

Article

The Analysis of NMR Magnetic Shieldings of Transition Metal (M)-Containing Molecules, M Belonging to Groups IIB, VIB and VIIIB, by Applying the LRESC-Loc Model

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Abstract

We studied the electronic origin of the NMR nuclear magnetic shieldings (σ) of compounds containing the following transition metal atoms: $M = \text{Zn, Cd, Hg, Co, Rh, Cr, Mo, W}$. The electronic mechanisms that underlie the relativistic effects on those shieldings were assessed with the LRESC-Loc model, which permits one to quantify the set of leading relativistic electronic mechanisms responsible for such effects in terms of well-known non-relativistic operators, and also allows for the determination of which molecular orbitals (MOs) are involved in each of those mechanisms. These MOs are such that the chemist's intuition associated with core, lone-pair (LP), and bonding MOs is satisfied. The LRESC model is a reliable semi-relativistic methodology that has been shown to reproduce, in a semiquantitative manner, the magnetic shieldings and experimental chemical shifts of transition metals in a large set of molecules. Several new features appear in the shieldings analyzed. Trends in the total shieldings within a given family of compounds depend on relativistic effects—the spin-orbit mechanism is one of the most involved—though, within it, one must consider the Fermi contact (FC) and the spin-dipolar (SD) mechanisms. We found that the contributions that are due to partially filled d atomic orbitals (AOs) become too large when the electron correlation is not properly included. This is overcome in our case using density functional theory. A large influence of lone-pairs of π -type on $\sigma(M)$ is also seen in some of the molecules studied.

Keywords: transition metals; LRESC-Loc; nuclear magnetic shielding; relativistic effects



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1. Introduction

Experimental measurements of the nuclear magnetic resonance (NMR) spectroscopic parameters of transition metal-containing molecules present several challenges, which include the percentage of abundance of naturally occurring metal isotopes. This fact is such that commercial spectrometers are unable to meet the stringent requirements for metal observation, together with the intrinsic sensitivity of a specific metal isotope in comparison to an equivalent number of protons, and the quadrupolar moments associated with metal nuclides where the nuclear spin of the metal, I_M , is greater than $1/2$ [1]. Therefore, accurate and detailed theoretical studies of the NMR shielding, $\sigma(M)$, and chemical shift, $\delta(M)$, in the nuclei of transition metals are of the utmost importance for the research community [2–10].

It is well-known that the inclusion of relativistic effects on heavy-atom-containing molecules, such as molecules with transition metal atoms, is mandatory for a proper analysis of such parameters [2–5,8–11]. These relativistic effects can be introduced within a four-component (4C) level of theory using the relativistic polarization propagator (RelPol-Prop) approach [12–14] at the random phase approximation (RPA). Meanwhile, at the two-component (2C) or semi-relativistic level of theory, the linear response with the elimination of small component (LRESC) model is among the most reliable methods available to calculate $\sigma(M)$ for atoms belonging up to the 5th period of the periodic table, and in some cases even for $\delta(M)$ for systems containing atoms of the 6th period [8,10,15–17]. In this model, the relativistic corrections are calculated as a sum of terms that include leading relativistic effects to reproduce, in a quantitative or semiquantitative manner, the 4C values of the diamagnetic and paramagnetic components of NMR properties, whereas the exact-two-component (X2C) model incorporates relativistic effects directly into the Hamiltonian rather than as a separate sum of correcting terms [18–20]. Therefore, LRESC allows for a more detailed description of the relativistic effects on NMR shieldings by decomposing them into contributions from the various electronic mechanisms. The last version of the LRESC model, the LRESC-Loc one, meaning the analysis of the LRESC mechanisms from localized MOs (LMOs), was published in 2022 [21]. This model provides a detailed description of each LRESC mechanism grounded on the chemist's intuition associated with core, lone-pair (LP), and bonding MOs [10,21].

Although experimental measurements of the NMR spectroscopic parameters of transition metal nuclei present some challenges, there are several studies involving these nuclei, like the ^{113}Cd and ^{199}Hg isotopes [22–28], which take care of their $I_M = 1/2$, sensitivity, and natural abundance that are comparable to those of ^{13}C . Therefore, the NMR spectroscopic parameters of these nuclei can be investigated with the same experimental techniques used for ^{13}C .

The MX_2 molecules ($M = \text{Cd}, \text{Hg}$ and $X = \text{Cl}, \text{Br}$, or I) are organometallic compounds whose chemical shifts of Cd and Hg have been measured under different conditions [24–28]. Moreover, the chemical shift of the zinc nucleus, which is an important nucleus among transition metals of interest for human health [29], has also been experimentally estimated for the molecule of ZnX_2 in different solvents [30,31]. Several theoretical studies, with or without relativistic corrections, have described the magnetic properties of these transition metals in the set of MX_2 molecules [9,21,32–35].

Another nucleus, cobalt-59, is one of the most important transition metal nuclei in the historical developments of NMR spectroscopy due to its favorable NMR properties: “Cobalt-59 occupies a unique place in NMR history, as it was one of the first nuclei for which it was observed that the resonance frequency depends on the compound” [36,37]. Furthermore, the magnetic properties of ^{59}Co are sensitive enough to allow for the description of the electronic structure, the geometrical parameters, and reactivities of cobalt-containing systems [38]. Cobalt is also an important transition metal for life, as it is present in vitamin B_{12} [39,40], as well as in model compounds of this biomolecule to study its properties and mechanism of action [41]. Other cobalt-containing organometallic compounds that have been widely studied experimentally and theoretically include $\text{CoH}(\text{CO})_4$ and $[\text{Co}(\text{CO})_4]^-$ carbonyl complexes, as well as $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ [36,42–52]. In addition, the VIIIB group of transition metals has gained interest in recent decades because these metals possess the necessary characteristics for the development of molecule-sized electronic components [53,54]. This feature, along with their importance in homogeneous catalysis [55,56], has motivated studies of the magnetic properties of rhodium-containing complexes, although it is well-known that this transition metal exhibits unfavorable NMR properties due to its very low magnetogyric ratio [57–62].

The transition metals that belong to group VIB of the periodic table constitute another set of elements that require special chemical conditions to measure their magnetic properties. These conditions are achieved in the oxides $[\text{MO}_4]^{2-}$ and carbonyl complexes $[\text{M}(\text{CO})_6]$, where $M = \text{Cr}, \text{Mo}, \text{W}$. Therefore, for these systems, it has been possible to describe the magnetic properties of these transition metals both experimentally and theoretically [63–74].

The analysis of NMR shieldings and chemical shifts in transition metal-containing molecules is an area of research that has matured over the last decade in the relevant research [8,10,21]. As a natural next step, we present here a detailed study of three sets of organometallic compounds. This work is motivated by various experimental and theoretical results that were reported recently for transition metals belonging to groups IIB, VIB, and VIIIB. Set I consists of the following molecules: $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, $\text{Hg}(\text{CH}_3)_2$, and MX_2 , where $M = \text{Zn}, \text{Cd}, \text{Hg}$ and $X = \text{Cl}, \text{Br}, \text{I}$. The complexes belonging to set II are $[\text{Co}(\text{CO})_4]^-$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{CO})_4]^-$, $[\text{Rh}(\text{Cp})(\text{CO})_2]$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$, while set III of molecules includes $\text{M}(\text{CO})_6$ and $[\text{MO}_4]^{2-}$ complexes, where $M = \text{Cr}, \text{Mo}, \text{W}$.

