-phase approximation (RPA) for second- and third-order ones. The hydrogen halides HX and methyl halides CH₃X (X = Br, I) are taken as model compounds. The nuclear magnetic shielding constant of the heavy and light nuclei are considered.

II. THEORETICAL APPROACH

In the LR-ESC approach,¹⁵ the starting point is the relativistic four-component RSPT(2)-like expression of magnetic molecular properties which are bilinear in the magnetic potential. Application of the ESC scheme to both the no virtual pair and the virtual pair creation parts of the four-component expression leads to a two-component formalism. In it, a whole set of one- and two-body operators describing the lowest order (in $1/c$) relativistic effects starting from the Schrödinger Hamiltonian are obtained. Relativistic corrections to both the diamagnetic and paramagnetic terms of the nuclear magnetic shielding tensor are expressed as first-, second-, and third-order RSPT corrections to the Schrödinger ground state molecular energy. In the present work all one-body operators thus obtained are considered. For the sake of clarity, following Ref. 9 they are separated as: (i) “passive” effects, i.e., those originated by considering relativistic effects on the magnetically unperturbed molecular states; and (ii) “active” effects, i.e., relativistic effects which are specific of the magnetic interaction and which are described by magnetic field-dependent operators.

The details of the theory in which the present work is based are extensively discussed in Ref. 15. Only a brief account is presented here. Although the same units as in Ref. 15 are used (atomic units), a constant factor β is introduced in all equations in order to make it simple to change to SI units. In a.u. $\beta = 1/2mc$ and in SI units $\beta = e/2m$. Additionally, in SI units a factor $\mu_0/4\pi$ must be added to the nuclear magnetic moment μ_M .

A. Passive relativistic effects

These correspond to inclusion of relativistic corrections to the (magnetically) unperturbed molecular states. One-body operators yielding this type of corrections can be divided into (a) spin-dependent operators; and b) scalar operators.

1. Passive spin-dependent operator

Here we consider the familiar spin-orbit correction

$$H^{\text{SO}} = \frac{1}{4m^2c^2} \sigma(\nabla V_C \times p), \quad (1)$$

where σ stands for the two-component Pauli matrices and V_C stands for the Coulomb potential of the (fixed) nuclei of the molecule. The spin-orbit relativistic correction to the magnetic shielding tensor is obtained within third-order perturba-

tion theory including the Fermi contact (FC), spin-dipolar (SD), and orbital Zeeman (OZ) operators. Taking into account the notation introduced in Ref. 15 the operators involved are

$$O^{1S}(B) = H^{\text{OZ}} = \beta LB, \quad (2)$$

$$O^{1T}(\mu_M) = H^{\text{FC}} + H^{\text{SD}}, \quad (3)$$

$$H^{\text{FC}} = \frac{8\pi}{3} \beta \sigma \mu_M \delta(r_M), \quad (4)$$

$$H^{\text{SD}} = \beta \sigma \left(\frac{3(\mu_M r_M) r_M - r_M^2 \mu_M}{r_M^5} \right), \quad (5)$$

where μ_M is the nucleus magnetic moment and r_M stands for the electron position with respect to nucleus M .

The corresponding correction to the magnetic shielding tensor will be identified as

$$\sigma^{\text{SO}} = \langle\langle H^{\text{FC}} + H^{\text{SD}}; H^{\text{OZ}}; H^{\text{SO}} \rangle\rangle, \quad (6)$$

where it must be understood that the tensor components of σ^{SO} are obtained by factoring out the vector components of μ_M to the left and those of B to the right. Taking this convention into account no explicit subscripts for tensor components will be included in what follows. The symbol $\langle\langle A; B; C \rangle\rangle$ is used to indicate the third-order energy correction corresponding to static perturbations A , B , and C .¹⁷

2. Passive scalar operators

Scalar one-body corrections correspond to the mass-velocity (Mv) and one-body Darwin (Dw) corrections

$$H^{\text{Mv}} = -\frac{1}{8m^3c^2} p^4, \quad (7)$$

$$H^{\text{Dw}} = \frac{1}{4m^2c^2} \nabla^2 V_C. \quad (8)$$

Relativistic corrections to the magnetic shielding tensor are obtained as third-order RSPT expressions for the paramagnetic component σ^p and as second-order RSPT expressions for the diamagnetic component σ^d , as follows:

$$\sigma(\text{Mv}) = \sigma^p(\text{Mv}) + \sigma^d(\text{Mv}), \quad (9)$$

$$\sigma(\text{Dw}) = \sigma^p(\text{Dw}) + \sigma^d(\text{Dw}). \quad (10)$$

Here

$$\sigma^p(\text{Mv}) = \langle\langle H^{\text{PSO}}; H^{\text{OZ}}; H^{\text{Mv}} \rangle\rangle, \quad (11)$$

$$\sigma^p(\text{Dw}) = \langle\langle H^{\text{PSO}}; H^{\text{OZ}}; H^{\text{Dw}} \rangle\rangle, \quad (12)$$

$$\sigma^d(\text{Mv}) = \langle\langle H^{\text{Dia}}; H^{\text{Mv}} \rangle\rangle, \quad (13)$$

$$\sigma^d(\text{Dw}) = \langle\langle H^{\text{Dia}}; H^{\text{Dw}} \rangle\rangle, \quad (14)$$

where

$$H^{\text{PSO}} = O^{1S}(\mu_M) = 2\beta \frac{\mu_M L_M}{r_M^3}, \quad (15)$$

$$H^{\text{Dia}} = \frac{\beta}{c} \left[(\mu_M B) \left(\frac{r_M r_0}{r_M^3} \right) - (\mu_M r_0) \left(\frac{r_M B}{r_M^3} \right) \right], \quad (16)$$

where L_M is the electron angular momentum with respect to nucleus M ; and r_0 is the electron position from the uniform magnetic field gauge origin. The symbol $\langle\langle A; B \rangle\rangle$ indicates the second-order energy correction for static perturbations A, B .¹⁷

B. Active relativistic effects

Magnetic field dependent operators yielding relativistic corrections at the lowest order in $1/c$ are obtained when the effects of the small component and “normalization” of the large component are taken into account within the ESC approach in the evaluation of the magnetic interaction matrix elements between four-component spinors yielding both the diamagnetic and paramagnetic terms.¹⁵ One-body operators thus obtained can also be classified as (a) spin-dependent operators and (b) scalar operators.

