

Relativistic study of nuclear magnetic shielding constants: mercury dihalides

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Abstract

Relativistic ab initio calculations of the ¹⁹⁹Hg nuclear magnetic shielding constant and the chemical shift of HgX₂ (X = Cl, Br, I) are presented. The method is a combination of the relativistic spin-free no-pair theory of Sucher and Hess and the spin-orbit unrestricted Hartree-Fock (SO-UHF) method reported previously. For the ¹⁹⁹Hg shielding constant, both the spin-free relativistic (SFR) term, like mass-velocity and Darwin terms, and the SO term are important and they strongly couple with each other. Without them the experimental trend in mercury dihalides cannot be explained even qualitatively. Since these relativistic terms stabilize the orbitals closer to the nucleus, a basis set having larger freedom near the nucleus is appropriate.

1. Introduction

Multinuclear NMR experiments have covered almost all the nuclei on the periodic table, and a large number of experimental data have been documented [1,2] even for heavy elements such as Hg, W and Pt. In a series of our studies [3–5], we have calculated NMR chemical shifts of a large number of molecules including transition metals and main-group elements, and elucidated their electronic mechanisms. We found that a major mechanism of the metal chemical shifts is an intrinsic property of the metal atom itself and therefore related with the position of the metal atom in the periodic table [4]. However, we have not extended our study to molecules including fifth-row atoms, since the relativistic effects are expected to be

of primary importance [6]. It is of great interest and of fundamental importance to study heavy metal NMR chemical shifts including full relativistic effects.

When the resonant nuclei are not heavy but are bonded to heavy elements like iodine, the spin-orbit (SO) effect is the most important relativistic effect [7]. We have developed the SO-unrestricted Hartree-Fock (UHF) method for a systematic calculation of the SO effect [8]. It is easier than the sum-over-state perturbation method [9,10]. We have demonstrated the importance of the spin-orbit effect for a number of halides such as HX [7,8], CH₃X [8], GaX₄⁻, InX₄⁻ [11], SiX₄, SiXI₃ [12], AlX₄⁻ [13]. The normal halogen dependence, classified by Kidd [1], is essentially due to the SO effect.

When the resonance nuclei are heavy, other spin-free relativistic effects like mass-velocity (MV) and

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Darwin (DW) terms [14] should become important [6]. We have reported [7] a relativistic method for calculating the magnetic shielding constants: we have combined the relativistic spin-free no-pair theory of Sucher [15] and Hess [16,17] and the SO-UHF method developed in our laboratory [8]. The so-called MV and DW terms are included in the former and the SO operator is handled in the latter. We have applied this theory to the calculations of the proton magnetic shielding constant of hydrogen halides HX (X = F, Cl, Br, I) and confirmed that the SO effect is dominant in the relativistic effects: the SFR terms were small since their effects are essentially local at the heavy halogen atoms [7].

In the present paper, we apply our relativistic method to calculations of the ^{199}Hg magnetic shielding constant of HgX_2 (X = Cl, Br, I), for which all the relativistic terms are expected to be important. In HgCl_2 the relativistic effect would mainly be due to Hg, but in HgI_2 the relativistic effects of both Hg and I should be important. We believe that this is the first relativistic calculation of the magnetic shielding constant for an element belonging to the fifth row of the periodic table.

2. Method

The details of the relativistic method for calculating the nuclear magnetic shielding constant have been given in a previous paper of this series [7]. It is in the Hartree-Fock (HF) level of approximation.

The zeroth-order hamiltonian is the relativistic hamiltonian and the magnetic field is dealt with as a perturbation. The relativistic hamiltonian is composed of the spin-free relativistic (SFR) no-pair hamiltonian [16,17] plus the SO interaction operator. The former is defined using the free-particle projectors [16] and the external-field projectors [17], and the conventional Breit-Pauli form is used for the latter. Our SO-UHF method is modified to include all of these terms, together with the external magnetic field.

The magnetic shielding constant is partitioned into diamagnetic term, σ^{dia} , paramagnetic term, σ^{para} , spin-dipolar term, $\sigma^{\text{SO}}(\text{SD})$, and the fermi contact term, $\sigma^{\text{SO}}(\text{FC})$ [7]. This partitioning is the same as that in the previous study on the SO effect [8]. No new term arises from the SFR terms, which affect the shielding constant only through the change in the electronic wave function.

