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Absolute NMR shielding scales and nuclear spin–rotation constants in ^{175}LuX and ^{197}AuX ($X = ^{19}\text{F}$, ^{35}Cl , ^{79}Br and ^{127}I)

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We present nuclear spin–rotation constants, absolute nuclear magnetic resonance (NMR) shielding constants, and shielding spans of all the nuclei in ^{175}LuX and ^{197}AuX ($X = ^{19}\text{F}$, ^{35}Cl , ^{79}Br , ^{127}I), calculated using coupled-cluster singles-and-doubles with a perturbative triples (CCSD(T)) correction theory, four-component relativistic density functional theory (relativistic DFT), and non-relativistic DFT. The total nuclear spin–rotation constants determined by adding the relativistic corrections obtained from DFT calculations to the CCSD(T) values are in general in agreement with available experimental data, indicating that the computational approach followed in this study allows us to predict reliable results for the unknown spin–rotation constants in these molecules. The total NMR absolute shielding constants are determined for all the nuclei following the same approach as that applied for the nuclear spin–rotation constants. In most of the molecules, relativistic effects significantly change the computed shielding constants, demonstrating that straightforward application of the non-relativistic formula relating the electronic contribution to the nuclear spin–rotation constants and the paramagnetic contribution to the shielding constants does not yield correct results. We also analyze the origin of the unusually large absolute shielding constant and its relativistic correction of gold in AuF compared to the other gold monohalides. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4934533>]

I. INTRODUCTION

For many nuclei, accurate gas-phase experimental nuclear spin–rotation constants have been used to determine absolute nuclear magnetic resonance (NMR) shielding constants. The common way to establish absolute shielding scales, based on the similarity between the equations for the nuclear spin–rotation and NMR shielding tensors, was first proposed by Ramsey¹ and further developed by Flygare.^{2,3} This approach establishes a non-relativistic relation between the electronic contribution to the nuclear spin–rotation constant $C_{K,\text{iso}}^{\text{el}}$ and the paramagnetic contribution to the absolute shielding constant $\sigma_{K,\text{iso}}^{\text{para}}$.^{2–4} Once $\sigma_{K,\text{iso}}^{\text{para}}$ is obtained this way, it is added to the calculated diamagnetic contribution $\sigma_{K,\text{iso}}^{\text{dia}}$ to provide an approximate value for the total isotropic absolute shielding constant of nucleus K. This can for a diatomic molecule be written as (NMR shielding constants are in ppm)

$$\sigma_{K,\text{iso}} = \sigma_{K,\text{iso}}^{\text{dia}} + \sigma_{K,\text{iso}}^{\text{para}} = \sigma_{K,\text{iso}}^{\text{dia}} + \left(\frac{10^9 m_p}{2m_e g_K B_r} \right) C_{K,\text{iso}}^{\text{el}}, \quad (1)$$

where m_p and m_e are the proton and electron masses, respectively; g_K is the nuclear g factor; $B_r = \hbar/(4\pi I_{\perp})$ is the molecular rotational constant in MHz; \hbar is the reduced Planck's constant; I_{\perp} is the perpendicular component of the moment of

inertia; and $C_{K,\text{iso}}^{\text{el}}$ is the electronic contribution to the isotropic spin–rotation constant in kHz.

Employing such an approach can give reasonable results for very light atoms (see, for instance, recent work^{5–7} and references therein); however, it fails when used for heavy atoms due to the neglected relativistic effects.^{8–14} Indeed, even for as light an element as oxygen, Eq. (1) gives an error in the absolute shielding constant of about 1–1.5 ppm.¹⁵ For heavy elements, these effects can make an order of magnitude difference, as shown, for instance, in a study of monocarbonyls of nickel, palladium, and platinum.¹⁴ Moreover, the relativistic effects often contribute significantly to the total absolute shielding and spin–rotation constants of light atoms in the vicinity of heavy atoms.^{16,17} For example, in hydrogen iodide, the relativistic correction to the spin–rotation constant of ^1H contributes by more than 100% to the total calculated value,¹⁶ but in this case, the validity of Eq. (1) remains rather good because the relativistic effects are approximately the same for both the spin–rotation and NMR shielding tensors.

These effects of relativity described above are in line with the observation that as the atoms become heavier, standard non-relativistic approaches based on the Schrödinger equation break down.^{17,18} Among the relativistic computational program packages used to calculate magnetic properties, the two-component spin-orbit zero-order-regular approximation (SO-ZORA)^{19,20} implemented in the Amsterdam Density Functional (ADF) package²¹ and the four-component Dirac-Coulomb Hamiltonian implemented in the ReSpect²² and the

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DIRAC²³ as well as the Beijing density functional (BDF)^{24–26} program packages can be mentioned.

Accurate experimental spin–rotation constants are useful for testing different computational methods. For instance, Teale *et al.*⁵ benchmarked different *ab initio* and density functional theory (DFT) methods in the calculation of spin–rotation and absolute shielding constants of 28 molecules. Accurate calculated results obtained by including relativistic corrections are important in their own rights for future benchmarking of approximate theoretical methods.^{12–14}

In this study, we report the non-relativistically and relativistically calculated nuclear spin–rotation constants and absolute shielding constants of all nuclei in ¹⁷⁵LuX and ¹⁹⁷AuX (X = ¹⁹F, ³⁵Cl, ⁷⁹Br, ¹²⁷I). The experimental studies of these lutetium and gold mono-halides have shown that all these molecules have a closed-shell singlet ¹Σ⁺ ground state.^{27–31} For all molecules except LuBr and LuI, experimental gas-phase nuclear spin–rotation constants have been reported by Gerry and co-workers.^{28–31} We compare spin–rotation constants calculated using non-relativistic coupled-cluster and relativistic DFT approaches with each other as well as with the corresponding experimental values. Absolute shielding constants are also calculated using the same non-relativistic approaches and compared with those obtained using two-component SO-ZORA and four-component Dirac-Kohn-Sham (DKS) for the relativistic corrections.

Because all the molecules studied in this work are diatomics, we follow the standard convention for spin–rotation constants of linear molecules and report the nonzero component (not the trace) of the tensor. For the purpose of simplicity, we use parentheses in Sec. III instead of the subscript K notation used for the nucleus in Eq. (1). In addition, we present the results with the signs from our calculations (consistent with the sign convention used by Flygare²) and put (+) or (–) for those signs of the experimental spin–rotation constants which we have changed, since different sign conventions are used in the literature.

II. COMPUTATIONAL DETAILS

The accurate non-relativistic coupled-cluster singles-and-doubles, CCSD, and CCSD with perturbative triples correction, CCSD(T), values of the magnetic properties were obtained using coupled-cluster analytic linear response methods, developed by Gauss and Stanton^{32,33} and implemented in the CFOUR program³⁴ (modified locally to include the g factors for the heavy nuclei). In the CCSD calculations, we used the uncontracted versions of the atomic natural orbital-relativistic correlation-consistent (ANO-RCC) basis sets, denoted as unc-ANO-RCC.^{35–37} In the CCSD(T) calculations, it was practically impossible to use the larger unc-ANO-RCC basis set, due to the large number of electrons in the molecules studied. Hence, in the CCSD(T) calculations, we used the uncontracted versions of the all-electron scalar relativistic Douglas–Kroll–Hess (denoted as unc-Cologne DKH2) basis set for lutetium (Lu),³⁸ double-ζ polarized Douglas–Kroll–Hess (denoted as unc-DZP-DKH) basis set for gold (Au),³⁹ and uncontracted augmented double-ζ polarized (denoted as unc-ADZP) basis sets for the halogen atoms.^{40–42}

We note that there are very few small all-electron basis sets available for the lutetium and gold atoms; therefore, at the CCSD(T) level, the above described literature basis sets were chosen and uncontracted to ensure increased flexibility in the region close to the nucleus. All the coupled-cluster calculations were performed applying gauge-including atomic orbitals (GIAOs^{43,44}).