1. Active spin-dependent operators

Spin-dependent operators were found to be [Eq. (44b) in Ref. 15]

$$O^{3T}(B) = H^{\text{SZ-K}} + H^{\text{BSO}}, \quad (17)$$

$$H^{\text{SZ-K}} = -\frac{\beta}{4m^2c^2} [3(\sigma B)p^2 - (\sigma p)(pB)], \quad (18)$$

$$H^{\text{BSO}} = \frac{\beta}{2mc^2} \nabla V_C \times (B \times r_0), \quad (19)$$

where the acronym SZ-K refers to the combination of the spin Zeeman and kinetic energy operators and BSO refers to the magnetic field dependent part of the spin-orbit operator. Corrections to the magnetic shielding tensor involving these operators are as follows:

$$\sigma(\text{SZ-K}) = \langle\langle H^{\text{FC}} + H^{\text{SD}}; H^{\text{SZ-K}} \rangle\rangle, \quad (20)$$

$$\sigma(\text{BSO}) = \langle\langle H^{\text{FC}} + H^{\text{SD}}; H^{\text{BSO}} \rangle\rangle. \quad (21)$$

2. Active scalar operators yielding relativistic corrections to the paramagnetic component of σ

Scalar field-dependent operators obtained when the effect of the small component and normalization of the large component of a given four-component spinor is expanded to order c^{-3} combine the PSO and OZ operators on one hand, and the kinetic energy operator on the other,

$$O^{3S}(B) = H^{\text{OZ-K}} = -\frac{\beta}{2m^2c^2} (LB)p^2, \quad (22)$$

$$O^{3S}(\mu_M) = H^{\text{PSO-K}} = -\frac{\beta}{2m^2c^2} \left\{ \frac{\mu_M L_M}{r_M^3}; p^2 \right\}, \quad (23)$$

where the curly brackets stand for the anticommutator. These operators yield relativistic corrections to the magnetic shielding tensor when combined with the OZ and PSO operators in RSPT(2) expressions. We thus define

$$\sigma(\text{OZ-K}) = \langle\langle H^{\text{PSO}}; H^{\text{OZ-K}} \rangle\rangle, \quad (24)$$

$$\sigma(\text{PSO-K}) = \langle\langle H^{\text{PSO-K}}; H^{\text{OZ}} \rangle\rangle. \quad (25)$$

3. Active relativistic corrections to the diamagnetic component of σ

A set of magnetic field dependent operators bilinear in μ_M and B are also obtained correcting the diamagnetic term of the magnetic shielding tensor,

$$H^{\text{Dia-K}} = -\frac{\beta^2}{mc^2} \left[\sum_{i,j=x,y,z} 4A_{Mi}A_{Bj}p_i p_j + 2(A_M A_B)p^2 + 2\pi(\mu_M B)\delta(r_M) \right], \quad (26)$$

where A_M and A_B stand for the vector potential of the nucleus magnetic field and uniform magnetic field, respectively. The last term expression holds only when the gauge origin is placed at the nucleus position.¹⁵ This operator can be reexpressed to give

$$H^{\text{Dia-K}} = -\frac{\beta^2}{mc^2} \left[2 \left(\frac{\mu_M L_M}{r_M^3} \right) (BL_M) + BB_M + 2(A_M A_B)p^2 + 2\pi(\mu_M B)\delta(r_M) \right], \quad (27)$$

where B_M stands for the nuclear magnetic field. The corresponding contribution to the magnetic shielding tensor is obtained within first-order perturbation theory and will be identified as $\sigma(\text{Dia-K})$.

In what follows, numerical results for all the above mentioned relativistic corrections to the isotropic magnetic shielding constants in HX and CH_3X ($X = \text{Br}, \text{I}$) are discussed. Calculations were carried out at the Hartree-Fock level for first-order quantities and at the RPA level for second- and third-order ones. Calculations of σ^{SO} , $\sigma(\text{Mv})$, $\sigma(\text{Dw})$, $\sigma(\text{SZ-K})$, and $\sigma(\text{BSO})$ were carried out with the DALTON program.¹⁸ As part of the present work, the program was modified to calculate the $\sigma(\text{Dia-K})$ term. Calculations of $\sigma(\text{OZ-K})$ and $\sigma(\text{PSO-K})$ were carried out with a modification of the SYSMO^{16,19} program. Matrix elements of $H^{\text{OZ-K}}$, $H^{\text{PSO-K}}$, and $H^{\text{Dia-K}}$ were calculated in an approximate way as the product of (at most two) matrix representations of suitable operators in the vector space spanned by the atomic orbitals (AOs) basis set. For $H^{\text{OZ-K}}$ and $H^{\text{PSO-K}}$ the products of the H^{OZ} and H^{PSO} operators with the kinetic energy operator were carried out. For $H^{\text{Dia-K}}$ the product of the H^{Dia} operator with the kinetic energy operator and the product of the PSO operator with the OZ operator were carried out. The numerical accuracy of matrix elements calculated in this way depends strongly on the basis set quality. However, it is worthy to note that the kinetic energy operator does not change the angular dependence of a given basis set function. As a consequence, if the kinetic energy operator acts on a basis set function belonging to a given “1” orbital angular momentum, the result is a function with the same 1. Therefore, in order for the approximate matrix elements to be correct, it is only needed that the basis set be flexible enough within a

given 1 angular momentum. The combination of the PSO and OZ operators in principle requires addition of 1+1 and 1−1 AOs in the basis set.

The basis sets used in this work are based on the Sadlej^{20,21} and aug-ccpVTZ^{22–24} basis sets. These basis sets have been optimized for the calculation of the Fermi contact (FC) term of J couplings by adding tight *s* functions and optimizing the contraction schemes in previous work.²⁵ These modified basis sets are identified by the acronyms Sad-J and aug-J and the contraction schemes in the (uncontracted/contracted) notation are as follows. For the Sad-J basis set they are: Br, [19*s*12*p*8*d*2*f*/11*s*9*p*8*d*2*f*]; I, [23*s*15*p*13*d*3*f*/16*s*13*p*13*d*3*f*]; C, [14*s*6*p*4*d*/9*s*5*p*4*d*]; H, [10*s*4*p*/6*s*4*p*]. For the aug-J basis set they are: Br, [21*s*15*p*10*d*3*f*/11*s*10*p*10*d*3*f*]; I, [25*s*18*p*13*d*3*f*/15*s*13*p*13*d*3*f*]; C, [15*s*6*p*3*d*1*f*/9*s*5*p*3*d*1*f*]; H, [10*s*3*p*1*d*/6*s*3*p*1*d*]. In some cases different uncontraction schemes have been carried out in order to analyze the numerical convergence of the obtained results. The acronyms Sad-J-un and aug-J-un are adopted for the fully uncontracted basis sets. In some instances, the fully uncontracted basis sets were further enlarged by adding three tight AOs of *s*, *p*, and *d* symmetry with exponents in the ratio 3:1 starting from the largest exponent, and three diffuse AOs of symmetry *d* and *f* with exponents in the ratio 1:3 starting from the smaller exponent in the original basis set. Such basis sets are identified by the acronyms Sad-J-un3 and aug-J-un3. Cartesian AOs obtained from the uncontracted Sadlej and aug-ccpVTZ basis sets were used to carry out the calculations in the SYSMO program. Geometric parameters of HX and CH₃X (X=Br,I) were taken from Ref. 26.

