The UKB prescription and the heavy atom effects on the nuclear magnetic shielding of vicinal heavy atoms

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Fully relativistic calculations of NMR magnetic shielding on XYH_3 (X = C, Si, Ge and Sn; Y = Br, I), XH_n (n = 1–4) molecular systems and noble gases performed with a fully relativistic polarization propagator formalism at the RPA level of approach are presented. The rate of convergence (size of basis set and time involved) for calculations with both kinetic balance prescriptions, RKB and UKB, were investigated. Calculations with UKB makes it feasible to obtain reliable results for two or more heavy-atom-containing molecules. For such XYH_3 systems, the influence of heavy vicinal halogen atoms on $\sigma(X)$ is such that heavy atom effects on heavy atoms (vicinal plus their own effects or HAVHA + HAHA effects) amount to 30.50% for X = Sn and Y = I; being the HAHA effect of the order of 25%. So the vicinal effect alone is of the order of 5.5%. The vicinal heavy atom effect on light atoms (HALA effect) is of the order of 28% for X = C and Y = I. A similar behaviour, but of opposite sign, is observed for $\sigma(Y)$ for which σ^{R-NR}(I; X = C) (HAHA effect) is around 27% and σ^{R-NR}(I; X = Sn) (HAVHA + HAHA effects) is close to 21%. Its electronic origin is paramagnetic for halogen atoms but both dia- and paramagnetic for central atoms. The effect on two bond distant hydrogen atoms is such that the largest variation of $\sigma(H)$ within the same family of XYH_3 molecules appears for X = Si and Y = I: around 20%. In this case σ(H; X = Sn, Y = I) = 33.45 ppm and σ(H; X = Sn, Y = H) = 27.82 ppm.

1. Introduction

Relativistic effects must be introduced when one wants to obtain reliable calculations of nuclear magnetic shieldings, σ, of heavy-atom containing molecules (atoms belonging to the forth row or down in the periodic table). Several methodologies were developed to include these effects. They can be divided into: (i) four-component or fully relativistic;[1–9] (ii) two-component or quasirelativistic[10–17] and (iii) perturbational or semirelativistic.[18–24] Some of them are still under development. The main difficulty concerning their validation is the fact that one cannot obtain proper experimental values for σ.[25]

Calculations of molecular properties using finite basis sets in relativistic quantum mechanics are usually contaminated with spurious states. In order to eliminate them *kinetically balanced* basis sets were suggested and are now routinely employed in 4-component methods. The use of this kind of basis set is a restriction that naturally arises in a matrix representation of the Dirac Hamiltonian. The large and small components are coupled in a precise way in its two-component formulation. Both components of the Dirac 2-spinor are related with an energy-dependent factor. So when one wants to express them in a finite basis set one should take care of that severe restriction; otherwise the matrix representation of the kinetic term is badly reproduced.[26] Only in the non relativistic limit that factor is such that one may discard its energy-dependent factor.

In the last few years several studies were oriented to develop new formalisms which include from the outset[9] or at the end,[8] a *magnetically balanced* basis set, also named a restricted magnetic balance basis set, RMB. From them it seems that RMB bases are the best option for the calculation of magnetic molecular properties. At the same time and strongly related with all this, the negative-energy branch of one-electron states that arise from the solution of the Dirac equation seems to introduce insurmountable difficulties in the calculations. Still it seems not to be clear enough that negative-energy solutions of the Dirac one-electron equation involve electronic states (as much as the solutions belonging to the positive-energy branch). When one does not include this branch of the spectra in fully relativistic calculations, a reliable theoretical value of molecular magnetic properties cannot be accomplished.[2,5,6,9] Then, the proper description of negative-energy electronic states is crucial in four-component methods. They are connected with positronic states through charge conjugation. But they are not, by themselves, positronic states.

In the development of the fully relativistic polarization propagator approach, RPPA,[2,5,27] the parameter space for the QED approach was considered to be identical with that of the empty Dirac sea approach.[28] In this way 'virtual' negative-energy electronic orbitals must be kept in calculations.

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Indeed only a small fraction of them should be considered.[29] This is not a drawback of the method. This is a natural consequence of being all the way through working within the relativistic domain in a consistent manner.

Then there are still several open questions which we address firstly, and can be formulated as follows. (i) Is it mandatory to resort to a magnetically balanced basis set for calculations of magnetic properties with perturbative fully relativistic methods? (ii) What kind of kinetically balanced basis set one should consider within the relativistic polarization propagator approach, or otherwise, shall one keep the condition $\mathbf{A} = 0$ for 4-component polarization propagator calculations, $\mathbf{A}$ being the external vector potential?

Searching for some criteria to ensure the convergence of fully relativistic calculations of σ we investigated the dependence of two kinetically balanced basis: restricted kinetic balanced, RKB; and unrestricted kinetic balanced, UKB,[5,6,30] with the size and type of basis sets. We assume as valid the completeness of a kinetically balanced basis for the matrix representation of the operators involved in our calculations. This is an important premise for relativistic molecular property calculations.[31] Kutzelnigg has shown that the exact relativistic wavefunction of the ground-state of H like ions is expandable in a kinetically balanced even-tempered Gaussian basis.[32] The second part of this paper is devoted to showing that one can obtain converged results by applying the UKB prescription with much smaller bases compared with the ones needed when applying the RKB prescription. We will also show that the working time for the calculations does not grow as one may expect. So, one can afford to calculate NMR magnetic shieldings of small and medium-size molecules containing one or more than one heavy atoms with the 4-component polarization propagator method. The UKB prescription makes it possible.

We shall emphasize the fact that, within the 4-component polarization propagator method, one should not impose the magnetic balance condition. Indeed one should be aware that there are two conditions to be fulfilled: the RKB prescription at the non-relativistic limit, and the very best representation of the negative-energy branch of one-electron states (molecular orbitals, MOs), which may or may not imply using quite large basis sets.

Right now most efforts to calculate and analyse nuclear magnetic shieldings with four-component methods were concentrated on molecules containing only one heavy atom. Relativistic corrections that contribute to the shielding of a light atom due to a neighboring heavy atom (HALA effects),[33,34] and relativistic corrections on the shieldings of the heavy atom itself (HAHA effects) were defined some time ago[35] and studied recently with *ab initio* methods.[36] On the other hand, the electronic effects of heavy atoms on the shielding of vicinal heavy atom (the HAVHA effects) are still quite unknown. Then in the third part of this article we address the study of HAVHA effects on XYH_3 (X = C, Si, Ge and Sn; Y = Br, I) molecular systems. There are several important questions that we try to answer: How important is the basis set convergence on both vicinal heavy atoms? Can one actually get convergence within RKB? or is it necessary to go to the UKB prescription for getting converged results?

Then, being sure about convergence one can ask about what kind of new effects can be expected in two-heavy atom containing molecules as compared with similar compounds where only one heavy atom is involved.

In Section 2 we give a brief introduction on kinetic balance prescriptions and fully relativistic polarization propagators, RPPA. We highlight the main differences between RKB and UKB, and give an answer on what kinetic balance prescription one should work-out within RPPA. Studies on convergence, performance and the way converged RKB and unconverged RKB calculations are related with UKB calculations are given in section 4.1. The analysis of electronic effects on $\sigma(X)$, $\sigma(Y)$ and $\sigma(H)$ are presented in sections 4.2 and 4.3. Remarks about our most important findings are given in section 5.

2. Theory

When the Dirac equation is written in terms of the so called large and small components it requires the fulfilment of a kinetic balance prescription. Otherwise the kinetic energy operator cannot be described adequately at the non relativistic limit.