In this work, we give results of NMR magnetic shieldings that cover new families of transition metal-containing systems, in a way that is intended to be a continuation of the previous work published few years ago [10]. This shows the capacity of the LRESC model to reproduce relativistic shielding constants and experimental chemical shifts for those systems. Our intention is not to give definitive benchmarks, since we did not include solvation effects, vibrational corrections, or other corrections that could be relevant to NMR shielding calculations. Consequently, a systematic discrepancy between theory and experiment cannot be unambiguously attributed to either the electronic structure method used here or to an incomplete description of the actual geometrical structure in solution. This concern is particularly relevant to set I of molecules, since it has long been recognized theoretically that, for Hg-containing systems, the explicit coordination of solvent molecules to this metal can substantially change, for example, computed NMR spin–spin coupling constants [75].

2. Theoretical Framework

The LRESC model was first proposed more than 20 years ago, with the aim of contributing to the calculations and analysis of the origin of relativistic effects involved in the NMR magnetic shieldings [15,16]. In the long time elapsed since its first development, the model has been used to generalize previous findings of non-relativistic (NR) relationships, like the Ramsey–Flygare relationship [13,76], or to include the analysis of some other effects—the most recent are parity-violation effects [77]. Furthermore, one of its newest applications was oriented to the calculation of the electric response in molecular properties [78,79].

Within the LRESC model, the 4C expressions of the isotropic magnetic shielding are written as a power series of the speed of light (using c^{-2} as a parameter), with one of its more fundamental procedures being the application of the Rayleigh–Schödinger perturbation theory (RSPT). Both the paramagnetic and diamagnetic components of $\sigma(\text{M})$ have been developed up to the second order in c^{-2} or to c^{-4} . The first-order terms correspond to the NR expressions, which are the NR paramagnetic (σ_p^{NR}) and the NR diamagnetic (σ_d^{NR}) components, while the second-order terms, with a dependence of c^{-4} , are due to the mechanisms associated with leading-order relativistic corrections. Additionally, these terms can also be categorized into ligand-dependent (LD) and non-ligand-dependent (NLD) terms [10,21,80], as shown in Table 1. The actual expressions for each of the terms written in this table were reported elsewhere [10,15,16].

Table 1. Paramagnetic and diamagnetic contributions to the shielding, as given in the LRESC model, expressed as the electronic mechanisms involved in the ligand-dependent and non-ligand-dependent terms until the order c^{-4} .

Mechanism	Ligand-Dependent (LD)		Non-Ligand-Dependent (NLD)	
	c^{-2}	c^{-4}	c^{-2}	c^{-4}
Paramagnetic-like	σ_p^{NR}	$\sigma_p^{PSOK}, \sigma_p^{(Mv+Dw)}, \sigma^{SO}$		$\sigma^{OZK}, \sigma^{BSO}, \sigma_p^{(FC+SD)}$
Diamagnetic-like			σ_d^{NR}	$\sigma_d^{FC}, \sigma^{PSO-OZ}, \sigma^{DiaK}, \sigma_d^{(Mv+Dw)}$

The paramagnetic mechanisms represent the NR paramagnetic term together with the mass-velocity (Mv) and Darwin (Dw) corrections, and the spin-orbit (SO), kinetic-paramagnetic spin-orbit (PSOK), kinetic-orbital Zeeman (OZK), and magnetic external field-induced spin-orbit (BSO) operators. On the other side, the diamagnetic mechanisms represent the NR diamagnetic term together with the diamagnetic mass-velocity (Mv) and Darwin (Dw) corrections, the Fermi contact (FC), and the kinetically corrected diamagnetic (DiaK) and paramagnetic spin-orbit operators (PSO-OZ).

As mentioned above, one of the latest developments in the LRESC model is the LRESC–Loc model [10,21]. Within it, it is possible to obtain the contributions from the core, LP, and LMOs to each mechanism shown in Table 1. Additionally, the contributions from the highest-energy d-orbitals of the transition metal atoms (d(M)) can also be calculated.

The chemical shifts in the transition metal atom, $\delta(M)$, are obtained with the following formula:

$$\delta(M) = \sigma^{ref}(M) - \sigma(M) \quad (1)$$

where $\sigma^{ref}(M)$ is the shielding of nucleus M of the transition metal atom in the system that is taken as reference.

3. Materials and Methods

In this work, we studied three families of molecules, divided into three sets, as shown in Table 2. In addition, the experimental distances between the halogen atoms and transition metal atoms for the bilinear MX_2 systems are shown in Table 3. For the rest of the molecules in set I ($Zn(NO_3)_2$, $Cd(ClO_4)_2$, $Hg(CH_3)_2$), the geometries were optimized at the Dirac–Hartree–Fock (DHF) level with the dyall.cv3z basis set [81].

Table 2. Molecular formulas of the families of studied molecules.

Set	Molecules
I	MX_2 , where $M = Zn, Cd, Hg$ and $X = Cl, Br, I$
II	$Zn(NO_3)_2^a$, $Cd(ClO_4)_2^a$, $Hg(CH_3)_2$
III	$[Co(CO)_4]^-$, $[Co(NH_3)_6]^{3+}$, $[Co(H_2O)_6]^{3+}$, $[Co(CN)_6]^{3-}$ $[Rh(CO)_4]^-$, $[Rh(Cp)(CO)_2]$, $[Rh(CO)_2Cl_2]^-$
	$M(CO)_6$, $[MO_4]^{2-}$ where $M = Cr, Mo, W$

^a The oxidation state of the transition metal atom is II.

Table 3. Bond distances between halogen atoms and transition metal atoms in the MX_2 molecules. All values are given in Å.

System	d(Zn–X)	System	d(Cd–X)	System	d(Hg–X)
$ZnCl_2$	2.07 ^a	$CdCl_2$	2.24 ^b	$HgCl_2$	2.25 ^c
$ZnBr_2$	2.20 ^a	$CdBr_2$	2.36 ^b	$HgBr_2$	2.41 ^d
ZnI_2	2.40 ^a	CdI_2	2.56 ^b	HgI_2	2.55 ^e

^a Reference [82]. ^b Reference [83]. ^c Reference [84]. ^d Reference [85]. ^e Reference [86].

For the molecules in set II, the experimental bond lengths of Co–C and C–O in the tetrahedral molecule $[\text{Co}(\text{CO})_4]^-$ are 1.752 Å and 1.153 Å, respectively [87]. The bond distances for the octahedral systems $[\text{Co}(\text{NH}_3)_6]^{3+}$ (Co–N 1.972 Å, N–H 0.98 Å) and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (Co–O 1.873 Å, O–H 0.993 Å) have been taken from Refs. [44–46]. For the $[\text{Co}(\text{CN})_6]^{3-}$ system, the experimental distances Co–C (1.890 Å) and C–N (1.160 Å) were obtained from Ref. [47]. Finally, the experimental structural parameters for $[\text{CoH}(\text{CO})_4]$ were obtained from Ref. [48]. The geometrical parameters for the Rh atom-containing systems were taken from Ref. [57].

Regarding set III of molecules, the geometrical parameters of the tetrahedral and octahedral systems obtained by experiments are shown in Table 4.

Table 4. Bond distances in set III of molecules. All values are given in Å.

System	d(M–O)	System	d(M–C)	d(C–O)
CrO_4^{2-}	1.632 ^a	$\text{Cr}(\text{CO})_6$	1.915 ^b	1.137 ^b
MoO_4^{2-}	1.674 ^c	$\text{Mo}(\text{CO})_6$	2.063 ^d	1.145 ^d
WO_4^{2-}	1.790 ^e	$\text{W}(\text{CO})_6$	2.058 ^f	1.148 ^f

^a Reference [63]. ^b Reference [64]. ^c Reference [65]. ^d Reference [66]. ^e Reference [67]. ^f Reference [68].