III. RESULTS

A. Passive relativistic effects

1. Passive spin-orbit corrections

The spin-orbit correction σ^{SO} is the most widely discussed contribution to relativistic effects on shieldings because of its importance in affecting the light nuclei in the vicinity of a heavy atom. Numerical results for this correction are available in the bibliography for HX within density functional theory (DFT) (Refs. 27–29), CHF (or RPA) (Refs. 30–32), and correlated complete active space (CAS)/RAS (Refs. 33 and 34) approaches and for the shieldings of the light nuclei in CH₃X (Refs. 27 and 33). From these works a clear idea on the relative importance of the SD and two-body SO operators can be conveyed,^{5,29,33} as well as on the sensitivity of these contributions to correlation effects.³³ Taking these facts into account, the most interesting results sought here are to analyze the performance of the aug-J and Sad-J basis sets in the calculation of this term at the RPA level, and to see the shift on the shieldings of the heavy nuclei when going from HX to CH₃X.

Results of the FC and SD contributions to σ^{SO} in HX and CH₃X (X=Br,I) are displayed in Table I. It is seen that very similar values are obtained with both the aug-J and Sad-J basis sets. The only exception occurs for the SD term of $\sigma(\text{I})$ in HI. Calculations with the fully uncontracted basis sets were carried out for HBr, HI, and CH₃Br. In all cases,

TABLE I. One body passive (third-order) spin-orbit correction to magnetic shielding constants σ in HX and CH₃X at the RPA level for the aug-J and Sad-J basis sets. Values in ppm.

| Molecule | Nucleus | FC | | SD | |
|--------------------|-------------------|--------|--------|-------|-------|
| | | aug-J | Sad-J | aug-J | Sad-J |
| HBr | Br ^{a,b} | 27.92 | 28.14 | 11.98 | 11.85 |
| | | 27.97 | 28.12 | 9.94 | 9.93 |
| | | 28.07 | 27.74 | 9.43 | 9.17 |
| CH ₃ Br | Br ^a | 18.55 | 17.66 | 22.87 | 22.41 |
| | | | 17.65 | | 20.45 |
| HI | I ^a | 109.67 | 110.45 | 69.76 | 57.52 |
| | | 109.77 | 110.58 | 47.41 | 52.29 |
| CH ₃ I | I | 83.44 | 84.85 | d | 85.21 |
| HBr | H ^{a,b} | 5.83 | 5.99 | 0.23 | 0.11 |
| | | 5.82 | 6.00 | 0.23 | 0.11 |
| | | 5.83 | 5.83 | 0.23 | 0.19 |
| HI | H ^a | 19.29 | 19.16 | 0.54 | 0.45 |
| | | 19.27 | 19.16 | 0.45 | 0.54 |
| CH ₃ Br | C ^a | 16.39 | 16.45 | −1.03 | −1.05 |
| | | | 16.44 | | −1.05 |
| CH ₃ I | C | 51.67 | 50.92 | −4.58 | −4.39 |
| CH ₃ Br | H ^a | −0.05 | −0.07 | c | c |
| | | | −0.06 | | |
| CH ₃ I | H | −0.65 | −1.03 | | |

^aCalculation with the fully uncontracted basis set.

^bCalculation with the fully uncontracted basis set, enlarged with three tight and three diffuse AOs. See text for details.

^cAbsolute value smaller than 0.01 ppm.

^dResponse calculation did not converge.

the FC contribution to σ^{SO} of all nuclei is hardly affected. This feature can be related to the optimization scheme of the aug-J and Sad-J basis sets.²⁵ Uncontraction of the basis sets has a significant effect on the SD contribution to σ^{SO} . This trend could be an indication of the need of higher angular momentum basis set functions at the inner shells in order to obtain reliable results of this term. In the case of HBr convergence of results was explicitly verified by enlarging further the basis sets. For both $\sigma(\text{Br})$ and $\sigma(\text{H})$ only minor changes are found with the aug-J-un3 and Sad-J-un3 basis sets.

Results for $\sigma(X)$ in HX (X=Br,I) are in excellent agreement with previous works.^{5,9,33} It is interesting to note that calculations within the DKH approach¹² agree well with the ESC-RPA ones. In CH₃X the shielding effect of the FC term of $\sigma^{\text{SO}}(X)$ is smaller by ≈ 10 ppm for X=Br and 25 ppm for X=I as compared to that in HX. The SD contribution nearly cancels this trend, as it changes oppositely by nearly the same amount for a given basis set. However, it has been shown that when correlation effects are taken into account, the SD contribution to $\sigma^{\text{SO}}(X)$ in HX is much smaller than the FC one.⁹ The RPA calculated change from HX to CH₃X could also be largely overestimated.

Results for the light nucleus directly bonded to the heavy atom are in excellent agreement with previous RPA results

TABLE II. Passive scalar corrections to the diamagnetic and paramagnetic terms of magnetic shielding constant of nucleus N in HX and CH_3X originating in the mass-velocity (Mv) and one-body Darwin (Dw) operators, at the RPA level, with the aug-J and Sad-J basis sets. Values in ppm.