For understanding the roles of the individual relativistic terms and the coupling thereof, we calculate in four levels of approximation [7]. They arise from the combinations of the "relativistic spin-free" and "non-relativistic" and "with" and "without" the spin-orbit interaction, namely,

- level I: non-relativistic Hamiltonian
- level II: non-relativistic Hamiltonian plus SO term
- level III: relativistic spin-free no-pair Hamiltonian (1)
- level IV: relativistic spin-free no-pair Hamiltonian plus SO term

Table 1
Total energy of HgX_2 at non-relativistic and relativistic levels with and without spin-orbit effect (in hartree)^a

Compound	non-relativistic Hamiltonian		relativistic Hamiltonian			
	without SO	with SO	external-field projection		free-particle projection	
			without SO	with SO	without SO	with SO
basis A						
HgCl ₂	-19312.273094	-19312.333206	-19438.921167	-19438.958603	-20116.384328	-20116.416656
HgBr ₂	-23533.847883	-23533.913920	-23698.287024	-23698.287024	-24393.693110	-24393.730574
HgI ₂	-32219.717066	-32219.804774	-32488.673471	-32488.733929	-33339.303327	-33339.358006
basis B						
HgCl ₂	-19312.596141	-19312.656265	-19729.646390	-19729.684390	-20664.185867	-20664.219027
HgBr ₂	-23534.170935	-23534.236983	-23988.807314	-23988.850615	-24941.493203	-24941.531529
HgI ₂	-32220.040146	-32220.127868	-32778.996386	-32779.057476	-33889.106919	-33889.162533

^a Total energy contribution of the SO term is calculated as a sum of the *x*, *y*, and *z* contributions.

Table 2
¹⁹⁹Hg magnetic shielding constants (ppm) and their analyses for HgX₂ calculated by the non-relativistic and relativistic methods and with and without the spin-orbit effect using basis A

Compound	without SO			with SO			total			δ^{exp}
	σ^{dia}	σ^{para}	σ^{tot}	σ^{dia}	σ^{para}	σ^{SO}	SD	FC	δ^{cal}	
non-Relativistic Hamiltonian										
level I										
HgCl ₂	9848	-1663	8185	9848	-1780	94	192	286	8354	0
HgBr ₂	9973	-1716	8257	9973	-1839	96	514	610	8744	-655
HgI ₂	10096	-2121	7975	10096	-2274	117	824	941	8763	-1609
Relativistic Hamiltonian (external-field)										
level III										
HgCl ₂	9970	-1193	8777	9970	-1251	55	198	253	8972	0
HgBr ₂	10095	-1181	8914	10095	-1240	54	678	732	9587	-655
HgI ₂	10218	-1421	8797	10218	-1493	64	1035	1099	9824	-1609
Relativistic Hamiltonian (free particle)										
level III										
HgCl ₂	10072	-1061	9011	10072	-1107	46	193	239	9204	0
HgBr ₂	10198	-1017	9181	10198	-1062	43	797	840	9976	-655
HgI ₂	10321	-1199	9122	10320	-1253	50	1201	1251	10318	-1114

Table 3
¹⁹⁹Hg magnetic shielding constants and their analyses for HgX₂ calculated by the non-relativistic and relativistic methods and with and without the spin-orbit effect using basis B

Compound	without SO			with SO			δ^{exp}			
	σ^{dia}	σ^{para}	σ^{tot}	σ^{dia}	σ^{para}	σ^{SO}	σ^{tot}	δ^{cal}		
				SD			FC			
non-Relativistic Hamiltonian										
level I										
HgCl ₂	9856	-1663	8193	9855	-1780	94	179	273	8348	0
HgBr ₂	9981	-1716	8265	9981	-1839	96	469	565	8707	-655
HgI ₂	10104	-2121	7983	10103	-2274	117	742	859	8688	-1609
Relativistic Hamiltonian (external-field)										
level III										
HgCl ₂	10714	-1202	9512	10714	-1263	57	623	680	10131	0
HgBr ₂	10839	-1184	9655	10839	-1245	55	2154	2209	11803	-655
HgI ₂	10961	-1422	9539	10961	-1496	65	3212	3277	12742	-1609
Relativistic hamiltonian (free-particle)										
level III										
HgCl ₂	11251	-1077	10174	11250	-1128	49	737	786	10908	0
HgBr ₂	11376	-1021	10355	11376	-1069	45	3171	3216	13523	-655
HgI ₂	11499	-1193	10306	11499	-1249	52	4641	4693	14943	-1609

The differences among these calculations serve to the understanding of the following features;

- level IV – level I: full relativistic effect
- level II – level I: SO effect in the non-relativistic environment
- level IV – level III: SO effect in the presence of the SFR terms
- level III – level I: SFR effects in the absence of the SO term (2)
- level IV – level II: SFR effects in the presence of the SO term

3. ^{199}Hg magnetic shielding constants in HgX_2

Many experimental data are accumulated on the magnetic shielding constants of fifth-row nuclei [1,2], but no theoretical study has been reported. We here report a relativistic calculation of the ^{199}Hg magnetic shielding constants of HgX_2 ($X = \text{Cl}, \text{Br}, \text{I}$). We choose HgCl_2 as a reference compound for chemical shift.