The 4C calculations of σ were carried out at the RelPolProp/RPA/dyall.cv3z level of approach [81], using the Dirac suite of programs [88]. The NR and leading relativistic corrections of LRESC were carried out with the Dalton code [89], using the same basis set. When LRESC results are expressed, they refer to the NR value plus the total of the leading relativistic corrections. As usual for calculations with the LRESC model, the gauge origin was placed at the site of the nucleus under study, though it was previously shown that LRESC is gauge-origin-independent in the limit of a complete basis set [90]. Moreover, in a study of SnI_4 , the difference resulting from placing the gauge with a robust basis set on Sn versus on I was 0.3% [17]. The contributions of the different occupied MOs to the electronic mechanism responsible for the relativistic effects were calculated by applying the LRESC–Loc model along with the Pipek–Mezey scheme [91] to localize the occupied MOs and by using the PySCF program [92]. Moreover, we used the BHandHLYP functional in the calculation of the 4C, LRESC, and NR shielding because it outperformed other density functionals in describing the LRESC relativistic corrections [17].

The system of reference for the calculation of the chemical shifts in ZnX_2 is the molecule $\text{Zn}(\text{NO}_3)_2$, while for CdX_2 and HgX_2 , the systems of reference are $\text{Cd}(\text{ClO}_4)_2$ and $\text{Hg}(\text{CH}_3)_2$, respectively. The system of reference for Co-containing molecules is $[\text{Co}(\text{CN})_6]^{3-}$.

4. Results and Discussion

In this section, the magnetic shielding constant and chemical shifts in metal transition nuclei in the molecules shown in Figure 1 are analyzed. Relativistic effects of these properties are given at LRESC and 4C levels, and the chemical shifts are compared with experimental results. The LRESC results are given on a basis of occupied MOs. In particular, the contributions from each LD mechanism are analyzed.

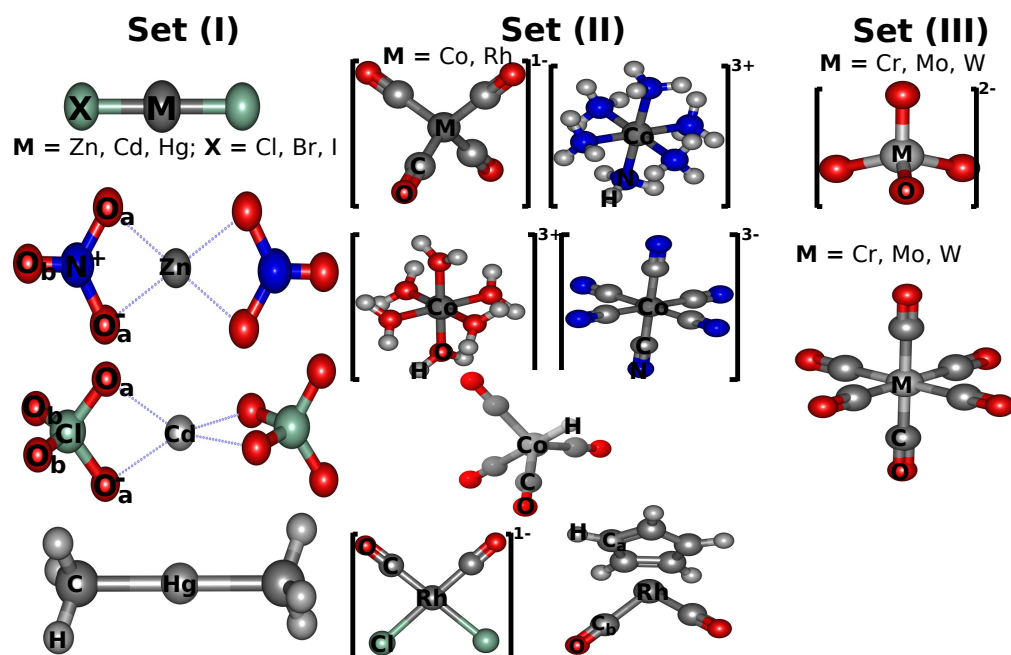


Figure 1. The three sets of molecules containing transition metal atoms that belong to groups IIB, VIIIB and VIB. (**Set I**) includes $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, $\text{Hg}(\text{CH}_3)_2$, and MX_2 molecules, where $M = \text{Zn, Cd, Hg}$ and $X = \text{Cl, Br, I}$. (**Set II**) includes $[\text{Co}(\text{CO})_4]^-$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{CO})_4]^-$, $[\text{Rh}(\text{Cp})(\text{CO})_2]$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$. (**Set III**) includes $[\text{MO}_4]^{2-}$ and $M(\text{CO})_6$ complexes, where $M = \text{Cr, Mo, W}$.

4.1. Set I of Molecules with Atoms Belonging to Group IIB

In Table 5, we show the results of calculations of $\sigma^{\text{NR}}(M)$, $\sigma^{\text{LRESC}}(M)$ and $\sigma^{\text{4C}}(M)$ for the following molecules: MX_2 ($M = \text{Zn, Cd, Hg}; X = \text{Cl, Br, I}$), $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 . As expected, relativistic effects increase as the atomic number of the transition metal (Z_M) grows.

Table 5. The shieldings of transition metal nuclei of the molecules MX_2 ($M = \text{Zn, Cd, Hg}; X = \text{Cl, Br, I}$), $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 . All values are given in ppm. These quantities were calculated using the Hartree–Fock (HF) and Dirac–Hartree–Fock (DHF) methodologies, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

	HF/DHF			BHandHLYP		
	$\sigma^{\text{NR}}(M)$	$\sigma^{\text{LRESC}}(M)$	$\sigma^{\text{4C}}(M)$	$\sigma^{\text{NR}}(M)$	$\sigma^{\text{LRESC}}(M)$	$\sigma^{\text{4C}}(M)$
$\text{Zn}(\text{NO}_3)_2$	1961.37	2109.84	2139.63	1839.27	1973.27	2004.38
ZnCl_2	1803.84	1947.27	1983.57	1705.31	1850.33	1886.09
ZnBr_2	1793.27	1992.87	2037.87	1693.38	1925.67	1972.06
ZnI_2	1840.69	2176.73	2235.78	1736.79	2170.33	2223.25
$\text{Cd}(\text{ClO}_4)_2$	4090.41	4721.57	4942.95	3982.54	4603.78	4824.60
CdCl_2	3662.22	4273.65	4514.26	3590.61	4200.19	4438.15
CdBr_2	3570.75	4243.14	4541.67	3531.51	4274.31	4600.14
CdI_2	3576.10	4433.56	4857.36	3484.17	4516.10	4973.56
HgMe_2	6844.56	9803.80	12,714.96	6502.75	9016.04	11,659.17
HgCl_2	7566.07	10,495.13	13,961.47	7377.01	10,208.76	13,297.81
HgBr_2	7562.80	10,618.85	15,037.06	7271.48	10,419.91	14,538.03
HgI_2	7281.31	10,505.37	16,167.79	7045.47	10,359.05	15,670.48

The LRESC results are in good agreement with the 4C ones for the molecules that contain atoms of zinc, with differences that are close to 2%, and for the Ccdmium-containing

molecules, where the differences grow up to 9%. However, for the molecules with atoms of mercury, the LRESC shielding calculations do not quantitatively reproduce the 4C results, with the differences close to 30%. This fact was previously reported for the nuclei of atoms that belong to the *p*-block of the periodic table [13,21,80].

In Figure 2, we show the paramagnetic, $\sigma_p(M)$, and diamagnetic, $\sigma_d(M)$, components of the magnetic shielding calculated at NR, LRESC, and 4C levels of theory, for transition metal atoms in MX_2 ($M = \text{Zn, Cd, Hg}$; $X = \text{Cl, Br, I}$), $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 molecular systems. The differences between $\sigma_d^{\text{NR}}(M)$, $\sigma_d^{\text{LRESC}}(M)$ and $\sigma_d^{\text{4C}}(M)$ are nearly constant for molecules containing the same transition metal, regardless of whether the electronic correlation was included or not, using DFT. The difference in results between LRESC and 4C is 82 ppm for ZnX_2 and $\text{Zn}(\text{NO}_3)_2$, while, for the molecules containing atoms of cadmium and mercury, such a difference is 430 and 2595 ppm, respectively. These numbers are due to the fact that the LRESC model overestimates the relativistic corrections for the diamagnetic component.