| Molecule | N | $\sigma(\text{Mv})$ | | $\sigma(\text{Dw})$ | | σ^{sc} | |
|--------------------|-------------------|---------------------|--------|---------------------|---------|----------------------|--------|
| | | aug-J | Sad-J | aug-J | Sad-J | aug-J | Sad-J |
| BrH | Br ^{a,c} | 166.43 | 159.35 | -101.19 | -95.12 | 65.24 | 64.22 |
| | | 154.20 | 159.06 | -101.57 | -101.42 | 52.63 | 57.64 |
| | | 153.51 | 154.85 | -101.57 | -101.48 | 51.94 | 53.37 |
| CH ₃ Br | Br ^{b,c} | 168.82 | 162.39 | -98.11 | -92.33 | 70.71 | 70.07 |
| | | 156.04 | 161.86 | -98.48 | -98.64 | 57.56 | 63.22 |
| | | 155.34 | 156.79 | -98.49 | -98.43 | 56.85 | 58.36 |
| IH | I ^{a,c} | 548.84 | 548.98 | -348.39 | -347.54 | 200.45 | 201.44 |
| | | 501.43 | 525.73 | -348.45 | -348.06 | 152.98 | 177.67 |
| | | 497.96 | 504.04 | -348.69 | -348.50 | 149.27 | 155.54 |
| CH ₃ I | I ^{b,c} | 565.10 | 515.95 | -318.95 | -320.38 | 246.15 | 195.57 |
| | | 483.14 | 511.98 | -333.05 | -332.48 | 150.09 | 179.50 |
| | | 479.42 | | | | | |
| BrH | H ^{a,c} | -1.21 | -0.48 | -0.30 | -0.69 | -1.50 | -1.17 |
| | | -1.61 | -0.99 | -0.13 | -0.44 | -1.74 | -1.43 |
| | | -1.25 | -1.63 | -0.31 | -0.13 | -1.56 | -1.76 |
| IH | H ^a | -3.53 | -2.65 | -0.19 | -0.52 | -3.72 | -3.35 |
| | | -3.75 | -2.98 | -0.11 | -0.73 | -3.86 | -3.71 |
| CH ₃ Br | C ^c | -2.04 | -1.54 | -0.28 | -0.55 | -2.32 | -2.09 |
| | | -2.15 | | -0.29 | | -2.44 | |
| CH ₃ I | C | -5.79 | -6.61 | -0.12 | 0.31 | -5.91 | -6.31 |
| CH ₃ Br | H | -0.91 | -0.49 | 0.04 | -0.19 | -0.87 | -0.68 |
| CH ₃ I | H | -1.29 | -1.99 | -0.28 | 0.06 | -1.57 | -1.93 |

^aFully uncontracted basis set.

^bBasis set uncontracted at the heavy atom.

^cFully uncontracted basis set plus three tight plus three diffuse AOs. See text for details.

for H in HX ^{5,9,33} and C in CH_3X .³³ It is worthy to note that for H in HX it has been shown that the two-body SO contributions are small but non negligible.^{5,29,33} DKH results are very similar in BrH and somewhat smaller in HI.¹² For the H nuclei two bonds away of the heavy atom in CH_3X small but non-negligible deshielding effects are found for $X=I$, in agreement with previous work.³³

2. Passive scalar relativistic corrections

Mv and Dw corrections [Eqs. (9) and (10)] yield the scalar correction σ^{sc} ,

$$\sigma^{\text{sc}} = \sigma(\text{Mv}) + \sigma(\text{Dw}). \quad (28)$$

In Table II we present results of $\sigma(\text{Mv})$, $\sigma(\text{Dw})$, and σ^{sc} calculated at the RPA level for all shielding constants in HX and CH_3X . Darwin corrections on $\sigma(X)$ ($X=Br,I$) can be considered converged for the uncontracted basis sets, as addition of tight and diffuse AOs to the uncontracted basis sets yields only minor changes in all cases. In CH_3Br a systematic shift in the Darwin correction to $\sigma(\text{Br})$ of ≈ 3 ppm with respect to HBr is obtained consistently with all basis sets. The shift of $\sigma(\text{I})$ from HI to CH_3I is 15.64 and 16.02 ppm for the aug-J-un and Sad-J-un basis sets, respectively.

Completely different conclusions hold for the mass-velocity correction on the shielding constants of Br, I. It is worthy to note that in all cases $\sigma(\text{Mv})$ and $\sigma(\text{Dw})$ carry opposite signs and the first roughly doubles the second in absolute value. Such relation can be traced to the existence of a δ -type contribution upon the action of the p^4 operator on s -type AOs. In fact, for an s -type AO in a Coulomb potential $V = -Z/r_N$ it holds (in a.u.),

$$p^2 \phi_s = 2(E - V) \phi_s \quad (29)$$

and

$$p^4 \phi_s = 2E p^2 \phi_s - p^2 V \phi_s \\ = 4(E - V)^2 \phi_s + 4\pi Z \delta(r_N) \phi_s - 2i(\nabla V) p \phi_s. \quad (30)$$

It can therefore be considered that in the mass-velocity correction there is a δ -type contribution with a factor of -2 compared to that in the Darwin term. Looking at the corresponding values of both corrections it can be concluded that such contribution plays an important role in $\sigma(\text{Mv})$. However, the action of p^4 on other type of inner shell AOs, especially p -type AOs, could also yield large contributions to $\sigma(\text{Mv})$. For this reason, as it is seen in Table II, values of $\sigma(\text{Mv})$ for the heavy nuclei change significantly when the flexibility of the basis set is augmented for the inner shell

TABLE III. Active spin-dependent corrections to the magnetic shielding constant of nucleus N in HX and CH_3X , at the RPA level, with basis sets aug-J and Sad-J. Values in ppm.

| Molecules | N | $\sigma(\text{SZ-K})$ | | | | $\sigma(\text{BSO})$ | | | |
|------------------------|--------------------------|-----------------------|--------|-------|-------|----------------------|---------|--------|--------|
| | | FC | | SD | | FC | | SD | |
| | | aug-J | Sad-J | aug-J | Sad-J | aug-J | Sad-J | aug-J | Sad-J |
| BrH | $\text{Br}^{\text{a,c}}$ | 731.86 | 699.82 | 4.14 | 2.98 | -189.25 | -181.23 | 9.76 | 8.66 |
| | | 733.80 | 732.92 | 4.15 | 2.99 | -189.67 | -189.43 | 9.74 | 8.63 |
| | | 733.80 | 732.92 | 18.81 | 18.32 | -189.67 | -189.43 | 29.21 | 28.37 |
| CH_3Br | $\text{Br}^{\text{a,c}}$ | 731.91 | 699.87 | 4.14 | 2.98 | -189.25 | -181.23 | 9.78 | 8.67 |
| | | 733.84 | 732.97 | | | -189.67 | -189.44 | 9.76 | 8.65 |
| | | | 732.99 | 18.81 | 18.32 | -189.68 | -189.45 | 29.23 | 28.38 |
| IH | $\text{I}^{\text{a,c}}$ | 2578.3 | 2573.8 | 27.50 | 20.06 | -646.3 | -647.1 | 48.14 | 41.12 |
| | | 2579.31 | 2576.9 | 26.98 | 21.25 | -661.97 | -661.4 | 48.62 | 42.54 |
| | | 2579.32 | 2576.9 | 70.08 | 69.10 | -661.97 | -661.4 | 111.50 | 109.09 |
| CH_3I | $\text{I}^{\text{b,c}}$ | 2516.0 | 2518.7 | 27.50 | 20.06 | -661.7 | -660.6 | 48.17 | 41.16 |
| | | | 2576.9 | | | | -661.4 | | 42.57 |
| | | 2579.4 | | 70.08 | | -662.0 | | 111.53 | |
| BrH | H^{a} | -0.02 | -0.02 | 0.0 | 0.0 | 0.05 | 0.05 | 0.0 | 0.0 |
| | | -0.02 | -0.02 | 0.0 | 0.0 | 0.05 | 0.05 | 0.0 | 0.0 |
| IH | H^{a} | -0.03 | -0.03 | 0.0 | 0.0 | 0.07 | 0.07 | 0.0 | 0.0 |
| | | -0.03 | -0.03 | 0.0 | 0.0 | | | | |
| CH_3Br | $\text{C}^{\text{a,c}}$ | 3.39 | 3.40 | 0.0 | 0.0 | -0.81 | -0.81 | 0.0 | 0.0 |
| | | | 3.40 | | | | | | |
| | | 3.40 | 3.40 | -0.0 | -0.0 | -0.81 | -0.81 | -0.0 | -0.0 |
| CH_3I | C^{c} | 3.39 | 3.39 | 0.0 | 0.0 | -0.75 | -0.76 | 0.0 | 0.0 |
| | | 3.40 | | 0.05 | | -0.75 | | 0.06 | |
| CH_3Br | H | d | ... | ... | ... | ... | ... | ... | |
| CH_3I | H | ... | ... | ... | ... | ... | ... | ... | |