2.1 The kinetic balance prescription

The time-independent one-electron Dirac equation in a static potential V provided by the nuclei in the Born–Oppenheimer frame can be written as

$$c(\alpha \cdot \mathbf{p}) \, \Psi + ((\beta - 1)mc^2 + V - E)\Psi = 0 \qquad (1)$$

where α and β are the 4×4 Dirac matrices. The relativistic wavefunction is a 4-spinor that can be written in terms of the so called *large* and *small* components

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \Psi^L(\mathbf{r}, t) \\ \Psi^S(\mathbf{r}, t) \end{pmatrix} \qquad (2)$$

Then eqn (1) can be written as a pair of two coupled equations

$$(V - E)\Psi^L + c(\sigma \cdot \mathbf{p})\Psi^S = 0$$
$$c(\sigma \cdot \mathbf{p})\Psi^L + (V - E - 2mc^2)\Psi^S = 0 \qquad (3)$$

From the second equation we have

$$\Psi^S = \frac{1}{2mc^2}\left[1 + \frac{E - V}{2mc^2}\right]^{-1} c(\sigma \cdot \mathbf{p})\Psi^L \qquad (4)$$

If the condition

$$\left|\frac{E - V}{2mc^2}\right| \ll 1 \qquad (5)$$

is fulfilled, eqn (4) becomes

$$\Psi^S = \frac{1}{2mc}(\sigma \cdot \mathbf{p})\Psi^L \qquad (6)$$

or

$$\lim_{c \to \infty} c\,\Psi^S = \frac{1}{2m}(\sigma \cdot \mathbf{p})\Psi^L \qquad (7)$$

This condition is valid for finite nuclei within the NR domain.[31,37] In such a case

$$\left| \frac{E - V}{2mc^2} \right| \approx \frac{T}{2mc^2} = \frac{v^2}{4c^2} \quad (8)$$

Another way to get an equivalent result is to replace the relation between large and small components of eqn (4) into the first of eqn (3)

$$(V - E)\Psi^L + (\sigma \cdot \mathbf{p}) \frac{1}{2m} \left(1 + \frac{E - V}{2mc^2} \right)^{-1} (\sigma \cdot \mathbf{p})\Psi^L = 0 \quad (9)$$

when $c \to \infty$ it becomes

$$\left(V - E + \frac{p^2}{2m} \right)\Psi^L = 0 \quad (10)$$

The condition of eqn (6) is called *kinetic balance* prescription because it ensures that the matrix representation of the kinetic energy operator of the unperturbed system will properly be described in the non-relativistic limit.

We can expand the large and the small component in a 2-spinor basis $\{\chi_\mu^L, \chi_\mu^S\}$

$$\Psi^L = \sum_{\mu=1}^{n_L} a_\mu^L \chi_\mu^L, \quad \Psi^S = \sum_{\mu=1}^{n_S} a_\mu^S \chi_\mu^S \quad (11)$$

where n_L and n_S need not be equal. The relationship between a_μ^S and a_μ^L depends on the kinetic balance prescription adopted.

In our calculations, Gaussian basis sets are used due to they give an straightforward manner to evaluate multicenter integrals. The Cartesian Gaussian functions can be written as

$$G_{ijk}^\alpha = N x^i y^j z^k e^{-\alpha \mathbf{r}_A^2} \quad (12)$$

where N is a normalization constant, A refers to the nuclear center, and the sum of indices i,j,k is related with the angular quantum number ℓ

$$G_\ell^\alpha = \{G_{ijk}^\alpha; \forall (i + j + k) = \ell\}$$

It is possible to transform them to a set of 2-spinor spherical Gaussian functions of the form

$$G_{nkm_j}^\alpha = N \mathbf{r}_A^{n-1} e^{-\alpha \mathbf{r}_A^2} \chi_{km_j}(\theta, \phi) \quad (13)$$

where χ_{km_j} is the angular part of the hydrogenic solution of the Dirac equation. Therefore this corresponds to the large component of the 4-spinor of the Dirac wavefunction. From the eqn (6), for each large component function with the angular quantum number ℓ, we get two small component functions with $\ell + 1$ and $\ell - 1$ angular quantum numbers:

$$\Psi^L \propto \chi^L \propto \eta^L(r) = \{G_\ell^\alpha\}$$
$$\Rightarrow \Psi^S \propto \chi^S \propto \eta^S(r) = \{c_{\ell-1} G_{\ell-1}^\alpha + c_{\ell+1} G_{\ell+1}^\alpha\} \quad (14)$$

where $c_{\ell-1}$ and $c_{\ell+1}$ are constants and $\eta^L(r)$ is the radial part of a spherical Gaussian 2-spinor.[28] In this case the kinetic balance prescription is known as *restricted kinetic balance*

(RKB). It is also possible to keep both type of small basis functions as separate functions *i.e.*

$$\Psi^L \propto \chi^L \propto \eta_\mu^L(r) = \{G_\ell^\alpha\}$$
$$\Rightarrow \Psi^S \propto \chi^S \propto \eta_\mu^S(r) = \{c_{\ell-1} G_{\ell-1}^\alpha\} \cup \{c_{\ell+1} G_{\ell+1}^\alpha\} \quad (15)$$

in which case the kinetic balance prescription is known as *unrestricted kinetic balance* (UKB). In the RKB prescription there is a $1:1$ relation between the large and the small component basis set. In the UKB prescription, each generated Gaussian function is independently used as a basis functions and then it produces, though not allways, a $2:1$ relation of the size between the large and small component basis. This increase the size of the small component basis set and so improve the description of the negative-energy space.

2.2. Fully relativistic polarization propagators

In order to get an answer on whether one is free to choose different kinetic balance prescriptions working with fully relativistic polarization propagators, we give a brief sketch on fundamentals. Within the polarization propagator method the object $\langle\!\langle ; \rangle\!\rangle$ replace the wavefunction of conventional quantum mechanics as the fundamental dynamical variable. Then the approximate schemes that arise from this formalism cannot often be related with that derived in a state function description.[38] In line with this the propagator equation of motion replace the time-dependent Schrödinger or Dirac equation in the state picture. The final form of the equation of motion obtained with superoperator algebra and the inner projection technique[39] is:

$$\langle\!\langle P; Q \rangle\!\rangle_E = (P^\dagger | \mathbf{h})(\tilde{\mathbf{h}} | E\hat{I} - \hat{H} | \mathbf{h})^{-1} (\tilde{\mathbf{h}} | Q) \quad (16)$$

$\mathbf{h}$ is a complete operator manifold of basic excitation operators from which it is possible to describe the whole branch of excited states that may come from a reference state $|0\rangle$. The operators P and Q should also be described in terms of basic excitation operators that belongs to that excitation manifold. This equation is exact provided that $\mathbf{h}$ is the complete manifold and $|0\rangle$ is the exact reference state. A detailed description of all elements of eqn (16) are given elsewhere.[27,38] Eqn (16) can be written in a more convenient way as

$$\langle\!\langle P; Q \rangle\!\rangle_E = \mathbf{b}^P \mathbf{M}^{-1} \mathbf{b}^Q \quad (17)$$

The term in the middle of the rhs of eqn (17) is the principal propagator. The other two are the property matrix elements.

One can develop approximate schemes expanding both terms of the polarization propagator in term of the fluctuational potential V.

$$H_0 = F + V \quad (18)$$

being

$$F = \sum_p \varepsilon_p a_p^\dagger a_p \quad (19)$$

and

$$V = 1/2 \sum \langle pq|rs \rangle a_p^\dagger a_q^\dagger a_s a_r - \sum_{pr} u_{pr} a_p^\dagger a_r \quad (20)$$

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The random phase level of approach, RPA, which is first order in the fluctuational potential is obtained when

$$|0\rangle = |HF \text{ (or DHF)}\rangle \tag{21}$$

being HF or DHF, Hartree–Fock or Dirac–Hartree–Fock ground states, respectively, and

$$|\mathbf{h}\rangle = |\mathbf{h}_2\rangle \tag{22}$$

being $\mathbf{h}_2 = \{a_a^\dagger a_i, a_i^\dagger a_a\}$ and $m,n,\ldots$ refer to unoccupied HF or DHF orbitals and $i,j,\ldots$ indices to occupied HF or DHF orbitals. Then the principal propagator of eqn (17) can be written at the RPA level as

$$M = \begin{pmatrix} \mathbf{A} & \mathbf{B}^* \\ \mathbf{B} & \mathbf{A}^* \end{pmatrix} \tag{23}$$

where

$$
\begin{aligned}
\mathbf{A}_{ia,jb} &= -\langle 0|[a_i^\dagger\, a_a,[a_b^\dagger\, a_j\, H_0]]|0\rangle \\
&= \delta_{ab}\,\delta_{ij}\,(\varepsilon_a - \varepsilon_i) + \langle aj||ib\rangle
\end{aligned} \tag{24}
$$

and

$$\mathbf{B}_{ia,jb} = -\langle 0|[a_i^\dagger\, a_a,[a_b^\dagger\, a_i\, H_0]]|0\rangle = \langle ji||ab\rangle \tag{25}$$

Matrix $\mathbf{A}$ do contain the average value of the unperturbed Hamiltonian H_0 between two singly excited states with respect to the reference state, and matrix elements of $\mathbf{B}$ are the matrix elements of H_0 between the reference state and doubly excited states. So matrix $\mathbf{A}$ have terms of order zero and one in V, while matrix $\mathbf{B}$ have a term of order one.