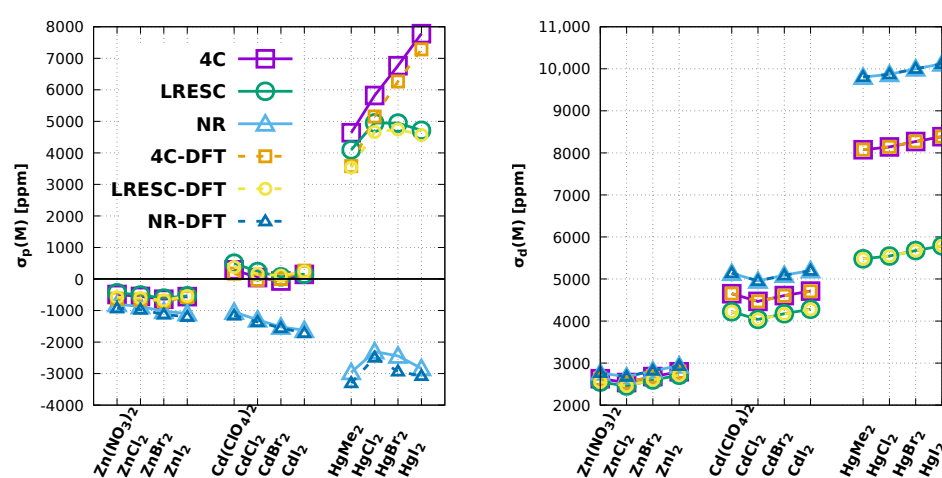


Figure 2. Paramagnetic, $\sigma_p(M)$, and diamagnetic, $\sigma_d(M)$, components of $\sigma(M)$ for MX_2 ($M = \text{Zn, Cd, Hg}$; $X = \text{Cl, Br, I}$), $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 molecules, calculated at NR, LRESC, and 4C levels of approach using HF and DHF methodologies, as well as the BHandHLYP functional. Dyall.cv3z basis set was used and the gauge origin was placed at the site of the atom under study. All values are given in ppm.

Regarding the paramagnetic component of σ , the differences between $\sigma_p^{\text{LRESC}}(M)$ and $\sigma_p^{\text{4C}}(M)$ for the molecules ZnX_2 , $\text{Zn}(\text{NO}_3)_2$, CdX_2 , and $\text{Cd}(\text{ClO}_4)_2$ arise due to the fact that the LRESC model slightly overestimates the paramagnetic components. However, these differences are smaller than those observed for the diamagnetic components. Thus, for the systems containing atoms of zinc and cadmium, the difference between the total $\sigma^{\text{LRESC}}(M)$ and $\sigma^{\text{4C}}(M)$ can be mainly attributed to the diamagnetic corrections of the LRESC model. For the molecules HgX_2 and HgMe_2 , the LRESC model underestimates the paramagnetic components, and the differences between $\sigma_p^{\text{LRESC}}(M)$ and $\sigma_p^{\text{4C}}(M)$ increase with Z_X to the point where it can no longer reproduce the 4C trend, becoming larger than the difference between $\sigma_d^{\text{LRESC}}(M)$ and $\sigma_d^{\text{4C}}(M)$ for the HgI_2 molecule. Hence, the main differences in the total value of $\sigma^{\text{LRESC}}(M)$ and $\sigma^{\text{4C}}(M)$ for an atom belonging to the 6th row of the periodic table are due to the two components of the shielding, although, as the atomic number of the substituent atoms increases, the paramagnetic component calculated with the LRESC model presents a larger deviation than the diamagnetic one with respect to the 4C values. Moreover, it is observed that the influence of the electronic correlation on σ increases as Z_M becomes higher.

In Table 6, we show the difference between $\sigma_d^{4C}(M)$ and $\sigma_d^{NR}(M)$, and between $\sigma_p^{4C}(M)$ and $\sigma_p^{NR}(M)$, representing the magnitude of the total relativistic correction for the diamagnetic and paramagnetic components, respectively ($\sigma_d^{Rel}(M)$ and $\sigma_p^{Rel}(M)$), along with the contributions coming from the ligand-dependent ($\sigma_p^{LD}(M)$) and non-ligand-dependent ($\sigma_p^{NLD}(M)$) relativistic corrections given by the LRESC model. It is observed that $\sigma_p^{NLD}(M)$ remains approximately constant for systems containing the same transition metal atom, while $\sigma_p^{Rel}(M)$ increases as Z_X increase. This behavior is reproduced by $\sigma_p^{LD}(M)$. Moreover, it is found that $\sigma_p^{NLD}(M) + \sigma_p^{LD}(M)$ overestimates the total relativistic correction for the paramagnetic component in systems that contain zinc and cadmium atoms, which explains why $\sigma_p^{LRESC}(M)$ is higher than $\sigma_p^{4C}(M)$ for these nuclei. In the case of the molecules HgX_2 and $HgMe_2$, an underestimation of $\sigma_p^{Rel}(M)$ is observed, which is also associated with the largest difference between $\sigma_p^{NLD}(M) + \sigma_p^{LD}(M)$ and $\sigma_p^{Rel}(M)$. When the electron correlation is included, this results in a reduction in this difference, which becomes more pronounced when Z_M increases. Thus, the difference between $\sigma_p^{LRESC}(Hg)$ and $\sigma_p^{4C}(Hg)$ as the atomic number of the substituents increases is mainly due to the changes in the chemical environment around the transition metal atom.

Table 6. Relativistic corrections to diamagnetic ($\sigma_d^{Rel}(M)$) and paramagnetic ($\sigma_p^{Rel}(M)$) on transition metal atoms for MX_2 ($M = Zn, Cd, Hg$; $X = Cl, Br, I$), $Zn(NO_3)_2$, $Cd(ClO_4)_2$, and $HgMe_2$ molecules, calculated as the difference between its 4C and NR values. Non-ligand-dependent (NLD) and ligand-dependent (LD) contributions are shown. All values are given in ppm.

	HF/DHF				BHandHLYP			
	$\sigma_d^{Rel}(M)$	$\sigma_p^{Rel}(M)$	$\sigma_p^{NLD}(M)$	$\sigma_p^{LD}(M)$	$\sigma_d^{Rel}(M)$	$\sigma_p^{Rel}(M)$	$\sigma_p^{NLD}(M)$	$\sigma_p^{LD}(M)$
$Zn(NO_3)_2$	−136.87	315.14	371.39	−4.60	−136.87	341.98	371.14	−18.88
$ZnCl_2$	−137.13	316.86	371.07	−9.13	−137.10	317.89	371.39	−7.78
$ZnBr_2$	−138.60	383.20	372.97	46.68	−138.57	417.25	373.38	79.05
ZnI_2	−141.06	536.15	375.50	183.44	−141.01	627.46	375.94	280.57
$Cd(ClO_4)_2$	−486.91	1339.44	1596.74	−49.22	−485.59	1327.65	1597.53	−59.79
$CdCl_2$	−485.69	1337.73	1596.43	−68.75	−485.41	1332.95	1597.40	−71.41
$CdBr_2$	−487.04	1457.96	1598.41	−8.30	−486.69	1555.32	1599.51	61.11
CdI_2	−489.28	1770.54	1600.92	176.90	−488.91	1978.30	1602.11	350.29
$HgMe_2$	−1728.43	7598.82	7105.30	−623.20	−1727.02	6883.44	7680.76	−843.33
$HgCl_2$	−1729.07	8124.47	7677.63	−424.60	−1727.40	7648.20	7680.60	−524.45
$HgBr_2$	−1730.24	9204.50	7679.63	−298.27	−1728.52	9195.07	7682.86	−308.71
HgI_2	−1732.38	10,618.86	7682.39	−130.37	−1730.65	10,355.66	7685.66	−43.68

The contributions of the different LD mechanisms to σ for the molecules MX_2 ($M = Zn, Cd, Hg$; $X = Cl, Br, I$), $Zn(NO_3)_2$, $Cd(ClO_4)_2$, and $HgMe_2$ are given in Figure 3 (also in the Supporting Information).