^aFully uncontracted basis set.^bBasis set uncontracted at the heavy atom.^cFully uncontracted basis set plus tight and diffuse AOs.^dAbsolute value smaller than 0.01 ppm.

AOs. It is seen that values calculated with the aug-J-un basis set are very similar to those of the aug-J-un3 one, but the addition of tight and diffuse AOs changes significantly the values of the Sad-J-un basis set.

The overall effect of the scalar corrections on the magnetic shielding constants of the heavy nuclei is a shielding effect, i.e., in all cases the corresponding value is positive and larger in absolute value than the spin-orbit correction discussed above. The change from HX to CH_3X can be estimated as a shielding effect of ≈ 5 ppm for $X = \text{Br}$, but only a very small change of 2 ppm is found for $X = \text{I}$. The chemical shift effect is smaller for the heavier element.

Results of σ^{sc} for the light nucleus directly bonded to the halogen atom displayed in Table II show small but non-negligible deshielding effects for both the H nucleus in HX and the C nucleus in CH_3X . Such contribution is opposite to that of the spin-orbit correction. It is worthy to note that in these calculations the gauge origin was placed at the nucleus of interest in each case. In all cases the scalar relativistic correction is dominated by the mass-velocity term. Even though results are not fully converged with respect to the basis set, differences in all calculated values of a given term

are less than 0.4 ppm. Results of the scalar correction σ^{sc} for the H nucleus two bonds away from the heavy nucleus in CH_3X are also small and negative but non negligible. In this case the spin-orbit correction was also small and negative.

Scalar relativistic effects were considered in early works.^{32,35} It was recognized that this contribution is very small in the relativistic correction of the magnetic shielding constant of a light nucleus in the vicinity of a heavy atom. Wolff and Ziegler²⁷ also included scalar effects in DFT calculations of the spin-orbit correction on magnetic shielding constants of light nuclei in HX and CH_3X . The present results for the heavy nucleus in HX are in very good agreement with recent work by Manninen *et al.*,⁹ but results for the H nucleus are not comparative, as the authors used a fixed gauge origin at the heavy nucleus position, and the present one considers a fixed gauge origin at the light nucleus position.

B. Active relativistic effects

1. Active spin-dependent terms

Contributions $\sigma(\text{SZ-K})$ and $\sigma(\text{BSO})$ [Eqs. (20) and (21)] are now considered. These terms are closely related to the

mass correction (MC) term first obtained by Fukui, Baba, and Inomata⁷ and evaluated explicitly in different works,^{5,9,36} and to the second-order spin-orbit term, also obtained by Fukui, Baba, and Inomata⁷ and numerically evaluated by Fukui, Baba, and Inomata⁷ and Manninen *et al.*⁹ and by Vaara, Ruud, and Vahtras in HX and CH₃X at the RPA and CAS/RAS levels.³⁴ It should be kept in mind that within the theory developed in Ref. 15 both terms carry different constant factors, there is a spin-dipolar (SD) contribution to $\sigma(\text{SZ-K})$ and there is no two-body contribution from the second-order spin-orbit term. These differences should be kept in mind when comparing numerical results from different works. It was explicitly shown in Ref. 15 that there is a sum rule connecting operators of the present work to those of Refs. 7 and 9.

In Table III we present results of the $\sigma(\text{SZ-K})$ and $\sigma(\text{BSO})$ terms calculated at the RPA level for all shielding constants in HX and CH₃X. It is worthy to note that basis sets Sad-J and aug-J were explicitly optimized for the calculation of the FC term of indirect spin-spin couplings and therefore they can be expected to be adequate for the calculation of the FC term of these relativistic effects.

Results for the heavy nuclei X ($X = \text{Br}, \text{I}$) show that the FC components of both $\sigma(\text{SZ-K})$ and $\sigma(\text{BSO})$ take very similar values for the aug-J and the uncontracted basis sets. The corresponding values can be considered to be converged with respect to the basis set, as further enlargement of the uncontracted basis sets yields only minor changes on the obtained results. Completely different comments apply to results of the SD component of both $\sigma(\text{SZ-K})$ and $\sigma(\text{BSO})$: in this case addition of tight and diffuse AOs to the uncontracted basis sets changes dramatically the obtained results. It can be concluded that in order to correctly reproduce the action of the SD operator on inner shell AOs of the heavy nuclei large flexibility of the AOs basis set is needed. A negligibly small shift of these relativistic effects is found from HX to CH₃X. This may be an indication that such terms are largely dominated by contributions from inner shell AOs. In fact it was explicitly shown by Gómez, Romero, and Aucar³⁶ that this is the case for the MC contribution by carrying out a localized molecular orbitals decomposition.

Values of $\sigma(\text{SZ-K})$ and $\sigma(\text{BSO})$ obtained for the H nucleus in both HX and CH₃X are negligibly small in all cases. The overall value of ≈ 2.5 ppm found for the C nucleus in both CH₃Br and CH₃I is found to be independent of the heavy nucleus. Therefore it can be speculated that this is not a relativistic effect originated in the heavy atom and transmitted to the C one, but this effect is strictly originated in the C electrons.