The RPA expressions at $E = 0$ are identical to those obtained in the fully coupled HF (DHF) method which is the same as the zero-field limit of the finite field method.[40,41] Following the same line of reasoning one could go one step up or down in the order of the fluctuation potential considered for calculations. The pure-zeroth order, PZOA, is obtained when matrix $\mathbf{B}$ is neglected and also all the two-electron matrix elements of $\mathbf{A}$. Then the principal propagator becomes the inverse of the first term in the last rhs of eqn (24). The PZOA level of approach coincide with uncoupled Hartree–Fock.

Within the relativistic domain the total Hamiltonian of an electronic system can be written as the sum of two terms, the unperturbed and the perturbed Hamiltonian (say H')

$$H = H^{DC} + H' \tag{26}$$

where H^{DC} is the Dirac–Coulomb N-electron Hamiltonian[28] and $\mathbf{A} = \mathbf{A}_M + \mathbf{A}_B$ is the vector potential that involve the sum of the nuclear and external vector potentials:

$$\mathbf{A}_M = \frac{1}{c^2}\frac{\mu_M \times \mathbf{r}_M}{r_M^3} \tag{27}$$

and

$$\mathbf{A}_B = \tfrac{1}{2}\,\mathbf{B} \times \mathbf{r}_G = \tfrac{1}{2}\,\mathbf{B} \times (\mathbf{r} - \mathbf{R}_G) \tag{28}$$

$\mathbf{R}_G$ is the gauge origin, $\mathbf{r}_M = \mathbf{r} - \mathbf{R}_M$ and $\mathbf{r}$ and $\mathbf{R}_M$ are the coordinates of the electron and the nucleus M, respectively.

The interaction of an N-electron system with an external magnetic field is accounted for by the minimal coupling prescription,[28] $\mathbf{p} \to \mathbf{p} + e\mathbf{A}$ leading to the introduction of the perturbative Hamiltonian

$$H' = e c \alpha \cdot \mathbf{A} \tag{29}$$

The vector potential $\mathbf{A}$ is, for describing the NMR spectroscopic parameters, the addition of both the nuclear and the external vector potential of eqn (27) and (28). Then, the second-order perturbative correction to the energy is written as

$$
\begin{aligned}
E^{(2)} &= \frac{1}{2} Re\langle\langle H'; H'\rangle\rangle \\
&= \frac{1}{2}\frac{e\hbar^2}{c} \sum_{MN} \gamma_M \gamma_N \mathbf{I}_M \cdot Re\left\langle\left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \frac{\alpha \times \mathbf{r}_N}{r_N^3}\right\rangle\right\rangle \cdot \mathbf{I}_N \\
&\quad + \frac{e^2\hbar}{2}\sum_M \gamma_M \mathbf{I}_M \cdot Re\left\langle\left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G\right\rangle\right\rangle \cdot \mathbf{B}
\end{aligned} \tag{30}
$$

The last term is related with the full relativistic expression of the NMR nuclear magnetic shielding

$$\sigma_M = e^2 Re\left\langle\left\langle \frac{\alpha \times \mathbf{r}_M}{r_M^3}; \alpha \times \mathbf{r}_G\right\rangle\right\rangle \tag{31}$$

It is observed that there is no distinction between dia and paramagnetic terms. They arise as an aproximation first shown in ref. 5. There was shown that

$$
\begin{aligned}
\langle\langle H'; H'\rangle\rangle &\approx \langle\langle H'; H'\rangle\rangle_{ee} + \langle\langle H'; H'\rangle\rangle_{pp} \\
&= (\Sigma_{is,jt}\, \mathbf{b}^*_{is}\, (\mathbf{M}_{ee}^{-1})_{is,jt}\mathbf{b}_{jt} + cc) \\
&\quad + (\Sigma_{i\bar{s},j\bar{t}}\mathbf{b}^*_{i\bar{s}}\, (\mathbf{M}_{pp}^{-1})_{i\bar{s},j\bar{t}}\, \mathbf{b}_{j\bar{t}} + cc)
\end{aligned} \tag{32}
$$

where ee and pp means that only excitations to positive-energy and negative-energy electronic orbitals are allowed, respectively. It is nicely seen that the $\langle\langle;\rangle\rangle_{ee}$ correspond to the equivalent paramagnetic term of any of both NMR spectroscopic parameters within the relativistic domain, and $\langle\langle;\rangle\rangle_{pp}$ correspond to the diamagnetic-like term. We can stress that within the relativistic domain there is no $\mathbf{A}^2$ term in the perturbed Hamiltonian, so diamagnetic contribution do not appears in the same manner as in the non relativistic regime. The virtual negative-energy MOs should be included in order to get the diamagnetic contribution.

In order to decide what kinetic balance one should consider within polarization propagator methods one should have a look on the matrix elements of eqn (32). The matrix that belongs to the principal propagator, i.e. $\mathbf{M}_{ee}$ and $\mathbf{M}_{pp}$ are clearly defined in terms of the unperturbed Hamiltonian (see eqn (24) and (25)). The other type of matrix elements, the property matrix elements (i.e. $\mathbf{b}_{is}$ and $\mathbf{b}^*_{i\bar{s}}$, s and $\bar{s}$ being virtual positive and virtual negative-energy MOs) are also defined in terms of the unperturbed molecular system (see ref. 27 and 38).

We can work a little more on these last matrix elements. The explicit NR expressions for $\mathbf{b}_{is}$ and $\mathbf{b}_{jt}$ are given, within the RPA level of approach and the RKB condition being imposed, as

$$\left\langle i \left| \frac{e}{c}\alpha \cdot \frac{\mu_M \times \mathbf{r}_M}{r_M^3} \right| s \right\rangle$$

$$= \left\langle i^L \frac{1}{2mc}(\sigma \cdot \mathbf{p}) i^L \left| \begin{pmatrix} 0 & \frac{e}{c}\sigma \cdot \frac{\mu_M \times \mathbf{r}_M}{r_M^3}(33) \\ \frac{e}{c}\sigma \cdot \frac{\mu_M \times \mathbf{r}_M}{r_M^3} & 0 \end{pmatrix} \right| \frac{1}{2mc}(\sigma \cdot \mathbf{p}) s^L \right\rangle$$

$$= \left\langle i^L \frac{1}{2mc}(\sigma \cdot \mathbf{p}) i^L \left| \begin{matrix} \frac{e}{2mc^2}\left(\sigma \cdot \frac{\mu_M \times \mathbf{r}_M}{r_M^3}\right)(\sigma \cdot \mathbf{p}) s^L \\ \frac{e}{c}(\sigma \cdot \frac{\mu_M \times \mathbf{r}_M}{r_M^3}) s^L \end{matrix} \right. \right\rangle$$

$$= \frac{e}{2mc^2} \left\langle i^L \left| \left\{ \sigma \cdot \frac{\mu_M \times \mathbf{r}_M}{r_M^3}, \sigma \cdot \mathbf{p} \right\}_+ \right| s^L \right\rangle$$

(33)

Then after solving the anticommutator one obtain the NR $\mathbf{b}_{is}$. In the same manner the NR expression of $\mathbf{b}_{jt}$ is obtained from

$$\left\langle j \left| \frac{ec}{2}\alpha \cdot (\mathbf{B} \times \mathbf{r}_G) \right| t \right\rangle \rightarrow \left\langle j^L \left| \frac{ec}{2}\{\sigma \cdot (\mathbf{B} \times \mathbf{r}_G), \sigma \cdot \mathbf{p}\}_+ \right| t^L \right\rangle \quad (34)$$

It is also clearly seen that one should consider the RKB or any variant of it but not the RMB prescription in order to get the proper NR limit of both matrix elements which intervene in the calculation of response properties within fully relativistic polarization propagators.