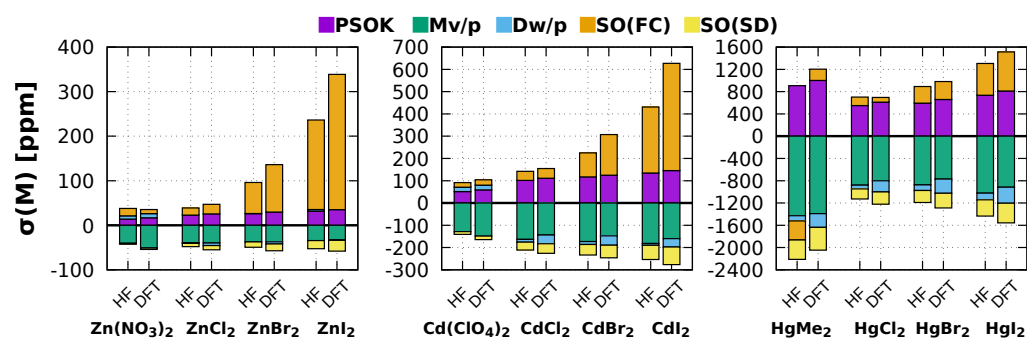


Figure 3. Contributions of LD mechanisms to $\sigma^{LD}(M)$ for MX_2 ($M = Zn, Cd, Hg$; $X = Cl, Br, I$), $Zn(NO_3)_2$, $Cd(ClO_4)_2$, and $HgMe_2$ molecular systems.

In most of the molecules studied here, the contributions to $\sigma^{LD}(M)$ from $\sigma_p^{Mv}(M)$, $\sigma_p^{Dw}(M)$, and $\sigma_p^{SO(SD)}(M)$ are negative, while $\sigma^{SO(FC)}(M)$ and $\sigma^{PSOK}(M)$ have positive values. For the molecules containing the heaviest halogen atoms and Zn and Cd transition metals, like ZnBr_2 , ZnI_2 , and CdI_2 , the positive value of $\sigma^{SO(FC)}(M) + \sigma^{PSOK}(M)$ is higher than the total value of the negative LD mechanisms, especially with the inclusion of electron correlation. This difference allows the LRESC model to reproduce the behavior of $\sigma_p^{AC}(M)$ for the systems containing zinc and cadmium atoms, as observed in Figure 2. For Hg-containing molecules, the $\sigma^{LD}(M)$ is negative, showing the necessity to develop additional LD mechanisms associated with positive values that could change the sign of $\sigma^{LD}(\text{Hg})$. Positive values of $\sigma^{LD}(\text{Hg})$, along with the positive value of $\sigma_p^{NLD}(\text{Hg})$, would allow the LRESC reproduce at least the slope of the $\sigma_p^{AC}(\text{Hg})$ values. These missing mechanisms can be associated with spin-orbit effects, or, more specifically, with a local angular momentum because, in Figure 3, it is possible to observe that the magnitude of the $\sigma^{PSOK}(\text{Hg})$ and $\sigma^{SO(FC)}(\text{Hg})$ contributions increases (both positive values) as the atomic number increases, and even more so with electronic correlation.

The contributions from the occupied MOs to the LD mechanisms for HgX_2 and HgMe_2 systems are shown in Figure 4. For this set, the value of each mechanism is determined by the bonds between the transition metal atom and the carbon or the halogen atoms, except for $\sigma^{SO(FC)}(\text{Hg})$ for the systems containing halogen atoms. This mechanism exhibits a higher contribution from $\text{LP}\sigma(\text{X})$ and $\text{LP}\pi(\text{X})$, which increases as the atomic number of the halogen atom increases. Furthermore, it is observed that the $\sigma_p^{Mv}(\text{Hg})$ and $\sigma_p^{Dw}(\text{Hg})$ mechanisms have the highest contribution from the $5d(\text{Hg})$ orbitals, while this contribution at $\sigma_p^{SO(FC)}(\text{Hg})$ changes sign with the halogen atomic number. Finally, the most sensitive occupied MOs to the chemical environment are the LP of the halogen atom and the $5d(\text{Hg})$ atomic orbitals, and it is observed that electron correlation only slightly changes the contribution from occupied MOs, especially bonds and LP, to the mechanisms. These behaviors for the HgX_2 molecules are reproduced by the ZnX_2 and CdX_2 ($\text{X} = \text{halogen atoms}$) systems.

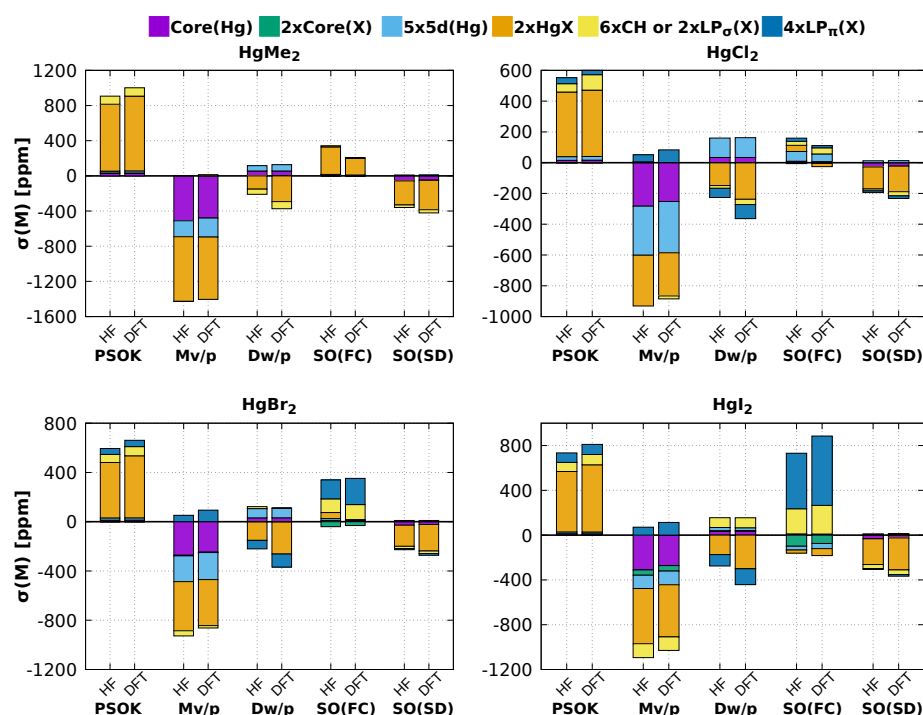


Figure 4. Contributions to the LD mechanisms from each occupied molecular orbital for HgX_2 ($\text{X} = \text{Cl, Br, I}$) and HgMe_2 systems with the BHandHLYP functional and HF/DHF methodologies.

The chemical shifts in transition metal atoms in MX_2 systems ($M = \text{Zn, Cd, Hg}$; $X = \text{Cl, Br, I}$), calculated at NR, LRESC, and 4C levels of theory, are shown in Figure 5 and Tables S3–S8. $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 molecules are taken as reference systems. Experimental results are also shown for comparison.