As mentioned above, contributions from operators closely related to those considered in the present work were numerically analyzed by different authors. The MC term⁷ was quantitatively analyzed by Visscher *et al.* in HX compounds.⁵ It was decomposed into molecular orbital (MO) contributions by Gómez, Romero, and Aucar.³⁶ Calculations of the second-order spin-orbit term were carried out in HX^{7,34} and CH₃X.³⁴ Recently, both the MC and second-order spin-orbit terms were carefully analyzed by Manninen *et al.*⁹ When the constant factors connecting different approaches

TABLE IV. Active scalar second-order relativistic effects $\sigma(\text{OZ-K})$ and $\sigma(\text{PSO-K})$ on nucleus N in HX and CH₃X ($X = \text{Br}, \text{I}$) at the CHF approximation with the Sadlej basis set^a. Values in ppm.

| Molecule | N | $\sigma(\text{OZ-K})$ | $\sigma(\text{PSO-K})$ | Total |
|--------------------|-----|-----------------------|------------------------|--------|
| BrH | Br | 34.97 | 22.43 | 57.40 |
| | | 35.48 ^b | 26.69 ^b | 62.17 |
| IH | I | 142.16 | 112.59 | 254.75 |
| | | 143.00 ^b | 125.45 ^b | 268.45 |
| CH ₃ Br | Br | 34.95 | 23.35 | 58.3 |
| CH ₃ I | I | 142.11 | 124.82 | 266.93 |
| BrH | H | 1.35 | 1.34 | 2.69 |
| IH | H | 3.00 | 2.98 | 5.98 |
| CH ₃ Br | C | 0.99 | 1.03 | 2.02 |
| CH ₃ I | C | 2.27 | 2.29 | 4.56 |
| CH ₃ Br | H | 0.78 | 0.78 | 1.56 |
| CH ₃ I | H | 1.82 | 1.81 | 3.63 |

^aCartesian basis set obtained from the fully uncontracted Sadlej basis set (Refs. 20 and 21).

^bCartesian basis set obtained from the fully uncontracted aug-ccpVTZ basis set (Refs. 22–24).

are taken into account, excellent agreement is found in all cases.

2. Active scalar contributions yielding relativistic corrections to the paramagnetic term

Relativistic effects identified as $\sigma(\text{OZ-K})$ and $\sigma(\text{PSO-K})$ in Eqs. (24) and (25) were considered in the bibliography only recently.^{9,15,16} Manninen *et al.*⁹ obtained numerical results of $\sigma(\text{OZ-K})$ for the noble gases, the hydrogen halides, and H₂X compounds. In recent work by Baba and Fukui within the DKH approach, terms closely related to those discussed here were also considered in the “level III” calculation.¹² In the present work, the calculation of both terms was implemented in the SYSMO program¹⁹ at the CHF level. Cartesian AOs obtained from the fully uncontracted Sadlej^{20,21} and aug-ccpVTZ basis sets^{22–24} were used. Results are displayed in Table IV. For the heavy nucleus a shielding effect is obtained from both terms. Values obtained for $\sigma(\text{OZ-K})$ in HX with different basis sets are very stable and in full agreement with those of Manninen *et al.*⁹ The $\sigma(\text{PSO-K})$ value is not fully converged. While the $\sigma(\text{OZ-K})$ term is insensitive to the change of chemical environment from HX to CH₃X, a non-negligible shift is found for $\sigma(\text{PSO-K})$. For the light nuclei non negligible positive values are also found. The value of 5.98 ppm obtained for H in HI is particularly worthy to note, as it represents a significant portion of the full heavy atom effect observed in this case. Values obtained for the H nucleus in CH₃X are also non negligible compared to the remainder relativistic effects.

3. Active scalar relativistic correction to the diamagnetic term

Scalar corrections to the diamagnetic component of the magnetic shielding tensor originated in field-dependent operators are obtained within first-order perturbation theory with the $H^{\text{Dia-K}}$ operator, Eq. (27), and gathered in the $\sigma(\text{Dia-K})$ term. We have separated the total value into two contributions. On one hand, $\sigma_1(\text{Dia-K})$ is the value obtained for the δ -type operators contained in $BB_{\mu N}$ and the last term

TABLE V. Active scalar relativistic corrections to the diamagnetic term of the magnetic shielding constant of nucleus N in HX and CH_3X calculated at the Hartree-Fock level with the aug-J and Sad-J basis sets. Values in ppm.

| Molecule | N | $\sigma_1(\text{Dia-K})$ | | $\sigma_2(\text{Dia-K})$ | | Total | |
|--------------------|-------------------|--------------------------|---------|--------------------------|----------------------|----------|---------|
| | | aug-J | Sad-J | aug-J | Sad-J | aug-J | Sad-J |
| BrH | Br ^{a,c} | -307.62 | -302.15 | -118.25 | -123.90 | -425.87 | -426.05 |
| | | | -307.38 | -153.75 | -153.64 | -461.37 | -461.02 |
| | | -307.62 | -307.38 | -153.76 | -153.66 | -461.38 | -461.04 |
| CH ₃ Br | Br ^{a,c} | -307.63 | -302.15 | -118.27 | -123.91 | -425.90 | -426.06 |
| | | -307.63 | -307.38 | -153.77 ^b | -153.65 | -461.40 | -461.03 |
| | | -307.62 | | | | | |
| IH | I ^{a,c} | -1092.9 | -1092.1 | -433.93 | -447.00 | -1526.8 | -1539.1 |
| | | -1092.9 | -1092.1 | -564.51 | -564.03 | -1657.4 | -1656.1 |
| | | -1092.9 | | -564.51 | | -1657.41 | |
| CH ₃ I | I ^a | -1091.5 | -1092.2 | -446.35 | -447.02 | -1537.9 | -1539.2 |
| | | -1092.9 | -1092.1 | | -564.05 ^b | | -1656.3 |
| BrH | H ^{a,c} | d | d | -1.43 | -1.41 | -1.43 | -1.41 |
| | | | | -1.50 | -1.41 | -1.50 | -1.41 |
| | | | | -1.52 | -1.50 | -1.52 | -1.50 |
| IH | H ^a | d | d | -3.23 | -3.41 | -3.23 | -3.41 |
| | | | | -3.47 | -3.41 | -3.47 | -3.41 |
| CH ₃ Br | C ^a | -1.31 | -1.31 | -1.54 | -1.55 | -2.85 | -2.86 |
| | | -1.31 | -1.31 | | -1.65 | | -2.96 |
| CH ₃ I | C ^a | -1.31 | -1.31 | -3.01 | -3.09 | -4.32 | -4.40 |
| | | -1.31 | | | -3.14 | | -4.45 |
| CH ₃ Br | H | d | d | -0.82 | -0.81 | -0.82 | -0.81 |
| CH ₃ I | H | d | d | -1.55 | -1.57 | -1.55 | -1.57 |

^aFully uncontracted basis set.^bBasis set uncontracted at the heavy atom.^cFully uncontracted basis set plus three tight and three diffuse AOs. See text for details.^dAbsolute value smaller than 0.01 ppm.

of Eq. (27), and is proportional to the electron density at the nucleus site in each case. On the other hand, the term dubbed $\sigma_2(\text{Dia-K})$ gathers the remainder two terms in $H^{\text{Dia-K}}$. Matrix elements of both operators involved have been calculated approximately as the product of the matrix representation of simpler operators, as indicated in Sec. II.