The formalism of polarization propagators do not include $\mathbf{A} \neq 0$ in the calculation of any NMR spectroscopic parameter. It was recently shown[27,42] that the coupling pathway which conduct the transmission of the external perturbation is based only on the unperturbed system. Another sound argument against the use of RMB in RPPA: we are able to calculate J couplings accurately.[27] The calculation of this property do not require the use of RMB as happens for other finite field based schemes.

3. Computational details

All calculations of NMR nuclear magnetic shieldings were performed with DIRAC program package[43] in a cluster of 9 nodes of Sun Fire X2200 M2 with two dual-core processors each. We want to stress that there is a large saving of computational efforts when calculations of σ^d are performed at PZOA level. The time saving is more than 50% when compared with calculations at RPA level of approach.

For NR calculations, the speed of light was taken as 10 times c ($c = 137.0359998$ a.u.). Experimental geometries were used for most of molecular models.[44] The geometries of H_2X and XH_3 were taken from ref. 45. The geometries for the SiBrH$_3$, SiIH$_3$, GeBrH$_3$ and GeIH$_3$ were optimized using the module OPTMIZE of the DIRAC code. In such a code all basis set are treated as uncontracted. For all XYH$_3$ model compounds the X atom was placed at the center of the molecule, and the gauge origin was assigned to the position of the center of coordinates. The Gaussian nuclear model was used in all calculations. Finally the geometries we have used are close to that of ref. 47 for XH$_4$ model compounds.

Both, the RKB and UKB prescriptions were applied to generate small components from large components in the four component basis set. Sadlej basis sets were chosen in most cases. Several more tight and diffuse Gaussian functions were included to get converged results; in particular for calculations with the RKB prescription. The scheme for including more Gaussian functions was the usual one: (i) tight basis functions were added to s, p, d and f blocks, with exponents related as $\alpha_{i+1}/\alpha_i = 3$ from the largest exponent of the each block; (ii) diffuse basis functions were not necessary to include in the d and f blocks because they do not change the shieldings values significantly; (iii) polarizations g-type functions were added in some cases, starting with an exponent of 0.5 and adding another functions with the same relation between exponents mentioned above. f-Type functions were also added starting with the smallest exponent of the previous block and from them larger exponent were chosen with the relation mentioned in (i). Faegri's basis sets[46] were used for As, Bi, Sn, Pb and noble gases with more tight and diffuse basis functions added following the scheme mentioned above.

4. Results and discussion

The rate of convergence for both kinetic balance prescriptions is shown first together with their time-consuming performance. Then we show the basis set dependence for two heavy-atom-containing molecules and the way the nuclear magnetic shielding depends on vicinal heavy atoms.

4.1 The shielding of noble gases and XH$_n$ systems with the UKB prescription

In Tables 1–3 we show calculations of dia- and paramagnetic components with both prescriptions and different basis sets for H_2O, PH$_3$ and GeH$_4$. The convergence threshold was taken when both, the difference within RKB calculations and between converged RKB and UKB calculations were less than 0.5%. It is observed that to get converged calculations with RKB requires a lot more effort than that with UKB, even for light atoms. As observed the basis set requirements are higher for diamagnetic components within RKB. This is due to the fact that they mostly arise within RPPA from contributions of matrix elements containing virtual negative-energy electronic wavefunctions. In such cases the description of small components becomes crucial.[29] The UKB prescription provides a much better performance for describing that branch of the electronic spectra.

In all cases calculations with Sadlej basis set and UKB is enough to get converged (within a few ppm) results. For $\sigma^d(O)$ in H_2O it gives 413.25 ppm which should be compared with the converged UKB value of 412.28 ppm. In the case of P in PH$_3$ its diamagnetic value with Sadlej basis set is 962.81 ppm and its converged value 960.78 ppm. In both cases the difference is of only -0.2%. The best total value of $\sigma(P)$ obtained with the UKB prescription can be compared with quite precise calculations of Antusek and Jaszunski[52] for equilibrium geometry at CCSD(T)/cc-pCVQZ level of approach: 605.83 ppm. Our result is 596.98 ppm at RPA level. Given that when including more correlation, say at SOPPA level, there is an increase of magnetic shieldings (around 5.4 ppm for

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Table 1 NMR σ (O) for OH$_2$ with both prescriptions, RKB and UKB

	RKB			UKB		
O (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
Sadlej-10s6p4d	323.20	−80.83	242.36	413.25	−80.83	332.42
11s6p4d	323.15	−80.76	242.39			
11s7p4d	323.21	−81.93	241.28			
11s7p5d	358.42	−81.95	276.46			
11s7p6d	386.10	−81.87	304.24			
11s7p6d1f	394.35	−81.69	312.66			
11s7p6d2f	396.22	−81.78	314.45			
12s8p7d2f	406.48	−82.14	324.34			
12s8p8d2f	409.23	−82.02	327.21	412.28	−81.82	330.45
12s8p8d3f	410.62	−81.91	328.71	412.28	−81.91	330.37
12s8p8d4f	411.14	−81.91	329.23	412.28	−81.91	330.37

Table 2 NMR σ (P) of PH$_3$ with both prescriptions, RKB and UKB

	RKB			UKB		
P (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
Sadlej-13s10p4d	704.54	−350.57	353.97	962.81	−350.57	612.24
14s10p4d	704.43	−350.20	354.23			
14s11p4d	704.47	−351.48	352.98			
14s11p5d	718.95	−359.75	359.19			
14s11p6d	730.18	−361.77	368.41			
14s11p7d	785.24	−362.45	422.79			
14s11p8d	846.75	−362.16	484.59			
14s11p8d1f	852.87	−365.65	487.22			
14s11p8d2f	873.02	−365.68	507.34			
15s12p9d3f	929.69	−365.21	564.48			
15s12p10d3f	942.75	−364.32	578.42			
15s12p11d3f	944.56	−363.79	580.77			
15s12p11d4f	957.25	−363.75	593.50	960.78	−364.51	596.27
15s12p11d5f	958.43	−363.72	594.71	960.76	−363.73	597.03
15s12p11d6f	959.02	−363.71	595.31	960.76	−363.73	597.03

Table 3 NMR σ (Ge) of GeH$_4$ with both prescriptions, RKB and UKB

	RKB			UKB		
Ge (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
Sadlej-15s12p9d	2118.74	−649.46	1469.29	2627.81	−649.26	1978.55
16s12p9d	2117.95	−645.53	1472.42			
16s13p9d	2118.03	−649.58	1468.45			
16s13p10d	2272.98	−647.04	1625.94			
16s13p11d	2348.19	−639.71	1708.48			
16s13p11d1f	2360.03	−643.58	1716.45			
16s13p11d2f	2368.95	−643.42	1725.53			
17s14p12d3f	2400.65	−634.51	1766.14			
17s14p13d3f	2404.97	−632.04	1772.93			
17s14p13d4f	2432.03	−631.94	1800.09			
17s14p13d5f	2506.39	−631.78	1874.62			
17s14p13d6f	2556.51	−631.18	1925.32			
17s14p13d7f	2559.22	−630.92	1928.31			
17s14p13d7f1g	2565.22	−633.19	1932.03			
17s14p13d7f2g	2583.94	−633.22	1950.72	2614.06	−633.60	1980.46
17s14p13d7f3g	2605.08	−633.44	1971.63	2614.04	−633.83	1980.21
17s14p13d7f4g	2612.18	−633.33	1978.85	2614.04	−633.72	1980.32
17s14p13d7f5g	2612.98	−633.31	1979.67	2614.02	−633.70	1980.32

N in NH$_3$[53]), one may expect that our best result would be close to that of Antusek and Jaszunski (within a 1% difference) when including equivalent correlation corrections. For σ^d(Ge) in GeH$_4$ the calculation with Sadlej basis set gives 2627.81 ppm which is close to its converged value of 2614.02 ppm. So in all these three cases the difference is less than 1% for atoms belonging up to the 4th row of the periodic table and systems of the type XH$_n$ (n = 2–4).