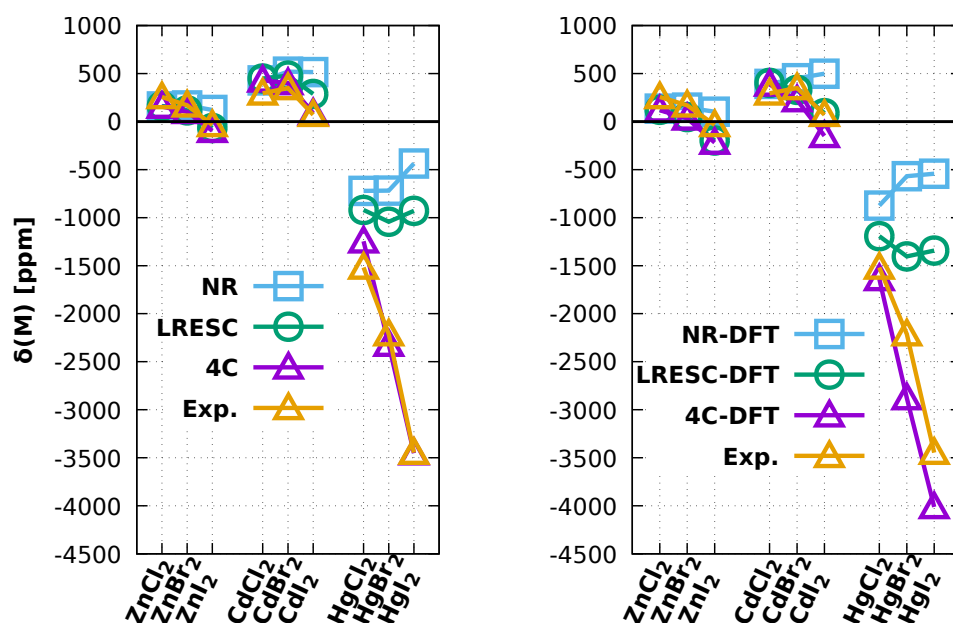


Figure 5. Chemical shifts (δ) in transition metal atoms in MX_2 ($M = \text{Zn, Cd, Hg}$; $X = \text{Cl, Br, I}$) systems, using $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 systems as reference, and calculated at NR ($\delta^{\text{NR}}(M)$), LRESC ($\delta^{\text{LRESC}}(M)$), and 4C ($\delta^{\text{4C}}(M)$) levels. For the systems containing Zn and Cd atoms the experimental results ($\delta^{\text{Exp.}}(M)$) with a concentration of 1.0 M were taken, while, for the HgX_2 systems, the results with the THF solvent were chosen. These quantities were calculated using the HF and DHF methodologies, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

The chemical shift calculated for the transition metal atoms in ZnX_2 and CdX_2 molecular systems ($X = \text{Cl, Br, I}$), regardless of the scheme of calculation, based on an ideal gas, reproduces the trend of $\delta^{\text{Exp.}}(M)$ at a concentration of 1.0 M. However, to reproduce the magnitude of $\delta^{\text{Exp.}}(M)$ with the highest accuracy, it is necessary to include the relativistic effects at a higher level, although the difference between $\delta^{\text{LRESC}}(M)$ and $\delta^{\text{Exp.}}(M)$ is minimal. For Hg-containing systems, it is observed that $\delta^{\text{Exp.}}(\text{Hg})$ in THF solvent is only reproduced by $\delta^{\text{4C}}(\text{Hg})$. The difficulty for LRESC in reproducing $\delta^{\text{Exp.}}(\text{Hg})$, as discussed earlier and shown in Figure 4, arises from its limitations in describing the influence of the chemical environment on the shielding of atoms belonging to the 6th row of the periodic table. Furthermore, it is observed that the contribution from $\text{LP}\pi(\text{I})$ to $\sigma^{\text{SO(FC)}}(\text{Hg})$ in the HgI_2 system causes LRESC to not reproduce the slope of $\delta^{\text{Exp.}}(\text{Hg})$ in systems that contain mercury atoms.

4.2. Set II of Molecules with Atoms Belonging to Group VIII B

The values of the shieldings at NR, LRESC, and 4C levels of theory for cobalt and rhodium atoms in $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{Cp})(\text{CO})_2]$, $[\text{Rh}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ systems are presented in Table 7. The differences between $\sigma^{\text{LRESC}}(M)$ and $\sigma^{\text{4C}}(M)$ for rhodium-containing systems are less than 12%; in contrast, for cobalt-containing systems, this difference is less than 10% when the electron correlation is not included, except for the $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ systems. The LRESC difference with the 4C value for the cobalt nuclei in the $[\text{Co}(\text{CO})_4]^-$ molecule

(−99,324 ppm) is the largest one, while such a difference in $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is around 45%. In general, the use of the BHandHLYP functional leads to a decrease in the magnitude of the values of the shieldings across all methodologies and molecular systems, except for $\sigma^{4C}(\text{Rh})$. Although we do not analyze in great detail the origin of quasi-instabilities (QIs) in this work, it is worth mentioning that the differences between the LRESC/HF and DHF values with respect to LRESC/BHandHLYP and 4C-BHandHLYP in the $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ molecules are due to a QI that arises in the calculation of the $\sigma^{SO(SD)}$ mechanism. This is briefly shown below.

Table 7. Shielding of the nuclei of transition metals (in ppm) for the molecules $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{Cp})(\text{CO})_2]$, $[\text{Rh}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$. These quantities were calculated using the HF and DHF methodologies, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

	HF/DHF			BHandHLYP		
	$\sigma^{NR}(M)$	$\sigma^{LRESC}(M)$	$\sigma^{4C}(M)$	$\sigma^{NR}(M)$	$\sigma^{LRESC}(M)$	$\sigma^{4C}(M)$
$[\text{Co}(\text{CN})_6]^{3-}$	−16,119.00	−15,508.44	−15,688.06	−8491.73	−8214.99	−8305.61
$[\text{CoH}(\text{CO})_4]$	−10,041.51	−12,600.16	−13,992.21	−4771.69	−4468.17	−4583.58
$[\text{Co}(\text{CO})_4]^-$	−31,415.12	88,080.35	−11,234.50	−4512.38	−4887.01	−4600.80
$[\text{Co}(\text{NH}_3)_6]^{3+}$	−34,738.19	−31,614.68	−33,957.49	−17,155.03	−16,503.63	−16,745.93
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	−58,972.46	−33,239.87	−60,856.96	−27,169.85	−25,396.77	−26,124.77
$[\text{Rh}(\text{Cp})(\text{CO})_2]$	−1204.08	−382.92	−428.23	−0.50	625.59	766.62
$[\text{Rh}(\text{CO})_4]^-$	−1373.51	−280.16	−250.55	−440.45	148.19	303.09
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$	−2629.26	−1869.93	−1785.17	−1381.66	−853.39	−729.74

In both $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ molecular systems, the consideration of electron correlation through the BHandHLYP functional leads to a reduction in the differences between LRESC/HF and DHF values (Table 7). For $[\text{Co}(\text{CO})_4]^-$, the $\sigma^{LRESC}(\text{Co})$ value reproduces the correct sign and is closer to the $\sigma^{4C}(\text{Co})$ value, with a difference of only 6%. Conversely, the LRESC difference with respect to 4C is reduced to 3% for $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ with the consideration of electron correlation. Furthermore, in the remaining systems, which contain one cobalt atom, the difference between $\sigma^{LRESC}(\text{Co})$ and $\sigma^{4C}(\text{Co})$ decreases to 2% when DFT is used, while, in the rhodium-containing systems, this difference increases.

Regardless of the methodology and the level of theory used, the deshielding effect on the cobalt atom increases with the number of the charge of the molecule. In systems containing a rhodium atom, the deshielding effect increases when the atoms interacting with rhodium atom vary, although there is no consistent bonding pattern, as observed in the $[\text{Rh}(\text{Cp})(\text{CO})_2]$ system.

The paramagnetic and diamagnetic components of σ , calculated at NR, LRESC, and 4C levels of theory for cobalt and rhodium nuclei in the $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{Cp})(\text{CO})_2]$, $[\text{Rh}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ systems, are presented in Figure 6.