The basis sets for HgX_2 are the gaussian functions given by Huzinaga et al. [18], which were optimized by the non-relativistic calculations. The Hg basis set is based on the (15s12p9d3f) set, and we used two different contractions: one is the [7s6p4d1f] contraction (basis A) in which the valence 6s and 6p orbitals are double-zeta but the core orbitals remain minimal, and the other is the [10s6p4d1f] contraction (basis B) in which the 1s orbital is uncontracted. The latter basis set is designed to see the relaxation of the inner core orbital due to the relativistic effect. For halogens we use (11s8p)/[4s3p] for Cl, (13s10p4d)/[4s3p2d] for Br,

and (16s13p7d)/[6s5p3d] for I, all taken from Huzinaga's book [18]. The FOBFs (first-order higher angular momentum functions) which work to diminish the gauge origin dependence [19] were not added, since the Hg magnetic shielding constants of HgX_2 are gauge origin independent for molecular symmetry and since the computational dimension becomes very large when we add FOBFs. The HgX_2 molecules are linear and the Hg–X distances are 2.252, 2.461, and 2.554 for $X = \text{Cl}, \text{Br},$ and I , respectively [20]. For the SO interaction we include only the one-electron term; the two-electron term was neglected in the present study.

The energies of HgX_2 at the non-relativistic and relativistic levels are summarized in Table 1. The relativistic correction to the Hg atomic energy is about 1200 au by the numerical HF and Dirac HF methods [21,22]. The corresponding energy for HgCl_2 is 804 au for basis A and 1352 au for basis B using the free-particle projection. The uncontraction of the 1s orbital of Hg in basis B allows a large relativistic reorganization effect, as expected. This indicates that the quality of the relativistic wave function is better for basis B than for basis A.

Tables 2 and 3 show the ^{199}Hg magnetic shielding constants and their analysis as defined by Eq. 12 of Ref. [7]. We calculated at the levels I–IV defined in Eq. (1). Table 2 is for basis A and Table 3 for basis B. Table 4 shows the analysis defined by Eq. (2) for the magnetic shielding constants of HgCl_2 and HgI_2 and for the chemical shift of HgI_2 , the reference compound being HgCl_2 . Fig. 1 shows the correlations between theory and experiment in different levels of approximation for ^{199}Hg chemical shifts calculated by the external-field projection in the

Table 4
Analysis of the relativistic effects for the ^{199}Hg shielding constant and chemical shift of HgCl_2 and HgI_2 (ppm)

Term	HgCl_2 shielding constant		HgI_2 shielding constant		$\text{HgI}_2 - \text{HgCl}_2$ chemical shift ^a	
	basis A	basis B	basis A	basis B	basis A	basis B
level IV – level I	787	1938	1849	4759	1062	2821
level II – level I	169	155	788	705	619	550
level IV – level III	195	619	1027	3203	832	2584
level III – level I	592	1319	822	1556	230	237
level IV – level II	618	1783	1061	4054	443	2271

^a Sign is different from the definition of the ordinary chemical shift in Tables 2 and 3.

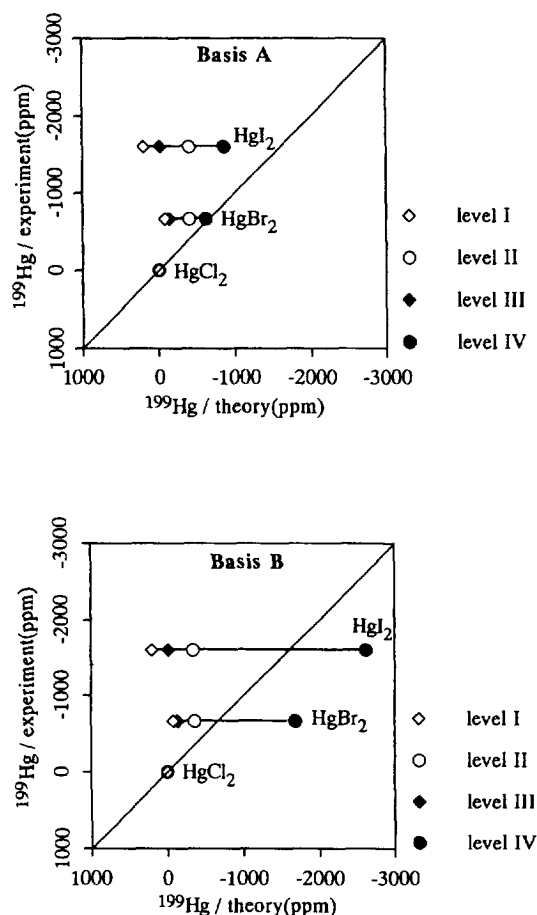


Fig. 1. Correlations between theory and experiment for ^{199}Hg chemical shifts in mercury dihalides. The upper and lower figures show the results calculated by bases A and B, respectively, using external-field projection.

relativistic calculations. The upper one is for basis A and the lower one for basis B.