The four-component relativistic DKS and the corresponding non-relativistic DFT results were obtained using the BP86^{45,46} and B3LYP^{47–50} exchange–correlation functionals implemented in a development version of the program package ReSpect.²² In the ReSpect calculations, restricted magnetic balance was used for the calculations of the NMR shielding constants^{51,52} and the restricted kinetic balance scheme in the case of the spin–rotation constant calculations.¹⁶ Rotational London orbitals (RLOs) are often used in calculations of spin–rotation constants to improve basis set convergence.^{53,54} The RLOs depend explicitly on the angular momentum and are generalizations of the conventional London orbitals (often referred to as GIAOs)^{43,44,53} introduced to improve basis set convergence and remove the gauge-origin dependence of the calculated properties. However, RLOs have not yet been implemented in ReSpect, and for this reason, the Common-Gauge Origin (CGO) approach was used in the calculations of the relativistic corrections to the nuclear spin–rotation constants. This does not significantly affect the final spin–rotation constants, since in this case, we used the larger basis sets and because the basis set convergence study shows that the results are well converged (*vide infra*). Furthermore, Xiao *et al.*⁵⁵ have shown that for large basis sets, the difference between spin–rotation constants obtained with and without rotational London orbitals is small. The GIAO^{43,44} approach was used for the absolute shielding constants calculations. Additional calculations using the CGO approach and the two DFT functionals were also performed for the analysis of the shielding constants and spans. The nuclear g-factors used in the calculations were taken from Ref. 56.

The basis set dependence of both the absolute shielding and spin–rotation constants was assessed by considering double, triple, and quadruple-ζ quality basis sets at the DKS/BP86 level. Specifically, we used Dyal’s relativistically optimized all-electron valence double-ζ (v2z),^{57–62} core–valence double-ζ (cv2z),^{57–62} valence triple-ζ (v3z),^{57,59–63} core–valence triple-ζ (cv3z),^{57,59–63} valence quadruple-ζ (v4z),^{57,59,60,62} and core–valence quadruple-ζ (cv4z)^{57,59,60,62} basis sets. The absolute shielding constants calculated within the two-component SO–ZORA scheme^{19,20} were obtained using the Amsterdam density functional (version 2014.01) program package²¹ employing the BP86 and B3LYP functionals and an all-electron quadruple-ζ quadruply polarized (QZ4P) Slater-type basis set, which is optimized for ZORA computations.⁶⁴ The unscaled ZORA method was used for the NMR shielding calculations including spin–orbit relativistic corrections. The zero-point vibrational (ZPV) corrections were calculated using the VIBROT program, a part of the MOLCAS program (version 3) package,⁶⁵ with the potential and the property curves obtained from DKS/BP86/cv4z calculations.

To consider only the scalar relativistic effects in the four-component calculations of the NMR shielding and

spin-rotation tensors, we have done the following: In perturbation-free calculations, we omit all SO integrals, while we keep all the four-component operators in the response calculations. This procedure will result in removing passive spin-orbit effects, keeping the scalar but spin-dependent Fermi contact/spin Zeeman-kinetic energy (FC/SZ-KE) terms, and partially retaining active spin-orbit effects; where passive spin-orbit effects feature magnetic field-free relativistic operators that provide first-order relativistic modifications of the wave function and active spin-orbit effects contain explicit dependence on the external or internal magnetic field perturbations (for definitions and more details, see Refs. 66 and 67). Thus, the definition of SO effects used in this work is consistent with Refs. 66 and 67 for light elements, where active spin-orbit effects are negligible,⁶⁶ while it differs for heavy elements. The SO contribution to the NMR shielding and spin-rotation tensors is calculated as the difference between full four-component calculations and calculations with SO effects removed as described above.

For direct comparison of the calculated spin-rotation constants with the corresponding experimental values, we used available experimental equilibrium geometries of $r_e(\text{Lu-F}) = 1.917\,118\,15\text{ \AA}$ and $r_e(\text{Lu-Cl}) = 2.373\,293\text{ \AA}$ taken from Ref. 31; $r_e(\text{Au-F}) = 1.918\,449\text{ \AA}$, $r_e(\text{Au-Cl}) = 2.199\,028\,7\text{ \AA}$, $r_e(\text{Au-Br}) = 2.318\,41\text{ \AA}$, and $r_e(\text{Au-I}) = 2.471\,102\,2\text{ \AA}$ taken from Refs. 29 and 30. For LuBr and LuI, geometries optimized using the SO-ZORA Hamiltonian, Grimme's dispersion-corrected⁶⁸ BP86 functional (BP86-D3) and the QZ4P basis set, $r_e(\text{Lu-Br}) = 2.530\,04\text{ \AA}$ and $r_e(\text{Lu-I}) = 2.772\,60\text{ \AA}$, were used. For LuF and LuCl,

geometry optimizations using the same approach lead to $r_e(\text{Lu-F}) = 1.915\,71\text{ \AA}$ and $r_e(\text{Lu-Cl}) = 2.370\,06\text{ \AA}$, with a deviation of $0.001\,41\text{ \AA}$ and $0.003\,233\text{ \AA}$ from the experimental values. This indicates that the optimized geometries of LuBr and LuI are sufficiently accurate for our purposes.

III. RESULTS AND DISCUSSION

A. Nuclear spin-rotation constants

The basis-set dependence of the calculated nuclear spin-rotation constants of all nuclei in LuX and AuX (X = F, Cl, Br, I) is collected in Table SI⁶⁹ of the supplementary material. In the LuX molecules with light halogens, basis set convergence can be achieved with the cv3z basis set. However, as the halogens become heavier—in particular for AuX—convergence is slower, and the cv4z basis is needed in order to reach convergence. Hence, DFT calculations have been performed using the cv4z basis set.

The non-relativistic and relativistic values of all the spin-rotation constants, calculated using different methods, are presented in Table I. For the LuX molecules, the coupled-cluster results differ significantly from the non-relativistic Hartree-Fock (HF) and DFT values. The same is also true for the AuX halides, but the differences are not so large for the gold atoms as for the lutetium atoms. For all the nuclei in all the molecules, the differences between the CCSD and CCSD(T) values are fairly small. Moreover, as shown in the table, for the nuclear spin-rotation constants in the AuX molecules, relativistic corrections are in general far more important than the correlation effects. Thus, we have not examined further the

TABLE I. Comparison of calculated values for nuclear spin-rotation constants (C , in kHz) of nuclei in LuX and AuX (X = F, Cl, Br, I) molecules at different computational levels.