Given that dia and paramagnetic components have a clear different electronic origin within the relativistic polarization propagator theory, they may deserves a separate way for being calculated. One can calculate diamagnetic components with
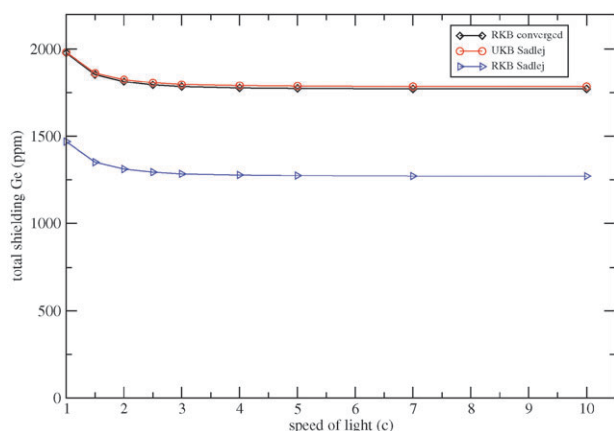
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Fig. 1 Non relativistic limit of $\sigma(Ge)$ for GeH_4. Calculations are performed with converged RKB, UKB with Sadlej basis set and unconverged RKB.

the small Sadlej basis set and the UKB prescription at PZOA level of approach getting reliable results.[29] They are quite close to calculations at RPA level of approach. If they were obtained with RKB prescription the basis set needed should be quite larger. Then by applying that recipe one can obtain large computational savings.

Paramagnetic components needs a different consideration. In our method they arise from excitations to virtual positive-energy electronic orbitals, which are mainly related to the large components of electronic orbitals. In this case calculations with RKB and UKB prescriptions depends on both, the size and type of the basis set. So $\sigma^p(O)$ for H_2O has an small difference between converged calculations and that performed with Sadlej basis set. It is observed then that one can get converged results for $\sigma(O)$ in H_2O calculating both components within the UKB prescription and using quite small basis set. A similar behaviour is obtained for $\sigma(P)$ in PH_3 where the difference between converged results and that obtained with Sadlej basis set is 2.5%. Finally $\sigma(Ge)$ for GeH_4 has a much smaller difference: 0.1%. This is not a general rule and one should be aware of this fact.

We have also studied the behaviour of $\sigma(Ge)$ in GeH_4 using both prescriptions when $c \rightarrow \infty$. As shown in Fig. 1 calculations with UKB and converged-RKB prescriptions follow a similar pattern when going from relativistic to their NR limit. On the other hand, non-converged RKB calculations give quite different numbers. In both domains the difference is close to 500 ppm.

The dependence of magnetic shieldings with both prescriptions and their comparison with previous calculations and experimental values are shown in Table 4. It is observed that the performance for calculations of $\sigma(X)$ of rare gases and XH_n ($n = 1...4$) molecular systems with UKB prescriptions are much better than that with the RKB prescription. Our results are in good agreement with that of Jaszunski and Ruud[47] for XH_4 and also with experiments. In all cases our calculations with UKB are closer to previous benchmark results, though with much smaller basis sets.

One needs to be very careful about the size of basis sets generated with both prescriptions. In all results presented in

Tables 1–4 the size of the large components for the UKB prescription is much smaller than their corresponding RKB. But this does not imply that the size of the total UKB basis set is smaller because one should consider the set of small components. As a first example we analyse calculations for the OH_2 system with Sadlej basis set. Working with RKB the total number of basis functions is 84 for each of both large and small components. In the case of UKB the number of large components is the same but the number of small components grows to 216. On the other hand when considering converged results with RKB the number of functions which are used to describe the large and small components is 133 each; then the total number is close to that of the UKB. A similar analysis for PH_3 system shows that, when Sadlej basis set (13s10p4d) is used together with the RKB prescription, 117 functions are generated for each of both components; if the same basis set together with the UKB prescription is considered the number of small components grows to 265. Finally, when converged RKB calculations are considered the total number of functions (large and small basis sets) is 390. Then the size of the basis sets for reliable calculations are equivalent. What about the computational time required? As shown in Fig. 2 the CPU time savings are larger when calculations are performed with the UKB prescription: they are around three times smaller than that of converged RKB calculations for PH_3 and GeH_4 systems.

4.2 The application of UKB prescription on shielding calculations of XYH_3 molecular systems

In the previous section we have shown that the UKB prescription ease the convergence of $\sigma(X)$ for XH_n systems. Now one may try to verify whether this is also fulfilled in the case of systems which contain more than one heavy atom, like the systems XYH_3 (X = C, Si, Ge y Sn; Y = F, Br and I). We studied with great care the convergence requirements of basis set for the shielding calculation of two system: $SnFH_3$ and $SnBrH_3$. On these grounds we got converged results for all other system of the serie. We may stress the fact that in such cases getting convergence is more difficult than in calculations on XH_n systems.

In Table 5 it is observed that σ^p of the light F atom, depends slightly on the size of the basis set for both prescriptions: 10% in each of both. This is not the case for its diamagnetic RKB contributions which varies around 30%. On the other hand, this last contribution is very well reproduced with UKB and an smaller basis set. Another interesting result is the vanishingly small dependence of $\sigma^p(F)$ and $\sigma^d(F)$ with the heavy atom basis set.

Let's consider now $\sigma(Sn)$. A less important dependence with the size of basis set is observed for diamagnetic RKB contributions, which is less than 15%. Its dependence with the light atom basis set is vanishingly small. Shall we expect that these general pattern would be the same when another heavy atom is bonded to the Sn atom? In Table 6 it is shown that this is fulfilled in all our cases. The convergence of UKB calculations is fulfilled due to the fact that calculations with RKB converge to them when they are performed with large enough basis sets. The convergence of diamagnetic

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Table 4 $\sigma(X)$ of rare gases and XH_n with both prescriptions, RKB and UKB

Rare gases	σ^p	σ^d	σ	σ (others)	Exp
Ne (RKB/11s8p7d3f)	14.25	538.55	552.80		
(UKB/9s6p4d)	13.47	544.99	558.46	561.3[a] 556.65[b]	
Ar (RKB/16s10p12d9f)	66.80	1197.95	1264.75		
(UKB/13s8p5d)	60.11	1204.71	1264.81	1274.30[a] 1273.27[b]	
Kr (RKB/17s14p11d8f5g)	557.91	2998.87	3556.78		
(UKB/16s13p8d)	537.91	3020.37	3558.29	3577.30[a] 3553.77[b]	
Xe (RKB/21s17p14d10f7g)	1947.96	4978.84	6926.80		
(UKB/20s16p11d)	1914.48	4994.46	6908.94	6938.0[a] 6718.53[b]	
Rn (RKB/24s18p16d10f8g)	11094.61	8617.88	19712.48		
(UKB/22s17p13d8f)	10759.64	8705.50	19465.14	19630.0[a] 15222.97[b]	
XH					
F (RKB/11s8p8d4f)	−57.25	474.21	416.96		
(UKB/10s6p4d)	−59.74	478.12	418.38	418.10[b]	410 ± 6[c]
Cl (RKB/15s11p10d6f)	−139.47	1119.02	979.56		
(UKB/14s10p4d)	−137.12	1124.59	987.46	977.09[b]	952[d]
Br (RKB/17s14p13d7f5g)	34.79	2913.39	2948.18		
(UKB/15s12p9d)	8.28	2932.71	2924.43	2921.98[b]	2617[d]
I (RKB /22s17p14d9f6g)	901.30	4881.46	5782.77		
(UKB/19s15p12d4f)	850.64	4923.22	5773.87	5598.19[b]	4510[d]
XH₂					
O (RKB/12s8p8d3f)	−81.91	410.62	328.71		
(UKB/10s6p4d)	−80.83	413.25	332.42	329.7[e] 330.81[b] 330.37[g]	323.6[f]
S (RKB/14s11p10d4f)	−300.08	1036.15	736.07		
(UKB/13s10p4d)	−288.15	1043.03	754.88	750.0[e] 748.37[i]	726 ± 12[h]
Se (RKB/16s13p12d7f3g)	−389.54	2810.57	2421.06		
(UKB/15s12p9d)	−414.92	2830.18	2415.27	2422.0[e] 2406.18[b]	2414[j]
Te (RKB/22s18p16d8f6g)	−28.12	4783.89	4755.77		
(UKB/19s15p12d4f)	−92.16	4817.20	4725.05	4769.4[e] 4569.37[b]	4954[k]
Po (RKB/26s21p18d11f7g)	6080.47	8287.51	14367.98		
(UKB/22s17p13d8f)	6859.05	8491.39	15350.44	15185.7[c] 11086.72[b]	
XH₃					
N (RKB/15s9p8d1f)	−88.27	353.25	264.98		
(UKB/10s6p4d)	−86.79	351.56	264.77		264.5 ± 0.05[l]
P (RKB/15s12p11d5f)	−363.72	958.43	594.71		
(UKB/13s10p4d)	−350.57	962.81	612.24	615.02[i] 669.09[m] 596.98[g]	599.93[n]
As (RKB/17s14p13d7f4g)	−513.04	2709.06	2196.02		
(UKB/19s16p11d3f)	−528.33	2728.49	2200.16	2457.82[m]	
Sb (RKB/21s17p16d8f6g)	−253.05	4681.92	4428.86		
(UKB/19s15p12d4f)	−355.64	4710.26	4354.61	5077.48[m]	
Bi (RKB/23s21p16d11f8g)	4416.21	8308.60	12724.81		
(UKB/22s17p13d8f)	4487.25	8382.73	12869.98	13500.86[m]	
XH₄					
C (RKB/12s8p7d1f)	−100.27	290.54	190.27		
(UKB/10s6p4d)	−98.47	294.47	196.00	201.81[o]	198.7
Si (RKB/15s12p11d4f)	−393.23	878.40	485.17		
(UKB/13s10p4d)	−382.58	884.78	502.20	500.87[o]	
Ge (RKB/17s14p13d7f4g)	−633.33	2612.18	1978.85		
(UKB/15s12p9d)	−635.66	2621.32	1985.65	1988.71[o] 1980.32[g]	
Sn (RKB/20s16p15d8f6g)	−380.06	4574.73	4194.67		
(UKB/19s15p12d4f)	−494.21	4604.60	4110.38	4017.54[o]	
Pb (RKB/26s22p17d12f4g)	4855.12	7835.03	12690.15		
(UKB/23s21p16d6f)	4340.42	8219.96	12560.38	10091.51[o]	