Fig. 1 shows that the relativistic effects are quite large and important for the ^{199}Hg chemical shift. Without the relativistic effects, the experimental trend of the chemical shift can not be explained: the normal halogen dependence (NHD) in Kidd's term [1], i.e., a compound containing a heavier halogen gives a higher-field shift, is far from explained when the relativistic effects are neglected. Though the non-relativistic results are rather independent of the uncontraction of the innermost $1s$ orbital of Hg, the relativistic results are strongly affected. Since the SFR terms as represented by the MV and DW terms and the SO term stabilize the orbitals close to the

nucleus, the roles of the inner primitive GTOs increase, in contrast to the non-relativistic case, resulting in a large increase of the FC term, as shown below. The present results with basis B overshoot the experimental values for HgBr_2 and HgI_2 mainly because the SO effect is overestimated in the present calculation due to the neglect of the two-electron term. Generally speaking, 20–40% of the one-electron term is canceled out by the two-electron term [16].

We now analyze the relativistic effect in more detail using the results shown in Table 4, in particular. We realize from this table that the various relativistic effects are much larger in HgX_2 than those in the previous case of HX [7].

We first examine the shielding constant of HgCl_2 . Since HgCl_2 is used as a reference compound in the chemical shift, the effect in HgCl_2 is hidden in Fig. 1. Since the relativistic effect of Cl is small, this molecule is regarded as showing the relativistic effect caused by mercury. From Table 4 we see that the most important relativistic effect on the ^{199}Hg shielding constant is the SFR term. In basis B the SO effect becomes important through the coupling with the SFR term. These effects are reflected mostly to the FC term as seen from Tables 2 and 3. This clearly shows that a full relativistic calculation is necessary for studying the heavy-nucleus magnetic shielding constants.

We next analyze the relativistic effect for the shielding constant of HgI_2 . From Table 4, we see that the SFR and SO terms are important and that they strongly couple with each other particularly in basis B. The SFR term is most important and next is the SO term. The SO term due to iodine would be larger than that due to Hg. On the other hand, for the chemical shift of HgI_2 , the reference compound being HgCl_2 , the importance of the SO term increases, since the relativistic effects local to the Hg atom cancel when we calculate the chemical shift.

Thus, we get the following picture of the relativistic effect in HgX_2 . The SFR terms of Hg couples strongly with the SO term of itself and of iodine. They stabilize and spin-polarize the inner orbitals near the ^{199}Hg nucleus and the resultant spin-polarization is detected by the FC term. Naturally, such stabilizations and polarizations of the inner orbitals are easier when such freedom is given near the

nucleus by uncontracting the inner 1s orbital of Hg (basis B). We note that in the present picture the role of the SO term may be exaggerated, since we neglect the two-electron SO term: the SFR term would actually be more important than it looks in the present study.

4. Concluding remarks

We have reported the first relativistic calculation of the heavy-nucleus magnetic shielding constant for HgX_2 ($X = \text{Cl}, \text{Br}, \text{I}$). Several important aspects are clarified.

(1) Relativistic calculations are necessary for the ^{199}Hg shielding constant of mercury dihalides since both SFR and SO terms are important and strongly couple with each other. This is in a sharp contrast to the previous case of the proton shielding constants in hydrogen halides [7], where only the SO effect of the heavy halogen atom is important. In both cases, the FC term is the most important.

(2) For the ^{199}Hg shielding constant, the SFR term of Hg is the largest and the second is the SO term of Hg and of the heavy ligands X. The SFR terms of X are less important since their effects are local on the atom X.

(3) For the ^{199}Hg chemical shift, a relative quantity, the SO term of X becomes more important for heavier halogens, and secondly the SFR term of Hg.

(4) Since both SFR and SO terms stabilize the orbitals closer to the nucleus, the coupling between them is so strong that their effects are far from additive. For adequately describing these effects, the basis set for the orbitals near the heavy nucleus should have a large flexibility.

Some problems are left for future study: 1. effect of the two-electron SO term, 2. use of the SO term as appearing in the no-pair theory, 3. similar expression for the fermi-contact term, and 4. electron correlation effect. The points 2 and 3 are related to the finite size of the nucleus. An examination of different relativistic theory would also be important.

Part of this study has been presented at the ESF Workshop on Calculation of NMR Parameters held in Helsinki [23].

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