		NR				DKS			
		HF ^a	BP86 ^b	B3LYP (0.2) ^b	CCSD ^c	CCSD(T) ^a	BP86 ^b	B3LYP (0.2) ^b	B3LYP (0.4) ^b
LuF	Lu	-6.301	-13.755	-11.982	-8.574	-8.773	-11.101	-9.698	-8.589
	F	-31.480	-46.357	-42.785	-34.590	-35.808	-44.816	-41.106	-37.166
LuCl	Lu	-5.188	-10.217	-9.398	-6.232	-6.401	-7.366	-6.502	-5.628
	Cl	-2.192	-3.054	-2.914	-2.334	-2.422	-2.908	-2.719	-2.457
LuBr	Lu	-3.120	-5.691	-5.341	-3.689	-3.608	-3.872	-3.453	-2.975
	Br	-5.740	-8.140	-7.778	-6.052	-6.402	-7.752	-7.223	-6.497
LuI	Lu	-2.709	-4.584	-4.443	-3.040	-2.990	-2.929	-2.654	-2.267
	I	-4.614	-6.312	-6.107	-4.753	-5.193	-6.157	-5.753	-5.165
AuF	Au	-1.266	-1.702	-1.669	-1.510	-1.508	8.237	11.377	14.248
	F	8.365	3.221	5.807	7.335	8.169	9.030	15.838	17.929
AuCl	Au	-0.694	-0.777	-0.789	-0.781	-0.700	-0.419	-0.217	-0.019
	Cl	0.411	-0.066	0.102	0.300	0.318	-0.913	-0.501	-0.166
AuBr	Au	-0.214	-0.337	-0.347	-0.356	-0.206	0.086	0.048	0.002
	Br	0.487	-0.643	-0.196	0.430	0.325	-3.343	-2.283	-1.316
AuI	Au	-0.201	-0.205	-0.214	-0.229	-0.181	0.435	0.359	0.250
	I	0.395	-0.869	-0.514	0.080	0.079	-3.694	-2.772	-1.829

^aBasis sets used: unc-Cologne DKH2 for Lu, unc-DZP-DKH for Au, and unc-ADZP for the halogen atoms.

^bNR and DKS values are from calculations using Dyall-cv4z and CGO. In parenthesis is the Hartree-Fock exchange contribution to B3LYP.

^cunc-ANO-RCC results; for LuX taken from Ref. 78.

dependence of the electron correlation effects on the basis set and on the method used.

Relativistic corrections are considerable, and the largest correction is observed in AuF. The results show that the non-relativistic DFT methods overestimate the magnitude of all the spin-rotation constants in the LuX series compared to the corresponding relativistic results. Changing the BP86 functional to the hybrid B3LYP functional also leads to a considerable change. For example in LuF, DKS/BP86 gives -11.101 kHz for $C(^{175}\text{Lu})$, whereas DKS/B3LYP gives -9.698 kHz. Similarly, $C(^{79}\text{Br})$ in AuBr obtained using DKS/BP86 is -3.343 kHz, whereas the DKS/B3LYP value is -2.283 kHz. Moreover, increasing the HF exchange contribution of B3LYP has a considerable effect for the DKS calculations. For instance, $C(^{197}\text{Au})$ in AuF calculated using the default DKS/B3LYP (20% HF exchange) is 11.377 kHz, whereas increasing the HF exchange to 40% increases the spin-rotation constant to 14.248 kHz. For $C(^{79}\text{Br})$ in AuBr, increasing the HF exchange from 20% to 40% changes the spin-rotation constant of Br by 42%. There are large differences between the results obtained with the non-relativistic DFT and coupled-cluster calculations and those using the four-component relativistic DFT calculations of the AuX molecules. For instance, $C(^{197}\text{Au})$ in AuF calculated using NR/BP86 is -1.702 kHz, whereas that obtained using DKS/BP86 is 8.237 kHz.

The total nuclear spin-rotation constants are compared to available experimental data in Table II. Our final theoretical results are obtained by adding $\Delta C(\text{rel})$, the difference

between the DKS and NR results obtained using either the BP86/cv4z or B3LYP/cv4z approach, to the non-relativistic CCSD(T) values. The zero-point vibrational corrections to the spin-rotation constants are negligible. From the table, one can see that for LuF and LuCl, the CCSD(T) results are already in agreement with the experimental values. For the nuclei in these two molecules, the HF results (shown in Table I) differ significantly from the corresponding coupled cluster results, showing that correlation effects may be of similar magnitude as the relativistic effects. For instance, the correlation effect [CCSD(T)-HF] on the spin-rotation constant of Lu in LuF is -2.472 kHz, whereas the BP86/cv4z calculated relativistic effect is 2.654 kHz. In these two cases, the additivity of electron correlation and relativistic effects becomes doubtful. For the AuX molecules, as shown in Table I, the HF results are close to the corresponding coupled cluster results; the electron correlation effects are small. However, the results obtained from the CCSD(T) calculations are far from the experimental values, because the relativistic corrections are much more important than the correlation effects. This demonstrates that non-relativistic methods are not suitable for the study of magnetic properties of the AuX molecules.

Comparing the final values for the AuX molecules, obtained using different DFT functionals for the relativistic contribution, shows that the BP86 results are in better agreement with experiment for AuF and AuCl, whereas B3LYP is slightly better than BP86 for the AuBr and AuI molecules. The total spin-rotation constants are in general in

TABLE II. Final nuclear spin-rotation constants (C , in kHz) of nuclei in LuX and AuX ($X = \text{F, Cl, Br, I}$) molecules calculated using the DFT and CCSD(T) approaches and the available experimental values.

		$\Delta C(\text{rel } 1)^a$	$\Delta C(\text{rel } 2)^b$	CCSD(T) ^c	ZPV ^d	Total 1 ^e	Total 2 ^f	Expt.
LuF	Lu	2.654	2.284	-8.773	0.035	-6.084	-6.454	(-) $8.763(25)^g$
	F	1.541	1.679	-35.808	0.196	-34.071	-33.933	(-) $35.56(19)^g$
LuCl	Lu	2.851	2.896	-6.401	0.014	-3.536	-3.491	(-) $5.563(12)^g$
	Cl	0.146	0.195	-2.422	0.005	-2.271	-2.222	(-) $2.141(42)^g$
LuBr	Lu	1.819	1.888	-3.608	0.004	-1.785	-1.716	...
	Br	0.388	0.555	-6.402	0.009	-6.005	-5.838	...
LuI	Lu	1.655	1.789	-2.990	0.003	-1.332	-1.198	...
	I	0.155	0.354	-5.193	0.007	-5.031	-4.832	...
AuF	Au	9.939	13.046	-1.508	-0.022	8.409	11.516	(+) $7.855(27)^h$
	F	5.809	10.031	8.169	-0.587	13.391	17.613	(+) $13.701(92)^h$
AuCl	Au	0.358	0.572	-0.700	0.014	-0.328	-0.114	(-) $0.334(85)^i$
	Cl	-0.847	-0.603	0.318	-0.021	-0.550	-0.306	(-) $0.261(76)^i$
AuBr	Au	0.423	0.395	-0.206	0.010	0.227	0.199	(-) $0.386(64)^i$
	Br	-2.700	-2.087	0.325	-0.033	-2.408	-1.795	(-) $1.418(66)^i$
AuI	Au	0.640	0.573	-0.181	0.008	0.467	0.400	...
	I	-2.825	-2.258	0.079	-0.020	-2.766	-2.199	(-) $1.99(17)^j$

^a $\Delta C(\text{rel } 1)$ is the difference between DKS and NR results calculated using the BP86/cv4z approach (see Table I).