[a] Relativistic calculation taken from ref. 48. [b] DHF calculations (non diamagnetic approximation) taken from ref. 49. [c] Combination of theoretically calculated diamagnetic shielding and experimental spin-rotation constant taken from ref. 50. [d] Estimate based on experimental spin-rotation constant and a model calculation for diamagnetic shielding taken from ref. 51. [e] Quasirelativistic results from a DKH calculation (ref. 54). [f] Calculations with CAS correlated method and experimental values taken from ref. 55. [g] This work. [h] Taken from ref. 56 and 57. [i] Results taken from ref. 52. They were obtained with equilibrium geometry at CCSD(T)/cc-pVTZ level plus relativistic correction calculated with DIRAC code and cc-pCVTZ basis set. [j] Experimental values taken from ref. 58. [k] Estimated value taken from the relation reported in ref. 59. [l] Estimated values derived from the spin-rotation tensor for the NH_3 molecule in its ground vibrational state taken from ref. 60. [m] Calculations with CAS correlated method taken from ref. 19. They are a sum of NR and semirelativistic corrections. [n] Experimental value with rovibrational corrections to the spin-rotation tensor from ref. 61. [o] CAS calculation taken from ref. 47.

contributions are critical for both atoms, Br and Sn. The total RKB value of σ(Sn) varies around 20% considering different basis sets, but 15% for σ(Br). The variation of the paramagnetic contribution considering both prescriptions is lower than 3%.

4.3 Analysis of the nuclear magnetic shieldings of XYH₃ molecular systems

In the previous Section it was shown that reliable results arise when UKB prescription is adopted for the calculation of nuclear magnetic shieldings in molecular systems that contain
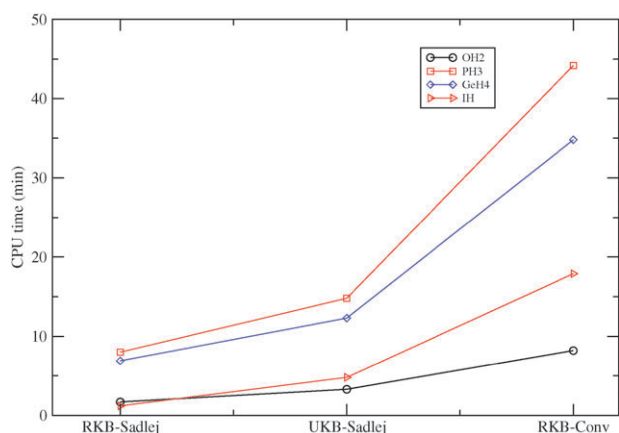
Fig. 2 Computational savings for calculations of $\sigma(X)$ (IH, H_2O, PH_3 and GeH_4) with both prescriptions, RKB and UKB.

more than one heavy atom. If RKB prescription is applied converged results are not easy to obtain. They would not be feasible to do for systems which contain more than two heavy atoms. Then one should work with the UKB prescription. Given that we want to analyse some of two heavy-atom containing molecular systems, there are several effects that

one can consider: the heavy atom effects on the central atom itself or on two-bond distant H atoms, and the effect of the central atom (that may be a heavy-atom) on vicinal heavy halogen atoms.

4.3.1 Halogen heavy-atom effects on the shielding of central atoms. We shall analyse first how much the total relativistic shielding, $\sigma^R(X)$, ($X = C$, Si, Ge, Sn) varies when the central atom is fixed and only one of its vicinal atoms change: Y ($Y = H$, Br, I). Its variation as compared with the corresponding shielding for the XH_4 molecules will show the influence of (heavy-) halogen atoms on $\sigma(X)$. For this purpose we define two parameters: 1) The absolute strength of the variation, $\Delta\sigma^R(X,Y) = (\sigma^R(X,Y)-\sigma^R(X, H))$, being this last shielding the one corresponding to the XH_4 molecule; and 2) $\delta\sigma^R(X,Y) = \Delta\sigma^R(X,Y)/\sigma^R(X, H)$ which measure the relative strength of the variation. From Table 7 it is observed that $\Delta\sigma^R(X, I)$ is above zero for $X = C$ and Si but goes below zero for $X = Ge$ and Sn; $\Delta\sigma^R(C, I) = 40.02$ ppm but $\Delta\sigma^R(Sn, I) = -50.53$ ppm. In these cases $\delta\sigma^R$ is 20.5% for $X = C$, 3.3% for Si and close to 1% for Ge and Sn. In the case of $Y = Br$, $\delta\sigma^R$ is between 4% and 6% for all X atoms. $\delta\sigma^R$ ($\delta\sigma^{R-NR}$) is a measure of the total (purely relativistic) effect on the shielding of an atom due to a vicinal atom. We can get an idea

Table 5 σ(Sn and F) of $SnFH_3$ systems with both RKB and UKB prescriptions

	RKB			UKB				RKB			UKB		
F (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t	Sn (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
10s6p4d	369.71	27.25	396.96	476.93	26.24	503.17	19s15p12d4f	3954.85	−727.42	3227.43	4641.48	−745.25	3896.22
11s7p6d1f	445.24	29.71	474.95				19s15p12d4f	3955.42	−727.84	3227.58			
12s9p8d3f	473.30	30.42	503.72	475.63	28.053	504.87	19s15p12d4f	3955.49	−728.05	3227.44	4641.51	−745.70	3895.80
12s9p8d3f	473.39	29.94	503.33	475.65	28.78	504.44	20s16p15d6f	4378.98	−677.80	3701.18	4615.44	−694.80	3920.64
12s9p8d3f	473.39	29.96	503.35	475.65	28.71	504.36	21s17p17d8f	4462.17	−653.39	3808.78	4613.38	−669.66	3943.72
12s9p8d3f	473.39	29.95	503.34				22s18p18d9f	4464.26	−658.61	3805.65			
12s9p8d3f	473.43	29.83	503.26				21s17p17d8f1g	4474.02	−653.21	3820.81			
12s9p8d3f	473.43	29.82	503.25				21s17p17d8f2g	4490.55	−653.17	3837.38			
12s9p8d3f	473.43	29.81	503.24				21s17p17d8f3g	4518.99	−653.13	3865.86			
12s9p8d3f	473.44	29.82	503.26				21s17p17d8f4g	4585.27	−653.03	3932.24			
12s9p8d3f	473.45	29.82	503.27				21s17p17d8f5g	4610.40	−652.82	3957.58			
12s9p8d3f	473.45	29.82	503.27				21s17p17d8f6g	4613.49	−652.79	3960.70			