It is observed that $\sigma_d^{4C}(\text{Co})$ is closely reproduced by $\sigma_d^{LRESC}(\text{Co})$ for all systems containing only one cobalt atom. Moreover, the effect of electron correlation on the diamagnetic component is negligibly small, regardless of the methodology used. In contrast, the relativistic effect on the paramagnetic component is overestimated, particularly at the LRESC/HF level of theory, as observed in the $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ molecular systems. Therefore, the inclusion of electron correlation is necessary in order to describe as accurately as possible the influence of the chemical environment and relativistic effects on the paramagnetic component in the Co-containing systems. The difference between $\sigma_p^{4C}(\text{Rh})$ and

$\sigma_p^{LRESC}(\text{Rh})$ is negligibly small at all theoretical levels, whereas LRESC overestimates the relativistic correction for the diamagnetic component, which changes slightly with the inclusion of electron correlation.

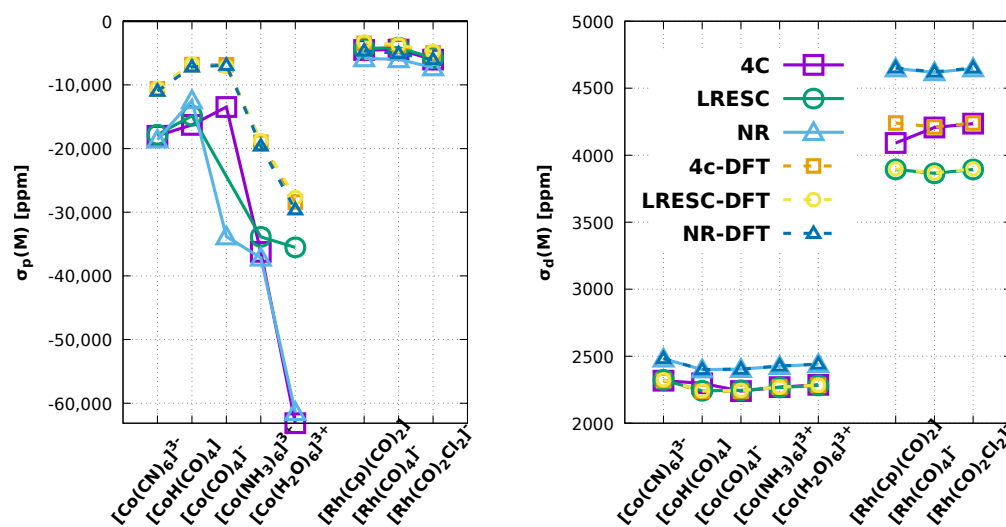


Figure 6. The paramagnetic and diamagnetic components, in ppm, of transition metal atoms in the $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Rh}(\text{Cp})(\text{CO})_2]$, $[\text{Rh}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ systems calculated at NR, LRESC, and 4C levels of theory. The values calculated using BHandHLYP functional are presented in dashed lines.

Table 8 shows, in ppm, the values of $\sigma_d^{RC}(M)$ and $\sigma_p^{RC}(M)$, along with the values of $\sigma^{LD}(M)$ and $\sigma_p^{NLD}(M)$ with the LRESC model (Table 1).

Table 8. Differences between NR and 4C diamagnetic and paramagnetic components of the shielding, along with the NLD and LD contributions to the paramagnetic component. Calculations were carried out at HF and DHF levels, as well as DFT with the BHandHLYP functional, and dyall.cv3z basis set. The gauge origin was placed at the site of the the atom under study.

	HF/DHF				BHandHLYP			
	$\sigma_d^{RC}(M)$	$\sigma_p^{RC}(M)$	$\sigma_p^{NLD}(M)$	$\sigma^{LD}(M)$	$\sigma_d^{RC}(M)$	$\sigma_p^{RC}(M)$	$\sigma_p^{NLD}(M)$	$\sigma^{LD}(M)$
$[\text{Co}(\text{CN})_6]^{3-}$	−163.61	594.55	279.90	489.01	−164.35	350.47	275.36	159.81
$[\text{CoH}(\text{CO})_4]$	−102.52	−3848.18	274.85	−2675.10	−162.30	350.41	273.66	188.29
$[\text{Co}(\text{CO})_4]^-$	−163.13	20,343.75	298.27	119,355.64	−163.49	75.17	276.76	−492.94
$[\text{Co}(\text{NH}_3)_6]^{3+}$	−156.14	936.84	290.20	2991.56	−157.32	566.42	279.62	530.12
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	−153.87	−1730.64	306.45	25,584.41	−158.51	1203.59	284.11	1647.34
$[\text{Rh}(\text{Cp})(\text{CO})_2]$	−555.68	1331.53	1311.25	262.85	−410.77	1177.90	1311.03	68.12
$[\text{Rh}(\text{CO})_4]^-$	−410.94	1533.90	1310.32	536.12	−410.92	1154.47	1310.61	31.18
$[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$	−411.11	1255.20	1311.67	200.82	−410.88	1062.80	1311.41	−29.85

The relativistic effect on the paramagnetic component, with or without electron correlation, is greater than that on the diamagnetic component. The largest relativistic corrections to $\sigma_p^{NR}(\text{Rh})$ within the LRESC model are associated with core MOs of the rhodium atom. In contrast, for systems containing one cobalt atom, the largest relativistic corrections to $\sigma_p^{NR}(\text{Co})$ are primarily influenced by the chemical environment. In the case of $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ systems, the unusually high $\sigma_p^{LD}(\text{Co})$ values arise from a significant overestimation, by several orders of magnitude, of the LD correction.

The contributions of different MOs to the LD corrections for $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ systems at the HF/cv3z and BHandHLYP/cv3z levels of theory are shown in

Table 9 and Table 10, respectively. We shall indicate with blue color the shielding behavior of a given mechanism, and with red color the deshielding behavior. A stronger blue (red) color means a higher shielding (deshielding) behavior. Additional details and values for the other cobalt-containing systems can be found in the Supporting Information. In the absence of electron correlation, the difference between $\sigma^{LRES C}(\text{Co})$ and $\sigma^{4C}(\text{Co})$ (Table 7) originates mainly from the contribution of the d-AOs of cobalt to $\sigma^{SO(SD)}(\text{Co})$.

Table 9. Isotropic values, in ppm, of the LD corrections within the LRESC approach for paramagnetic components with LMOs on the Co atom in the $[\text{Co}(\text{CO})_4]^-$ molecular system. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

HF									
	Core (Co)	4 × Core (C)	4 × Core (O)	5 × 3d (Co)	4 × CoC	4 × CO	8 × C=O	4 × LP _σ (O)	Σ
σ^{PSOK}	0.82	0.48	0.02	90.94	7.61	1.95	1.92	1.01	104.75
$\sigma^{Mv/p}$	12.12	3.41	−1.59	−98.29	204.03	−54.89	70.52	−18.63	116.68
$\sigma^{Dw/p}$	2.54	−4.41	0.65	−636.39	−37.48	20.46	10.30	8.59	−635.74
$\sigma^{SO(FC)}$	−2.87	−0.36	−0.05	−1187.30	20.00	−5.91	−74.98	−2.34	−1253.81
$\sigma^{SO(SD)}$	−67.16	77.79	16.51	123,326.40	−2604.43	817.43	−689.81	147.03	121,023.76
BHandHLYP									
	Core (Co)	4 × Core (C)	4 × Core (O)	5 × 3d (Co)	4 × CoC	4 × CO	8 × C=O	4 × LP _σ (O)	Σ
σ^{PSOK}	0.78	0.15	0.07	16.30	7.93	2.18	−0.76	0.20	26.84
$\sigma^{Mv/p}$	−1.80	0.53	−0.48	5.73	−1.90	−12.74	3.89	−1.35	−8.12
$\sigma^{Dw/p}$	0.07	−0.61	0.27	−25.91	0.38	3.97	0.30	−0.02	−21.56
$\sigma^{SO(FC)}$	−0.25	−1.21	−0.34	−701.79	42.59	−22.61	23.17	−0.96	−661.40
$\sigma^{SO(SD)}$	0.31	0.30	0.09	183.30	−12.39	4.80	−5.34	0.23	171.30