^b $\Delta C(\text{rel } 2)$ is the difference between DKS and NR results calculated using the B3LYP/cv4z approach (see Table I).

^cBasis sets used: unc-Cologne DKH2 for Lu, unc-DZP-DKH for Au, and unc-ADZP for the halogen atoms.

^dZero-point vibrational correction.

^eThe sum of relativistic corrections from BP86/cv4z, zero-point vibrational correction, and the CCSD(T) values.

^fThe sum of relativistic corrections from B3LYP/cv4z, zero-point vibrational correction, and the CCSD(T) values.

^gTaken from Ref. 31.

^hTaken from Ref. 27, in Ref. 28, $C(^{197}\text{Au}) = -7.85(52)$ kHz and $C(^{19}\text{F}) = 16.5(17)$ kHz are reported.

ⁱTaken from Ref. 30.

^jTaken from Ref. 29.

quite good agreement with the corresponding experimental data. The computational approach followed allows us to estimate the unknown spin–rotation constants in LuBr and LuI molecules. For these constants, although DFT overestimates the electron correlation effects at the non-relativistic level, both functionals yield very similar values of the required DFT relativistic corrections. In AuI, the difference between BP86 and B3LYP relativistic corrections is large; the agreement of $C(^{127}\text{I})$ with experiment suggests that using B3LYP provides a better estimate of the unknown gold spin–rotation constant, $C(^{197}\text{Au})$.

B. NMR shielding constants

The basis set dependence of the computed shielding constants is depicted in Table SII⁶⁹ of the supplementary material. Basis set convergence is achieved with the cv4z basis set, and this basis is therefore used in the DFT calculations. Similarly, we used the QZ4P basis set for the calculations performed in ADF. Compared to the results for the LuX molecules, those for AuX show a slightly larger basis set dependence.

The absolute shielding constants calculated using the different methods are presented in Table III. It is important to note that the DKS/B3LYP results were obtained using a CGO approach. BP86 test calculations employing GIAOs and CGOs showed that these two approaches give approximately the same isotropic shielding constants when the cv4z basis set is used (the largest difference being 0.4% for $\sigma(\text{Cl})$ in LuCl, see Table SII⁶⁹). The first observation from the results

in Table III is the huge magnitude of the relativistic effects for both the LuX and AuX series of molecules. The non-relativistic results are much smaller than the relativistic values, in most cases by (approximately) a factor of two. Only for the shielding constants of the light nuclei in the AuX series are the relativistic effects smaller, their magnitude and sign depending on X and the functional used. Treatment of the relativistic effects using the two-component ZORA Hamiltonian is not sufficient, as shown by comparing the results obtained from the four-component DKS Hamiltonian. For instance, $\sigma(\text{Lu})$ in LuF calculated using the non-relativistic, SO-ZORA and DKS approaches and the BP86 functional are 6604.1 ppm, 9741.9 ppm, and 10 771.6 ppm; the corresponding results for $\sigma(\text{Au})$ in AuF are 8210.5 ppm, 15 712.9 ppm, and 16 377.0 ppm, respectively. Another interesting observation is the effect of HF exchange in the case of AuF, where the results change considerably compared to those of the other molecules— $\sigma(\text{Au})$ in AuF calculated using DKS/B3LYP increases by 13% when the HF exchange increases from the default 20% to 40%, whereas $\sigma(\text{Lu})$ in LuF changes by only 1%. Also, the differences between $\sigma(\text{Au})$ in AuF obtained from the BP86 and B3LYP functionals using the non-relativistic approach are very small (8210.5 ppm versus 8236.2 ppm, respectively), whereas large differences are observed between these functionals at the DKS level (16 377.0 ppm versus 19 353.5 ppm, respectively).

In Table IV, it is shown that as the amount of HF exchange increases, the occupied-virtual orbital energy gaps widen. We observe a direct correlation with the results listed in Table III; this widening of the energy gaps significantly increases the

TABLE III. Comparison of calculated absolute shielding constants (σ , in ppm) of nuclei in LuX and AuX (X = F, Cl, Br, I) molecules at different computational levels.

		NR					SO-ZORA		DKS		
		HF ^a	BP86 ^b	B3LYP(0.2) ^b	CCSD ^c	CCSD(T) ^a	BP86 ^d	B3LYP ^d	BP86 ^b	B3LYP(0.2) ^b	B3LYP(0.4) ^b
LuF	Lu	7496.1	6604.1	6816.2	7223.9	7199.1	9741.9	9942.2	10 771.6	10 942.4	11 066.2
	F	16.1	-200.2	-148.1	-29.2	-47.4	-172.5	-117.9	-174.7	-120.0	-62.3
LuCl	Lu	6631.6	5064.4	5320.0	6305.6	6253.0	8699.9	9035.7	9791.1	10 070.2	10 339.6
	Cl	348.5	36.0	86.8	296.9	264.7	113.4	183.3	118.7	187.8	283.4
LuBr	Lu	6186.1	4487.4	4718.6	5810.6	5863.3	8381.4	8755.7	9517.0	9807.3	10 123.0
	Br	1398.7	678.2	787.0	1305.0	1199.5	985.3	1159.9	1107.9	1268.3	1486.3
LuI	Lu	5341.2	3327.6	3479.0	4985.6	5038.8	7684.5	8127.0	8880.5	9212.6	9638.3
	I	2694.9	1661.9	1786.7	2610.2	2342.0	2544.0	2854.7	3040.2	3291.6	3649.1
AuF	Au	8573.6	8210.5	8236.2	8382.7	8383.1	15712.9	17322.9	16377.0	19353.5	21815.3
	F	598.0	519.6	559.5	582.2	594.1	653.9	726.4	611.9	715.0	746.3
AuCl	Au	8339.8	8169.1	8150.6	8187.7	8330.1	11867.2	12122.8	12618.9	13348.1	13944.8
	Cl	1275.5	1120.2	1177.3	1239.9	1245.5	909.8	1021.9	892.0	1022.6	1126.8
AuBr	Au	8371.4	8287.3	8253.0	8241.8	8414.4	13422.7	13390.6	14887.7	14931.4	14840.5
	Br	3314.0	2950.2	3070.7	3235.0	3249.7	2464.6	2737.1	2577.9	2855.0	3103.5
AuI	Au	8403.7	8338.0	8306.1	8238.3	8517.9	15356.3	15118.7	17081.4	16764.2	16230.6
	I	5703.5	5059.3	5242.0	5543.3	5543.0	4345.3	4873.6	4847.5	5331.2	5828.2

^aBasis sets used: unc-Cologne DKH2 for Lu, unc-DZP-DKH for Au, and unc-ADZP for the halogen atoms.

^bNR and DKS values are from calculations using Dyal-cv4z basis set. In parenthesis (0.2 or 20%, and 0.4 or 40%) is the Hartree-Fock exchange contribution to B3LYP (note that the NR/DFT and B3LYP results were obtained employing CGO whereas all the others were obtained using GIAO, see Table SII⁶⁹ for the gauge-origin dependence).