Results are displayed in Table V. The very large overall deshielding effect found for the heavy nuclei has its major contribution from $\sigma_1(\text{Dia-K})$. This highly local contribution is insensitive to the change of chemical environment from HX to CH_3X . The $\sigma_2(\text{Dia-K})$ contribution is also very significant for the heavy nuclei. Very stable values are obtained with different basis sets and negligibly small shifts from HX to CH_3X are found. For the H nucleus in HX , a negligibly small value is found for $\sigma_1(\text{Dia-K})$, and a small deshielding effect is given by $\sigma_2(\text{Dia-K})$. For C in CH_3X , the value given by $\sigma_1(\text{Dia-K})$ is very similar for both $X=\text{Br}$ and $X=\text{I}$. Therefore, it can be considered that this is not a relativistic effect originated in the heavy nucleus and transmitted to the light one, but this value is certainly originated in the inner shell electrons of the C atom. The $\sigma_2(\text{Dia-K})$ contribution is small and negative. Small negative overall values are also found for the H nucleus in CH_3X .

This relativistic correction to the diamagnetic term was

not explicitly considered within the ESC approach until recent work.^{9,15,16} In DKH calculations by Baba and Fukui, terms similar to the ones here presented are considered in the level III calculation.¹²

IV. DISCUSSION

The total relativistic effect on the magnetic shielding constants in HX and CH_3X are summarized in Table VI. The most reliable value of each contribution as discussed in the corresponding section is considered to obtain the total values quoted in Table VI. As mentioned above, the only contributions for which significant differences are found when calculated with the enlarged basis sets are the $\sigma(\text{Mv})$ term and the SD term of the SZ-K and BSO corrections. The shift from HX to CH_3X in the full relativistic correction of the magnetic shielding of the heavy nuclei is very small compared to the individual contributions. It may be seen that relativistic effects yielding the largest corrections are not those yielding the most important contributions to the shift from HX to CH_3X . This is the case, for instance, of $\sigma(\text{SZ-K})$, $\sigma(\text{BSO})$, and $\sigma(\text{Dia-K})$. This fact suggests that such terms originate mainly in the inner-shell electrons, as it was explicitly discussed for the MC term in Ref. 36 and for the Dia-K one in

TABLE VI. Summary of relativistic corrections to the magnetic shielding constant of nucleus N in HX and CH_3X .^a Results in ppm.

| Molecule | N | σ^{NR} | SO | σ^{sc} | SZ-K +BSO | OZ-K+ PSO-K | Dia-K | Total effect | σ^{TOT} |
|------------------------|-----|----------------------|-------------------------------|----------------------|--------------|----------------|----------|-----------------|-----------------------|
| HBr | Br | 2643.54 | 37.50 | 51.94 | 592.15 | 57.40 | -461.38 | 277.61 | 2921.15 |
| CH_3Br | Br | 2619.78 | 38.10 | 56.85 | 591.35 | 58.30 | -461.40 | 286.52 | 2906.30 |
| HI | I | 4540.77 | 157.18 167.97 ^b | 149.27 | 2098.93 | 254.75 | -1657.41 | 1002.73 | 5543.50 |
| CH_3I | I | 4380.57 | 170.06 ^b | 150.09 | 2099.01 | 266.93 | -1656.3 | 1029.78 | 5410.35 |
| HBr | H | 30.94 | 6.06 | -1.56 | 0.03 | 2.69 | -1.52 | 5.70 | 36.64 |
| HI | H | 31.21 | 19.72 | -3.86 | 0.04 | 5.98 | -3.47 | 18.41 | 49.62 |
| CH_3Br | C | 168.30 | 15.39 | -2.44 | 2.58 | 2.02 | -2.96 | 14.59 | 182.89 |
| CH_3I | C | 190.06 | 47.09 | -5.91 | 2.59 | 4.56 | -4.45 | 43.88 | 233.94 |
| CH_3Br | H | 28.49 | -0.07 | -0.87 | <-0.1 | 1.56 | -0.81 | -0.19 | 28.30 |
| CH_3I | H | 29.08 | -0.65 | -1.57 | <-0.1 | 3.63 | -1.57 | -0.53 | 28.92 |

^aThe most reliable values of each term according to results of the corresponding section are considered.

^bValue of the Sad-J basis set.

Ref. 16. A small shielding of the heavy nucleus is obtained from the SO, σ^{sc} , and $\sigma(\text{PSO-K})$ terms. The calculated shift of the nonrelativistic shielding constant calculated at the RPA level with the aug-J-un basis set is a deshielding of 23.76 ppm for $X=\text{Br}$ and 160.20 ppm for $X=\text{I}$. Very close results are obtained with the enlarged basis sets. It is thus seen that the shift from HX to CH_3X of the full shielding constant is largely dominated by the nonrelativistic terms. The effect of the relativistic corrections is to reduce the corresponding values in both cases.

For the light nucleus directly bonded to the heavy atom, we obtain, in agreement with previous studies,³⁰ that the overall relativistic effect is closely reproduced by the SO one in the case of the H nucleus. However, we stress the importance of the other contributions $\sigma(\text{PSO-K})$ and $\sigma(\text{Dia-K})$ to obtain the correct results when the gauge origin is placed at the light nucleus position in fixed gauge origin calculations. For $\sigma(\text{C})$ in CH_3I , the non-SO contribution is of about -3 ppm, which is non negligible.

In Table VII the total magnetic shielding constants in HX are displayed and compared to values from the bibliography. It is important to recall that all calculations in the present work were carried out at the Hartree-Fock and RPA levels of approximation. In doing so we intend to obtain uncorrelated results which can be compared with benchmark four-component results within the RPA-DHF approach.⁵ Other numerical results obtained within the *ab initio* self consistent approach are as follows: ZORA,¹¹ DKH,¹² quasirelativistic DKH,¹⁴ and calculations by Manninen *et al.* based on the Breit Pauli Hamiltonian.⁹

The work by Manninen *et al.*⁹ is based in a formalism which is the closest to that of the present work, and therefore it will be considered with special care. The main differences to be expected in numerical results are as follows: In first place, different expressions for several closely related operators are obtained. However, the existence of a sum rule connecting both formalisms was explicitly proven as part of Ref. 15. When the constant factors of closely related operators are taken into account, excellent agreement is found between both works. Second, Manninen *et al.* did not present numerical results of the PSO-K contribution. And, in third place, the

only relativistic effect on the diamagnetic term explicitly calculated is the one consistent with the diamagnetic approximation of Ref. 5, i.e., only "passive" effects are included. This means that only corrections due to the mass-velocity and Darwin effects on the unperturbed molecular state are considered. In the present work, the $\sigma(\text{Dia-K})$ term collects the remainder relativistic effects on the diamagnetic term. It is very interesting to compare the obtained results. When the PSO-K contribution obtained in this work is added to the total magnetic shielding of the heavy nuclei X in HX ($X=\text{Br},\text{I}$) of Manninen *et al.* (see Table VII), the obtained value is in very close agreement with the four-component results of Visscher *et al.*⁵ It is thus verified that the ESC formalism is an excellent approximation to the full relativistic effect on magnetic shielding constants within the diamagnetic approximation at least for Z of the order of 50.