Table 6 σ(Sn) and Br) of SnBrH3 systems with both RKB and UKB prescriptions

	RKB			UKB				RKB			UKB		
Br (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t	Sn (basis set)	σ^d	σ^p	σ^t	σ^d	σ^p	σ^t
15s12p9d	2384.05	573.30	2957.35	2931.84	566.24	3498.09	19s15p12d4f	4028.45	−757.14	3271.31	4739.27	−776.16	3963.10
16s13p10d	2521.90	584.97	3106.87				19s15p12d4f	4028.46	−757.13	3271.33			
17s14p11d1f	2619.51	581.65	3201.16				19s15p12d4f	4032.93	−762.21	3270.72			
18s15p12d2f	2647.39	581.01	3228.39				19s15p12d4f	4041.80	−777.12	3264.68			
18s15p14d3f	2677.29	580.16	3257.45				19s15p12d4f	4050.60	−803.46	3247.13			
17s15p15d4f	2725.42	581.86	3307.28				19s15p12d4f	4052.47	−813.94	3238.53			
18s15p15d6f	2843.97	583.18	3427.15	2915.67	583.18	3488.85	19s15p12d4f	4052.57	−814.95	3237.62	4739.28	−838.85	3900.43
18s15p15d6f1g	2865.27	583.00	3448.26				19s15p12d4f	4052.58	−815.08	3237.49			
15s12p9d	2384.05	573.35	2957.39	2931.85	566.28	3498.13	20s16p14d5f	4307.64	−715.98	3591.66	4714.15	−737.62	3976.53
15s12p9d	2384.05	573.41	2957.46				21s17p15d5f	4309.56	−689.19	3620.37			
15s12p9d	2384.05	573.43	2957.48				21s17p16d6f	4454.35	−685.59	3768.76			
15s12p9d	2384.05	573.43	2957.48				21s17p17d7f	4520.77	−682.54	3838.23			
15s12p9d	2384.11	571.45	2955.56				21s17p17d8f1g	4547.47	−681.60	3865.86			
15s12p9d	2384.11	571.31	2955.42				21s17p17d8f3g	4592.37	−681.63	3910.74			
15s12p9d	2384.11	571.29	2955.40				21s17p17d8f4g	4658.67	−681.46	3977.21			
15s12p9d	2384.11	571.29	2955.40				21s17p17d8f5g	4683.76	−681.21	4002.56			

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Table 7 $\sigma(X)$ and $\sigma(Y)$ of XYH_3 molecular systems with the UKB prescription. NR values are given between parenthesis

XYH$_3$	RPA σ^p	σ^d	σ^t	PZOA σ^d
CH$_4$				
C	−98.72	294.27	195.55	294.88
	(−98.13)	(295.33)	(197.20)	(295.33)
H	2.91	27.87	30.78	27.97
	(2.89)	(27.87)	(30.76)	(27.87)
CBrH$_3$				
C	−269.55	453.05	183.50	453.10
	(−282.38)	(455.25)	(172.87)	(455.25)
Br	25.80	2915.38	2941.19	2916.30
	(−476.50)	(3122.18)	(2645.68)	(3122.53)
H	−86.88	116.55	29.67	116.56
	(−87.56)	(117.10)	(29.54)	(117.10)
CIH$_3$				
C	−279.19	514.76	235.57	514.81
	(−320.04)	(518.35)	(198.31)	(518.35)
I	747.83	4888.27	5636.10	4890.34
	(−1064.92)	(5494.27)	(4429.34)	(5494.29)
H	−123.68	157.59	33.91	157.61
	(−124.69)	(158.98)	(34.29)	(158.98)
SiH$_4$				
Si	−395.43	885.04	489.61	885.56
	(−413.63)	(899.11)	(485.49)	(899.12)
H	2.09	25.73	27.82	25.83
	(2.10)	(25.76)	(27.86)	(25.75)
SiBrH$_3$				
Si	−580.64	1039.53	458.89	1039.68
	(−616.97)	(1055.32)	(438.35)	(1055.32)
Br	334.69	2915.43	3250.12	2916.46
	(−163.89)	(3122.58)	(2958.69)	(3122.59)
H	−68.45	96.74	28.29	96.75
	(−69.23)	(97.20)	(27.98)	(97.20)
SiIH$_3$				
Si	−591.23	1096.89	505.66	1097.05
	(−646.21)	(1114.00)	(467.80)	(1114.01)
I	1572.06	4888.38	6460.44	4890.10
	(−292.35)	(5494.63)	(5202.28)	(5494.66)
H	−109.44	142.89	33.45	142.90
	(−111.43)	(144.15)	(32.72)	(144.15)
Ge	−649.26	2627.81	1978.55	2628.55
	(−993.46)	(2778.86)	(1785.40)	(2778.87)
H	2.60	25.24	27.84	25.24
	(2.47)	(25.43)	(27.91)	(25.43)
GeBrH$_3$				
Ge	−903.68	2753.98	1850.29	2754.70
	(−1292.88)	(2915.79)	(1622.91)	(2915.80)
Br	364.60	2915.16	3279.75	2916.16
	(−139.66)	(3122.05)	(2982.39)	(3122.06)
H	−64.03	91.74	27.72	91.75
	(−64.74)	(92.37)	(27.63)	(92.37)
GeIH$_3$				
Ge	−851.72	2806.04	1954.32	2806.76
	(−1295.08)	(2969.02)	(1673.94)	(2969.03)
I	1482.81	4888.22	6371.02	4890.20
	(−329.21)	(5494.11)	(5164.90)	(5494.15)
H	−92.33	124.52	32.20	−78.82
	(−94.56)	(125.79)	(31.22)	(125.79)
SnH$_4$				
Sn	−494.44	4604.60	4110.16	4606.26
	(−1811.97)	(5099.14)	(3287.17)	(5099.15)
H	2.93	24.65	27.58	24.65
	(2.75)	(25.19)	(27.95)	(25.19)
SnBrH$_3$				
Sn	−776.27	4709.73	3933.47	4711.28
	(−2192.84)	(5234.07)	(3041.24)	(5234.10)
Br	567.67	2915.28	3482.96	2916.28
	(61.92)	(3122.16)	(3184.08)	(3122.17)
H	−58.80	86.35	27.54	86.35
	(−59.03)	(87.35)	(28.32)	(87.35)

Table 7 (*continued*)

| XYH$_3$ | RPA | | | PZOA |
	σ^p	σ^d	σ^t	σ^d
SnIH$_3$				
Sn	−716.78	4776.41	4059.63	4777.90
	(−2175.02)	(5286.46)	(3111.44)	(5286.51)
I	1754.15	4898.60	6652.74	4909.30
	(10.62)	(5494.49)	(5505.12)	(5494.61)
H	−83.23	114.79	31.56	114.80
	(−84.96)	(116.34)	(31.38)	(116.34)

of what $\delta\sigma^R$ and $\delta\sigma^{R-NR}$ means comparing their numbers for X = Sn and Y = I. In such a case $\delta\sigma^R$ = 1.23% but $\delta\sigma^{R-NR}$ = 15.21%. So, even when relativistic effects are important, the total effect is quite small.

It should be mentioned that the paramagnetic variation is larger than its diamagnetic counterpart in both systems, though their changes are quite similar in magnitude. One should consider the diamagnetic variation if wants to get reliable final results: $\Delta\sigma^{R,d}$(C, I) = 220.49 ppm and $\delta\sigma^{R,d}$(C, I) = 74.93%; and $\Delta\sigma^{R,d}$(Sn, I) = 171.81 ppm and $\delta\sigma^{R,d}$(Sn, I) = 3.73%.