^cunc-ANO-RCC results; for LuX taken from Ref. 78.

^dSO-ZORA values are from calculations using ZORA/QZ4P basis sets.

TABLE IV. HOMO and LUMO energies and band gap (E_g) of LuX and AuX (X = F, Cl, Br, I) molecules calculated using DKS/BP86/cv4z and DKS/B3LYP/cv4z (all in eV).

	BP86			B3LYP(0.2) ^a			B3LYP(0.4) ^a			$\Delta E_g(1)^c$	$\Delta E_g(2)^d$
	HOMO	LUMO	E_g^b	HOMO	LUMO	E_g^b	HOMO	LUMO	E_g^b		
LuF	-4.69	-2.56	2.13	-5.06	-1.56	3.50	-5.60	-1.07	4.53	1.04	1.37
LuCl	-4.72	-2.83	1.89	-5.10	-1.83	3.26	-5.66	-1.25	4.41	1.14	1.38
LuBr	-4.72	-2.89	1.82	-5.10	-1.90	3.20	-5.67	-1.31	4.36	1.16	1.37
LuI	-4.70	-2.98	1.71	-5.08	-2.00	3.08	-5.67	-1.40	4.27	1.19	1.36
AuF	-7.00	-5.23	1.78	-7.87	-4.36	3.51	-8.89	-3.54	5.35	1.84	1.73
AuCl	-6.68	-4.87	1.81	-7.56	-4.07	3.48	-8.60	-3.35	5.26	1.77	1.68
AuBr	-6.38	-4.77	1.61	-7.15	-4.00	3.15	-8.09	-3.30	4.79	1.64	1.55
AuI	-5.96	-4.58	1.38	-6.60	-3.83	2.76	-7.41	-3.18	4.23	1.46	1.38

^aIn parenthesis (0.2 or 20%, and 0.4 or 40%) is the Hartree-Fock exchange contribution to B3LYP.

^b $E_g = E(\text{LUMO}) - E(\text{HOMO})$.

^c $\Delta E_g(1) = E_g(\text{B3LYP}(0.4)) - E_g(\text{B3LYP}(0.2))$.

^d $\Delta E_g(2) = E_g(\text{B3LYP}(0.2)) - E_g(\text{BP86})$.

magnitude of the paramagnetic shielding. For instance in AuF, $\sigma^{\text{para}}(\text{Au})$ for DKS/B3LYP (20% HF exchange) is 9427.3 ppm, whereas for DKS/B3LYP (40% HF exchange), it is 11 888.3 ppm (a 26% increase). This is mainly due to a strong stabilization of the occupied molecular orbitals (MOs) and destabilization of the virtual MOs, see Table IV. Such an effect has also been noticed for some organic and organometallic complexes.^{70–72}

The electronic contribution to the spin–rotation constants, the perpendicular and parallel components of the paramagnetic contribution to the shielding, and span and perpendicular component of the isotropic spin–rotation constants (all in ppm and calculated employing CGO) in the AuX molecules are listed in Table V. From the table, we can see that $\sigma_{\perp}^{\text{para}}$ (paramagnetic contribution to σ_{\perp} , the perpendicular component of σ with respect to the bond axis) of Au in AuF is dominated by the spin–orbit contribution (1532.5 ppm for ΔSC , scalar relativistic contribution, and 11 186.5 ppm for ΔSO , spin–orbit contribution). In contrast, in AuCl, AuBr, and AuI, the SC dominates even though SO effects are as large as the SC for Au in AuI. This leads to large relativistic corrections to the total shielding constants of gold in AuF and AuI, 8166.5 ppm and 8743.4 ppm, respectively (see Table VI). Test calculations using SO-ZORA/BP86/QZ4P also show that the sum of scalar and SO contributions to the absolute shielding of Au in AuF amounts to 10 410.3 ppm, whereas that of Au in AuI is 6244.3 ppm (see Table SIII⁶⁹ for details). In addition, there is a large difference between the Au results in AuF obtained using the BP86 and B3LYP functionals. This difference mainly originates from the spin–orbit coupling contribution in AuF. In the case of $\sigma_{\parallel}^{\text{para}}$ (paramagnetic contribution to σ_{\parallel} , the parallel component of σ with respect to the bond axis), there is a partial cancellation between the scalar and the SO contributions in all the AuX molecules leading to relatively small relativistic effects for this component compared to $\sigma_{\perp}^{\text{para}}$. There is a large relativistic correction to C^{el} of Au in AuF, compared to the other molecules, which mainly originates from spin–orbit coupling (see Table V). Except for Au in AuI, there is partial cancellation between scalar and SO contributions to C^{el} , but the net relativistic contributions are nonetheless large for all the nuclei of the AuX series.

We recall that the values of the paramagnetic contribution to the total absolute shielding constant calculated and obtained from the electronic contribution to the spin–rotation constant are identical in the non-relativistic theory, since the magnetic and angular momentum operators have the same form. On the other hand, in the four–component relativistic theory, these operators are fundamentally different since the magnetic momentum operator couples the large and the small component of the wave function, whereas the total angular momentum operator does not.^{8,73} As a consequence, values obtained directly from the four–component relativistic calculations are different. This indicates that determining the total absolute shielding constants based on spin–rotation constants leads to wrong results, since the error in σ^{para} is directly transferred to σ_{iso} . The overall analysis of the spin–orbit effects on the absolute shielding constants calculated using BP86/cv4z in the AuX molecules shows that the spin–orbit effect observed for $\sigma(^{197}\text{Au})$ in AuF is 31% of σ_{iso} , whereas it is 5% in AuCl, 7% in AuBr, and 16% in AuI; and similarly it contributes 7% of $\sigma(^{19}\text{F})$, 5% of $\sigma(^{35}\text{Cl})$, 3% of $\sigma(^{79}\text{Br})$, and 7% of $\sigma(^{127}\text{I})$ for the AuX series.

The final absolute shielding constants are listed in Table VI. In the case of the LuX molecules, relativistic contributions to the absolute shielding constants of both Lu and the halogen atoms increase as the halides become heavier. The same is also true for Au in the AuX series, with the exception of AuF, which has an unexpectedly large relativistic effect for $\sigma(\text{Au})$, as seen from Figure 1. From the figure, one can also see that for the LuX molecules, the use of coupled-cluster calculations is very important, whereas correlation effects are described relatively better by DFT for the AuX molecules. There is no definite trend for the relativistic corrections to the absolute shielding constants of the halogens in AuX. In all molecules, the zero-point vibrational corrections are negligible.

In a previous study using the second-order Douglas-Kroll-Hess Hamiltonian (DKH2) together with the BP86 functional, Yoshizawa and Sakaki⁷⁴ reported the absolute shielding constants of gold in AuF to be 23 747 ppm, 14 196 ppm in AuCl, 15 891 ppm in AuBr, and 18 194 ppm in AuI. The results obtained in our study for these nuclei are

TABLE V. Comparison of the calculated electronic contributions to C , paramagnetic contributions to σ , shielding spans (Ω), and the perpendicular component of the total C for nuclei in AuX (X = F, Cl, Br, I) (all in ppm); BP86/cv4z using the CGO approach for all calculations.