TABLE VII. Total relativistic magnetic shielding constant of nucleus N in HX ($X=\text{Br},\text{I}$) obtained in this work compared with other values from the bibliography.

| Molecule | N | Present | Four- | ZORA ^b | DKH ^{c,d} | ESC ^e |
|----------|-----|-----------------------------|-------------------------------|-------------------|--------------------|----------------------|
| | | work | component RPA ^a | | | |
| HBr | Br | 2921.15 ^f | 3224.6 | 2851.0 | 3295.4 | 3222.8 |
| | | | | | 3164.9 | 3245.23 ^f |
| HI | I | 5543.50 | 6768.4 | 5487.3 | 7128.9 | 6652.5 |
| | | | | | 6508.5 | 6765.09 ^f |
| HBr | H | 36.64 36.02 ^g | 36.08 | 33.30 | 36.60 | 36.93 |
| | | | | | 37.15 | |
| HI | H | 49.62 48.30 ^g | 47.98 | 41.93 | 48.31 | 50.45 |
| | | | | | 49.72 | |

^aReference 5.

^bReference 11.

^cReference 12.

^dReference 14.

^eReference 9.

^fThe PSO-K contribution obtained in this work is added to Manninen *et al.* (Ref. 9) total relativistic correction.

^gThe two-body spin-orbit contribution taken from Ref. 5 is added to the total value.

However, in the present work very large negative contributions from the $\sigma(\text{Dia-K})$ term are found for the heavy nuclei. As a consequence the full relativistic effect within the present ESC formalism comes very close to the values obtained within the ZORA approach.¹¹ At this point the question whether the ESC and ZORA formalisms yield good approximations to the relativistic magnetic shielding constant including the effect of so called “electron-positron rotations”⁶ remains open. But these values suggest that such effect cannot be neglected when accurate results are sought. Recent work on the noble gas atoms seems to confirm this assertion.⁶ For instance it was found that the Dirac-Fock linear response DF-LR value for the magnetic shielding constant of Xe ($Z=54$) is 6938 ppm,⁶ but the sum of the relativistic shielding considering only “electronic” rotations plus the diamagnetic contribution obtained with the diamagnetic approximation is 7985 ppm. It is thus seen that within this last approach the magnetic shielding constant is overvalued by ≈ 1000 ppm. This result is fully consistent with the findings of the present work for I ($Z=53$): the total value of the ZORA and present LR-ESC approach are ≈ 1200 ppm smaller than the four-component result of Visscher *et al.*⁵ A deeper analysis of this problem is clearly necessary and work along this line is under progress in our group.

Results for the light H nucleus in HX show excellent agreement between the present calculations and those of Manninen *et al.*⁹ and DKH ones.^{12,14} Comparison of individual contributions must be carried out with care as different gauge origins were considered by Manninen *et al.* (gauge origin at the heavy nucleus) and in the present work (gauge origin at the nucleus of interest in each case). It can be concluded that all the neglected contributions in the work by Manninen *et al.* should yield negligibly small or mutually cancelling values when calculated with the gauge origin at the heavy nucleus. For comparison with four-component results of Visscher *et al.* (gauge origin at the heavy nucleus), it is interesting to point out that in four-component RPA calculations two-body effects originating in the Coulomb interaction are taken into account within the mean field approach. Therefore, small differences originating in these contributions should be expected. For instance, the two-body (third-order) spin-orbit contribution yields -1.32 ppm for H in HI and -0.61 ppm for H in HBr.⁵ Although only the spin-same orbit contribution is included in Dirac-Coulomb calculations, these values can be taken as indicative of the differences to be expected. In fact, if such values are added to the total relativistic correction found in this work, agreement with four-component values of Visscher *et al.* becomes excellent. This very important result indicates that the ESC approach is an excellent approximation for the magnetic shielding constant of the light nucleus in the vicinity of a heavy atom for Z as large as 50.

V. CONCLUDING REMARKS

In this work the capability of the LR-ESC approach to reproduce four-component results of the nuclear magnetic shielding constants of the heavy and light nuclei in HX compounds was analyzed. It is seen that LR-ESC results within the diamagnetic approximation match closely four-

component results of Visscher *et al.*⁵ for the magnetic shielding constant of the heavy nucleus. However, when the effect of electron-positron rotations is included within the LR-ESC approach, there are very large negative contributions correcting the diamagnetic term. The numerical accuracy of such contributions should be verified carrying out the corresponding four-component calculations. Results for the H nucleus are also in excellent agreement with four-component values of Visscher *et al.*⁵ It is worthy to mention that in four-component Dirac-Hartree-Fock calculations, two-body effects are included within the mean-field approach. Therefore, a detailed comparison with LR-ESC values may be carried out only if such two-body effects are estimated within the LR-ESC approach. This will be the subject of future work. However, looking at the obtained results it can be expected that such contributions will be very small.

Calculations of the relativistic effect on the nuclear magnetic shielding constant of the heavy nucleus in HX and CH_3X allowed to analyze the sensitivity of different contributions to the change in chemical environment. In fact, some of the largest contributions to the absolute nuclear magnetic shielding constant showed negligibly small shifts from HX to CH_3X . The overall shift is dominated by nonrelativistic effects. A decomposition into molecular orbitals contributions could be a valuable tool to determine the relative importance of inner and valence shell electrons in defining a given relativistic effect.^{16,36}

In the present work all calculations were carried out at the RPA level and compared to RPA four-component calculations.⁵ For comparison with experimental values, correlation effects should also be taken into account, as it is known that such effects may be very important for some relativistic effects discussed in the present work.³³ It is worthy to mention that the theoretical framework in which the present work is based is a four-component many-body RSPT(2) expression of magnetic properties. The inclusion of correlation effects is therefore consistent with the LR-ESC approach and work along these lines is under progress in our research group.

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