On the other hand, as observed in Fig. 3 and 4, relativistic effects due to vicinal (heavier) halogen atoms are larger when central atoms are lighter. This means that HAVHA effects are much less important than HALA effects, or HAVHA and HAHA are opposite for central atoms. For substituent iodine $\delta\sigma^{R-NR}$(C, I) = 21.58% which is larger than $\delta\sigma^{R-NR}$(Sn, I) = 15.21%. The same behaviour though more pronounced is observed for the total shielding: $\delta\sigma^R$(C, I) = 20.50% which is much larger than $\delta\sigma^R$(Sn, I) = 1.23%.

Then we include the traditional way to analyse relativistic effects on the central (heavy or light) atom itself: $\sigma^{R-NR}(X,Y)/\sigma^{NR}(X,Y)$. In the case of XH$_4$ these relativistic effects are less than 1% for X = C (−0.84%) and Si (0.85%), but then they increase (HAHA effect) to 10.82% for Ge and to 25.04% for Sn. These effects also increase when there are (heavier) halogen as substituent: for iodine, relativistic effects on C (HALA effect) amount 18.79% and that on
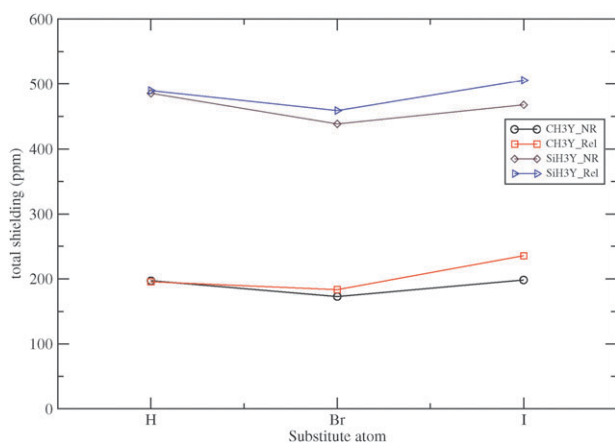

Fig. 3 Relativistic (HALA) effects on the shielding of central atoms of XYH$_3$ molecular systems when X = C, Si and Y = H, Br and I.
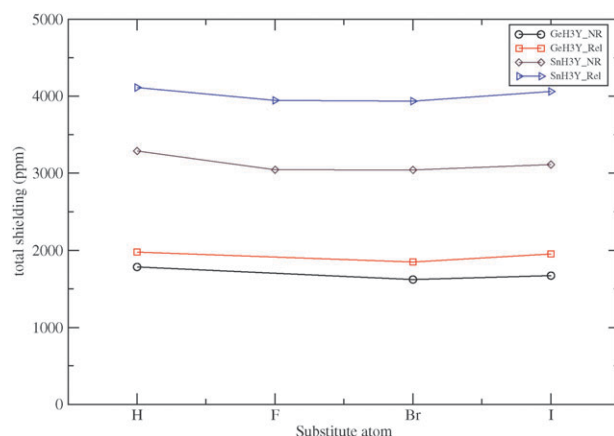

Fig. 4 Relativistic (HAVHA + HAHA) effects on the shielding of central atoms of XYH$_3$ molecular systems when X = Ge, Sn and Y = H, (F) Br and I.

Sn (HAVHA + HAHA effects) increase to 30.47%. The HAVHA effect is then 30.47–25.04% or close to 4.5%.

4.3.2 Central atom effects on the shielding of (heavy-) halogen atoms. Following the same line of reasoning as in the last section we will analyse here how much relativistic effects modify the shieldings of the halogen atoms when the central atoms becomes heavier. The pattern of variation of both dia and paramagnetic terms are found to be completely different. The diamagnetic contribution to σ(Y; Y = Br and I) do not change much even for the heaviest central atom. This is not the case for paramagnetic terms: they change for iodine more than 100% between X = C (747.83 ppm) and X = Sn (1754.15 ppm).

The total relativistic (NR) magnetic shielding for Br increase 18.42 (20.35)% when the central atom changes from C to Sn. A similar behaviour is observed for iodine though more pronounced for NR calculations: 18.04 (24.29)%. On the other hand, for X = C (Sn) relativistic effects (R-NR) increase σ(I) from 4429.34 (5505.12) ppm to 5636.10 (6652.74) ppm or 27.24 (20.84)%. A similar behaviour, though quantitatively smaller, is observed for Br. It means that either relativistic effects on the shielding of halogen atoms are more pronounced when the central atoms are lighter, or HAVHA and HAHA effects have opposite sign in these cases.

4.3.3 Halogen (heavy)-atom effects on two-bond distant hydrogen. In this section we show the effects of heavy-halogen atoms on the shielding of two-bond distant H atoms when the central atom becomes heavier. We need to define a new

parameter: $\eta_{X,Y} = (\sigma^R(H; X,Y) - \sigma^R(H; X,Y = H))/\sigma^R(H; X,Y = H)$ which would measure the effects on $\sigma(H)$ when the halogen Y (central atom X) is modified, being the central (halogen) atom fixed. In the case of Y = I, $\eta_{X,I}$ have the values 0.1017, 0.2024, 0.1566 and 0.1443 for X = C, Si, Ge and Sn, respectively. For Y = Br the same serie of Xs gives the values: −0.0361, 0.0169, −0.0036 and −0.0015. Then, for Iodine the largest effects (of 20%) is observed for X = Si. It is also interesting to observe that $\sigma(H)$ varies 3.13, 5.63, 4.36 and 3.98 ppm when X = C, Si, Ge and Sn, and Y = I.

5. Concluding remarks

In this article we addressed several still open questions related with: (i) the application of different kinetic balance prescriptions on the calculation of magnetic molecular properties within the relativistic polarization propagator approach; (ii) the performance of the UKB prescription on such calculations; and (iii) some new electronic effects that appears on the shielding of heavy (or light atoms two-bond distant from heavy atoms) atoms due to the presence of vicinal heavy atoms.

Working with relativistic polarization propagators there is no formal requirement to enforce the application of magnetic kinetic balance prescription. On the contrary the RKB prescription is a necessary condition, but is not enough to obtain reliable results. Applying the UKB prescription, more-flexible basis sets are obtained but UKB calculations are more time-consuming than RKB when equivalent basis sets are used. On the other hand the UKB prescription ensure convergence with quite smaller basis sets and so the time saving is large.

We have shown that calculations with both prescriptions converge to the same value, though UKB is much more efficient. One can obtain reliable results working with Sadlej basis sets for calculations of paramagnetic components at RPA level of approach, and diamagnetic components at PZOA level of approach. In this way we have obtained reliable results for systems with more than one heavy-atom-containing molecule, like SnIH$_3$, and without large computational cost. Then in the near future we will be able to afford fully relativistic *ab initio* calculations of shieldings for systems with more than two heavy-atom-containing molecules.

Converged results for the shielding calculation of two vicinal heavy atoms needs large enough basis set for both atoms. The quality of the basis set of the vicinal heavy atom only influence the paramagnetic contribution of a given heavy atom but diamagnetic contributions are more sensitive to the quality of its own basis set.

A new electronic mechanism arise when two heavy atoms are bonded each other. This mechanism applies on both vicinal atoms, the halogen Y and the central atom X in molecular systems like XYH$_3$. Relativistic effects (R-NR) on central atoms due to vicinal heavy-halogen atoms are larger when the central atoms are lighter. This means that HAVHA effects are much less important than HALA effects or HAVHA and HAHA effects have opposite sign for central atoms. A similar rationale though for halogen atoms may explain why relativistic effects on the shielding of heavy halogen atoms are more important when the central atoms are lighter. Another related finding is on the HAVHA effects which modify both components of the shielding of the central atom but only the paramagnetic component of the shielding of the halogen vicinal atom.

Relativistic effects on central atoms can be important (15% for X = Sn and Y = I, and 8.4% for Y = Br), but the total effect, which measure how much $\sigma(X)$ varies with respect to its value for XH$_4$ molecule, is much less important (1.2% and 4.3% for X = Sn, and Y = I and Br, respectively). This means that for the systems analysed here the chemical shift will be small though measurable: $\delta(Sn) \approx \sigma(Sn; SnIH_3) - \sigma(Sn; SnH_4) = -50.53$ ppm.

When analizing the heavy-atom effects on two-bond distant hydrogen atoms, we found an up-field effect for (Y) = I. Such effect is more pronounced when the central atom is X = Si: $\sigma(H)$ varies 20%. The mininum was found for X = C: 10%.

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