	NR ^a	SC ^b	DKS ^c	Δ SC ^d	Δ SO ^e	Δ rel ^f	NR ^a	SC ^b	DKS ^c	Δ SC ^d	Δ SO ^e	Δ rel ^f
AuF												
C_{\perp}^{el}	-2089.6	-6112.5	9760.7	-4022.9	15873.2	11850.3	19.2	220.9	147.9	201.7	-73.0	128.7
$\sigma_{\perp}^{\text{para}}$	-2089.6	-557.1	10629.4	1532.5	11186.5	12719.0	19.2	225.6	9.3	206.4	-216.3	-9.9
$\sigma_{\parallel}^{\text{para}}$	0.0	5547.7	-1811.1	5547.7	-7358.8	-1811.1	0.0	4.3	300.5	4.3	296.2	300.5
Ω	2033.6	6051.9	12493.4	4018.3	6441.5	10459.8	34.4	233.1	279.5	198.7	46.4	245.1
C_{\perp}	-2029.3	-6052.2	9820.9	-4022.9	15873.1	11850.2	71.0	272.1	199.0	201.1	-73.1	128.0
AuCl												
C_{\perp}^{el}	-2178.8	-3291.2	-1219.6	-1112.4	2071.6	959.2	-107.9	-427.3	-510.9	-319.4	-83.6	-403.0
$\sigma_{\perp}^{\text{para}}$	-2178.8	2269.6	2743.7	4448.4	474.1	4922.5	-107.9	-396.7	-587.1	-288.8	-190.4	-479.2
$\sigma_{\parallel}^{\text{para}}$	0.0	5552.0	2619.4	5552.0	-2932.6	2619.4	0.0	29.9	268.5	29.9	238.6	268.5
Ω	2095.5	3201.7	202.0	1106.2	-2999.7	-1893.5	56.4	377.2	806.4	320.8	429.2	750.0
C_{\perp}	-2086.2	-3198.7	-1127.1	-1112.5	2071.6	959.1	-31.2	-350.9	-434.6	-319.7	-83.7	-403.4
AuBr												
C_{\perp}^{el}	-2062.1	-2568.6	335.5	-506.5	2904.1	2397.6	-389.2	-1529.6	-1447.2	-1140.4	82.4	-1058.0
$\sigma_{\perp}^{\text{para}}$	-2062.1	2997.7	5229.5	5059.8	2231.8	7291.6	-389.2	-1233.9	-1193.7	-844.7	40.2	-804.5
$\sigma_{\parallel}^{\text{para}}$	0.0	5552.4	4344.4	5552.4	-1208.0	4344.4	0.0	294.4	434.2	294.4	139.8	434.2
Ω	1922.1	2417.5	1022.7	495.4	-1394.8	-899.4	273.4	1414.9	1514.7	1141.5	99.8	1241.3
C_{\perp}	-1910.2	-2416.7	487.4	-506.5	2904.1	2397.6	-251.7	-1392.3	-1309.8	-1140.6	82.5	-1058.1
AuI												
C_{\perp}^{el}	-1993.7	-1690.3	3652.6	303.4	5342.9	5646.3	-837.4	-3604.2	-2987.1	-2766.8	617.1	-2149.7
$\sigma_{\perp}^{\text{para}}$	-1993.7	3881.4	8552.5	5875.1	4671.1	10546.2	-837.4	-2412.3	-1604.5	-1574.9	807.8	-767.1
$\sigma_{\parallel}^{\text{para}}$	0.0	5553.4	4338.9	5553.4	-1214.5	4338.9	0.0	1191.0	659.6	1191.0	-531.4	659.6
Ω	1825.6	1506.8	4379.5	-318.8	2872.7	2553.9	678.8	3447.1	2108.1	2768.3	-1339.0	1429.3
C_{\perp}	-1809.9	-1506.5	3836.3	303.4	5342.8	5646.2	-660.7	-3427.6	-2810.5	-2766.9	617.1	-2149.8

^aNR—non-relativistic BP86/cv4z results.^bSC—BP86/cv4z results calculated without spin-orbit coupling.^cDKS—full four-component BP86/cv4z relativistic results.^d Δ SC—scalar relativistic correction (difference between SC and NR).^e Δ SO—spin-orbit relativistic correction (difference between DKS and SC).^f Δ rel—total relativistic correction (difference between DKS and NR).

16547.6, 12807.3, 15064.2, and 17308.7 ppm, respectively (see Table VI). Considering only the levels of theory (pure two-component DFT vs four-component DFT combined with CCSD(T) approach), our final values of the shielding constants should be more accurate. Recently, Maldonado *et al.*⁷⁵ in a study of different relativistic methods computed the shielding constants of Au in the AuX series. Using a four-component (4c-) approach at the B3LYP level, they obtained 18222.70, 13443.57, 14701.90, and 16374.60 ppm for X = F, Cl, Br, and I, respectively, and similar results for the 4c-PBE0 approximation. Considering the role of various approximations they proposed 15000–16000 ppm as the best theoretical estimate of the Au shielding constant in AuF, which agrees well with our final result (16547.6 ppm). Moreover, the authors stated that the unusually large values earlier obtained for this constant were due to quasi-instability problems. Our relativistic DFT results listed in Table III also show that B3LYP overestimates the shielding constant of Au in AuF (19353.5 ppm), while that obtained from BP86 (16377.0 ppm) is close to the proposed range.

C. NMR shielding spans

When the electronic density surrounding the nucleus is asymmetric, the magnitude of the chemical shielding components becomes different. For the linear molecules considered here, this leads to $\sigma_{\parallel} \neq \sigma_{\perp}$, where σ_{\parallel} (σ_{\perp}) defines the parallel (perpendicular) component of σ with respect to the bond axis (a similar notation is used for C). Taking into account the relativistic effects and the two Flygare relations,^{2,4} the isotropic shielding and the span of the shielding tensor (Ω_K in ppm) can be expressed as¹⁴

$$\sigma_{K,\text{iso}} \approx \sigma_K^{\text{dia,FA}} + \left(\frac{10^9 m_p}{2m_e g_K B_r} \right) C_{K,\text{iso}} + \sigma_{K,\text{iso}}^{\text{para,rel}} - \left(\frac{10^9 m_p}{2m_e g_K B_r} \right) C_{K,\text{iso}}^{\text{el,rel}}, \quad (2)$$

$$\Omega_K \approx \left| \left(\frac{10^9 m_p}{2m_e g_K B_r} \right) C_{K,\perp} + \sigma_{K,\perp}^{\text{para,rel}} - \sigma_{K,\parallel}^{\text{para,rel}} - \left(\frac{10^9 m_p}{2m_e g_K B_r} \right) C_{K,\perp}^{\text{el,rel}} \right|. \quad (3)$$

TABLE VI. Final absolute shielding constants in LuX and AuX (X = F, Cl, Br, I) molecules calculated using the DFT and CCSD(T) approaches (in ppm).

		$\Delta\sigma(\text{rel } 1)^a$	$\Delta\sigma(\text{rel } 2)^b$	CCSD(T) ^c	ZPV ^d	Total 1 ^e	Total 2 ^f
LuF	Lu	4167.5	4 126.2	7199.1	-5.4	11 361.2	11 319.9
	F	25.5	28.1	-47.4	-1.4	-23.3	-20.7
LuCl	Lu	4726.7	4 750.2	6253.0	-1.3	10 978.4	11 001.9
	Cl	82.7	101.0	264.7	-0.7	346.7	365.0
LuBr	Lu	5029.6	5 088.7	5863.3	-1.1	10 891.8	10 950.9
	Br	429.7	481.3	1199.5	-0.8	1628.4	1680.0
LuI	Lu	5552.9	5 733.6	5038.8	-0.8	10 590.9	10 771.6
	I	1378.3	1 504.9	2342.0	-0.7	3 719.6	3 846.2
AuF	Au	8166.5	11 117.3	8383.1	-2.0	16 547.6	19 498.4
	F	92.3	155.5	594.1	-11.1	675.3	738.5
AuCl	Au	4449.8	5 197.5	8330.1	27.4	12 807.3	13 555.0
	Cl	-228.2	-154.7	1245.5	-9.5	1 007.8	1 081.3
AuBr	Au	6600.4	6 678.4	8414.4	49.4	15 064.2	15 142.2
	Br	-372.3	-215.7	3249.7	-13.8	2 863.6	3 020.2
AuI	Au	8743.4	8 458.1	8517.9	47.4	17 308.7	17 023.4
	I	-211.8	89.2	5543.0	-19.4	5 311.8	5 612.8

^a $\Delta\sigma(\text{rel } 1)$ —difference between DKS and NR results calculated using BP86/cv4z (see Table III for the BP86 results).

^b $\Delta\sigma(\text{rel } 2)$ —difference between DKS and NR results calculated using B3LYP(0.2)/cv4z (see Table III for the B3LYP results).

^cBasis sets used: unc-Cologne DKH2 for Lu, unc-DZP-DKH for Au and unc-ADZP for the halogen atoms.

^dZero-point vibrational correction.

^eThe sum of relativistic corrections from BP86/cv4z, zero-point vibrational correction and the CCSD(T) results.

^fThe sum of relativistic corrections from B3LYP(0.2), zero-point vibrational correction and the CCSD(T) results.

The superscript “rel” indicates the relativistic contribution to the corresponding tensor, $\sigma_K^{\text{dia,FA}}$ is the shielding constant of the free atom K in ppm, $\Omega = |\sigma_{\perp} - \sigma_{\parallel}|$, and σ_{\parallel} (σ_{\perp}) are in ppm, B_r in MHz and the spin-rotation constants in kHz. Note that Eq. (3) is correct under the assumption that the Flygare relation for the diamagnetic shielding,⁴ in its relativistic extension, holds not only for the isotropic values but also for the diagonal tensor components. This assumption introduces an error of

less than 1% for the systems studied in this work (except Au in AuCl where the error is about 7%).

The shielding spans of the nuclei in the molecules studied in this work calculated using the relativistic and non-relativistic approaches are presented in Table VII. The trends of the shielding spans obtained from the two- and four-component relativistic calculations show that in the LuX molecules, both the Lu and X shielding spans increase as the X atom becomes heavier. This is also true for the halogen atoms in AuX, but not for the gold atoms. The non-relativistic results for the AuX molecules show in general decreasing shielding spans for the gold atoms and an increasing trend for the halogens as the atoms become heavier. The SO-ZORA and DKS values for the spans of the nuclei in LuX are comparable when using the same functional. However, this is not true for the AuX molecules, see Table VII. The relativistic corrections to the span of the nuclei in the LuX molecules are relatively small compared to the relativistic corrections to the total absolute shielding constants. The case of the LuX molecules can be explained using Eqs. (2) and (3). From Eq. (3), we see that unlike in the case of σ_{iso} , there is partial cancellation of the relativistic effects in Ω (see Table VII). For instance, in LuF, the relativistic contributions are 14% for $\Omega(^{175}\text{Lu})$ and 3% for $\Omega(^{19}\text{F})$, to be compared with 39% for $\sigma(^{175}\text{Lu})$ and 17% for $\sigma(^{19}\text{F})$ (a similar case has been reported previously¹⁴). However, this is very different for AuF, for which the spin-orbit coupling dominates the shielding constant and as a consequence this cancellation of the relativistic effects becomes less pronounced.

If we omit the relativistic corrections from Eq. (3), we get the relation which has been used to determine the span from the experimental spin-rotation constant. However, in most of

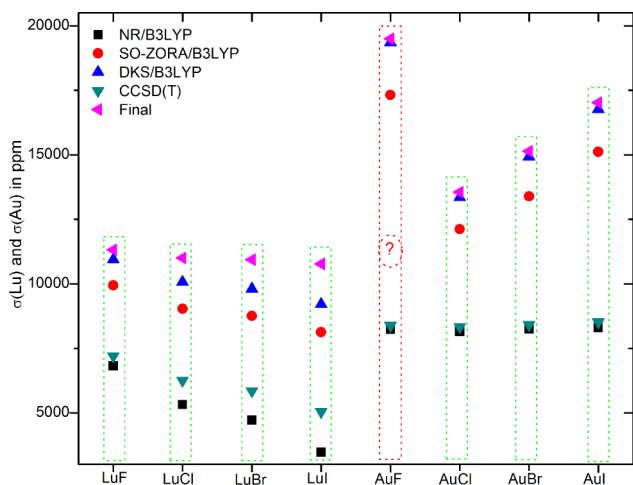


FIG. 1. Comparison of absolute shielding constants of LuX and AuX (X = F, Cl, Br, I) molecules: calculated using B3LYP functional combined with non-relativistic and relativistic Hamiltonians, as well as using CCSD(T) and final corrected values. For the description of the methods, see footnotes of Table III. The question mark in the figure shows the expected place of $\sigma(\text{Au})$ if AuF follows the trend of the AuX molecules.

TABLE VII. Comparison of the calculated shielding spans (Ω , in ppm) of nuclei in LuX and AuX (X = F, Cl, Br, I) molecules using different computational levels and the final total shielding spans.

		NR		SO-ZORA		DKS		$\Delta\Omega(\text{rel } 1)^c$	$\Delta\Omega(\text{rel } 2)^d$	CCSD(T) ^e	Total 1 ^f	Total 2 ^g
		BP86 ^a	B3LYP ^a	BP86 ^b	B3LYP ^b	BP86 ^a	B3LYP ^a					
LuF	Lu	2470.5	2152.3	2162.7	1 875.9	2 135.8	1 881.3	-334.7	-271.0	1576.2	1 241.5	1 305.2
	F	1043.5	965.9	1011.7	929.7	1 018.6	936.1	-24.9	-29.8	814.4	789.5	784.6
LuCl	Lu	4782.6	4399.3	3722.8	3 250.8	3 629.8	3 220.3	-1 152.8	-1 179.0	2997.8	1 845.0	1 818.8
	Cl	1682.2	1606.3	1608.2	1 502.6	1 621.5	1 515.6	-60.7	-90.7	1339.1	1 278.4	1 248.4
LuBr	Lu	5649.8	5303.2	4204.6	3 682.5	4 052.9	3 636.3	-1 596.9	-1 666.9	3584.2	1 987.3	1 917.3
	Br	3683.1	3520.1	3569.6	3 306.6	3 565.5	3 317.3	-117.6	-202.8	2 900.9	2 783.3	2 698.1
LuI	Lu	7391.6	7164.5	5238.3	4 629.9	4 982.2	4 540.9	-2 409.4	-2 623.6	4823.1	2 413.7	2 199.5
	I	5775.0	5587.8	5868.8	5 405.5	5 773.1	5 375.0	-1.9	-212.8	4754.1	4 752.2	4 541.3
AuF	Au	2033.8	1994.1	8108.3	11 472.8	12 445.2	16 209.5	10 411.4	14 215.4	1772.8	12 184.2	15 988.2
	F	31.9	91.7	14.4	114.1	280.9	23.1	249.0	-68.6	72.0	321.0	3.4
AuCl	Au	2100.5	2127.3	616.2	213.7	158.6	494.0	-1 941.9	-1 633.3	1857.2	84.7	223.9
	Cl	61.9	23.8	636.4	439.4	808.9	523.7	747.0	499.9	63.1	810.1	563.0
AuBr	Au	1925.9	1976.3	156.2	90.0	971.0	705.2	-954.9	-1 271.1	1733.4	778.5	462.3
	Br	280.6	99.7	1421.3	1 003.8	1 520.6	1 047.7	1 240.0	948.0	84.5	1 324.5	1 032.5
AuI	Au	1853.6	1900.4	3419.5	3 126.9	4 266.3	3 669.1	2 412.7	1 768.7	1582.1	3 994.8	3 350.8
	I	684.3	409.8	2400.2	1 686.0	2 115.5	1 524.9	1 431.2	1 484.1	21.1	1 452.3	1 505.2

^aUsing cv4z basis sets (all using GIAO, except B3LYP where CGO was used).

^bUsing ZORA optimized QZ4P basis sets.

^c $\Delta\Omega(\text{rel } 1)$ —difference between DKS and NR results calculated using BP86/cv4z (relativistic corrections).

^d $\Delta\Omega(\text{rel } 2)$ —difference between DKS and NR results calculated using B3LYP/cv4z (relativistic corrections).

^eBasis sets used: unc-Cologne DKH2 for Lu, unc-DZP-DKH for Au and unc-ADZP for the halogen atoms.

^fSum of the CCSD(T) results and $\Delta\Omega(\text{rel } 1)$ from BP86/cv4z, absolute values.

^gSum of the CCSD(T) results and $\Delta\Omega(\text{rel } 2)$ from B3LYP/cv4z, absolute values.

the AuX molecules, where the relativistic correction is very large, determining the shielding span from the spin-rotation constants causes unrecoverable errors. In Table V, the scalar and spin-orbit contributions to the shielding span of the nuclei in the AuX molecules calculated using DKS/BP86/cv4z were listed. In the case of AuCl, AuBr, and AuI, these two relativistic contributions partly cancel, having opposite sign, which as a result decreases the span of the gold nuclei. However, in AuF, they are both positive and hence the total relativistic contribution ($\Delta\text{SC} + \Delta\text{SO}$) to the shielding span of gold in AuF increases (see Table V and Fig. S1⁶⁹ of the supplementary material). The same is also true for the halogens with the exception of the iodine shielding span.

The common way of determining the shielding span in diatomic molecules is based on estimation from the perpendicular spin-rotation constant (see, e.g., Refs. 76 and 77), in theory corresponding to the use of Eq. (3) without the relativistic correction terms. This is correct in the non-relativistic theory, see Table V. For instance, the non-relativistic C_{\perp} of Au in AuF gives -2029.3 ppm whereas its Ω is 2033.6 ppm, but those calculated using DKS/BP86 are 9820.9 ppm and 12 493.4 ppm, respectively. Unexpectedly, the relation between the span and the spin-rotation constant also works if only scalar relativistic corrections are included. If we insert the ΔSC terms listed in Table V into Eq. (3), we see that the scalar relativistic corrections cancel each other and as a result the span is approximately the same as given by the perpendicular component of the spin-rotation constant.

For example, in AuF $C_{\text{Au},\perp}^{\text{el},\Delta\text{SC}}$ is -4022.9 ppm, $\sigma_{\text{Au},\perp}^{\text{para},\Delta\text{SC}}$ is 1532.5 ppm and $\sigma_{\text{Au},\parallel}^{\text{para},\Delta\text{SC}}$ is 5547.7 ppm. When we insert these values into Eq. (3) ($1532.5 - 5547.7 + 4022.9$), we get a net scalar relativistic correction of 7.7 ppm, which makes the relation between the span and spin-rotation constant valid also in the presence of only scalar relativistic corrections ($\Omega_{\text{Au}}^{\text{SC}}$ in AuF is 6051.9 ppm and $C_{\text{Au},\perp}^{\text{SC}}$ is -6052.2 ppm, see Table V). However, the relation becomes invalid when spin-orbit relativistic corrections are included. For instance, the sum of the ΔSO relativistic corrections in Eq. (3) for Au in AuF ($11 186.5 + 7358.8 - 15 873.2$) is 2672.1 ppm, which is the major contribution to Δrel (2679.8 ppm) (see Table V).

The final spans of all nuclei are obtained by adding $\Delta\Omega(\text{rel})$, the difference between the DKS and NR results obtained using DFT/cv4z, to the non-relativistic CCSD(T) values. These results show that, with the exception of $\Omega(\text{Au})$ in AuF, the span increases as the nuclei become heavier.

IV. CONCLUSIONS

In this contribution, we presented the nuclear spin-rotation and absolute shielding constants of all nuclei in the LuX and AuX (X = F, Cl, Br, I) molecules, calculated at the non-relativistic (CCSD(T) and DFT) and four-component relativistic DFT levels of theory. Our final theoretical results are obtained by adding $\Delta(\text{rel})$, the difference between DKS and NR results obtained using either BP86/cv4z or B3LYP/cv4z, to

the non-relativistic CCSD(T) values. Even though in principle the relativistic DFT approach gives simultaneously an estimate of electron correlation and relativistic effects, we have adopted this procedure, assuming that at the non-relativistic level the electron correlation effects are more reliably described by coupled-cluster methods than by DFT.

For the LuF and LuCl molecules, the CCSD(T) spin-rotation constants are in good agreement with the experimental values, adding the DFT-calculated relativistic corrections to these results deteriorates the agreement. In this case, DFT significantly overestimates the electron correlation effects at the non-relativistic level, indicating that adding DFT relativistic corrections to the CCSD(T) results may not be appropriate. For all the AuX molecules, the final calculated nuclear spin-rotation constants are in quite good agreement with the corresponding available experimental data. For LuBr and LuI, the computed nuclear spin-rotation constants are the first to be reported. The relativistic effects on the shielding constants are large compared to the effects on the nuclear spin-rotation constants and shielding spans for the LuX molecules. However, due to considerable spin-orbit coupling in the AuX molecules, the relativistic correction to the span is in some cases larger than that to the shielding.

For most of the molecules studied, including relativistic effects in the calculations leads to a very significant change of the absolute shielding constants. The relativistic correction to the shielding span of gold in AuF is unexpectedly large compared to the other molecules. This is due to the signs of the scalar and spin-orbit relativistic contributions, which add up and as a result increase the total relativistic correction, whereas in the other molecules there is a partial cancellation of these two contributions, leading to a smaller total relativistic correction.

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