Table 10. Isotropic values, in ppm, of the LD correction within the LRESC approach for paramagnetic components with LMO on the cobalt atom in the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ system. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

HF							
	Core (Co)	6 × Core (O)	3 × 3d (Co)	6 × CoO	12 × OH	6 × LP _π (O)	Σ
σ^{PSOK}	0.78	0.11	144.92	2.30	0.78	−1.16	147.74
$\sigma^{Mv/p}$	49.68	−6.02	823.33	−54.98	14.12	258.53	1084.65
$\sigma^{Dw/p}$	−2.06	4.39	−637.58	18.34	−12.67	−86.04	−715.61
$\sigma^{SO(FC)}$	−0.77	−0.05	−110.46	−2.90	−1.78	−1.61	−117.57
$\sigma^{SO(SD)}$	−306.68	0.00	25,495.12	−2.34	25.13	−26.03	25,185.20
BHandHLYP							
	Core (Co)	6 × Core (O)	3 × 3d (Co)	6 × CoO	12 × OH	6 × LP _π (O)	Σ
σ^{PSOK}	−0.20	0.14	32.86	0.27	30.97	23.08	87.11
$\sigma^{Mv/p}$	12.40	−3.67	−108.94	0.57	−93.41	246.36	53.32
$\sigma^{Dw/p}$	−0.60	2.66	−3.54	−0.47	−9.46	−113.79	−125.20
$\sigma^{SO(FC)}$	0.03	−0.01	−4.39	0.48	−10.52	−10.03	−24.44
$\sigma^{SO(SD)}$	−2.20	0.00	482.74	0.35	654.93	520.72	1656.55

The bonds, LPs, and especially the d-AOs, in contrast to the MX_2 molecular systems, which have fully occupied d-AOs, are influenced by the electron correlation. Although the total value of $\sigma^{SO(SD)}(\text{Co})$ retains its sign with the change in methodology, $\sigma^{LD}(\text{Co})$ for $[\text{Co}(\text{CO})_4]^-$ becomes associated with a deshielding effect due to the contribution of the d-AOs to $\sigma^{SO(FC)}(\text{Co})$.

The contributions of the occupied LMOs to the LD mechanisms for $[\text{Rh}(\text{Cp})(\text{CO})_2]$, $[\text{Rh}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ molecular systems are shown in Figure 7 and in the

Supporting Information. The influence of the chemical environment on the shielding of Rh is governed primarily by the d -AOs, as in the cobalt-containing systems, followed by the bonds between the transition metal and the p -block elements of the periodic table. In the case of the $[\text{Rh}(\text{CO})_4]^-$ system, which exhibits five $4d$ -AOs centered on the rhodium atom, $\sigma^{\text{SO}(\text{FC})}(\text{Rh})$ is the principal contributor to $\sigma^{\text{LD}}(\text{Rh})$. In contrast, for $[\text{Rh}(\text{Cp})(\text{CO})_2]$ and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$, which each exhibit four $4d$ -AOs centered on the rhodium atom, the main contributions arise from $\sigma_p^{\text{Mv}}(\text{Rh})$ and $\sigma^{\text{SO}(\text{SD})}(\text{Rh})$. Moreover, considering electron correlation effects, the contributions of the rhodium d -AOs and bonds to $\sigma^{\text{SO}(\text{FC})}(\text{Rh})$ and $\sigma_p^{\text{Mv}/p}$, respectively, are mainly responsible for the reduction in the difference between $\sigma_p^{\text{RC}}(\text{Rh})$ and $\sigma^{\text{LD}}(\text{Rh})$ (Table 8).

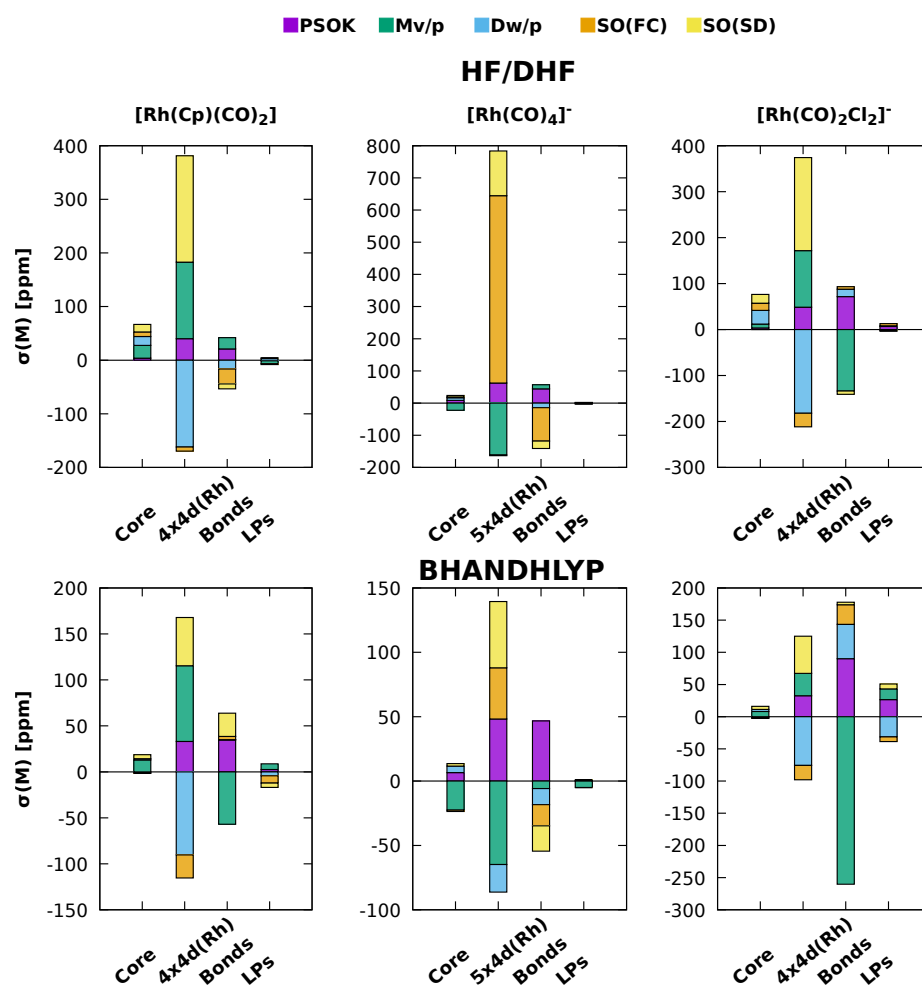


Figure 7. Isotropic values, in ppm, of the LD correction within the LRESC approach for paramagnetic components with LMOs on the rhodium atom in the $[\text{Rh}(\text{Cp})(\text{CO})_2]$, $[\text{Rh}(\text{CO})_4]^-$, and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ systems. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

The chemical shifts, in ppm, on transition metal atoms in $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, and $[\text{Co}(\text{NH}_3)_6]^{3+}$ molecular systems, using the $[\text{Co}(\text{CN})_6]^{3-}$ molecular system as the reference, calculated with NR ($\delta^{\text{NR}}(M)$), LRESC ($\delta^{\text{LRESC}}(M)$), and relativistic ($\delta^{\text{4C}}(M)$) levels of theory, along with experimental results ($\delta^{\text{Exp}}(M)$), are shown in Figure 8 and Tables S28–S37. The chemical shifts for rhodium-containing molecular systems are not discussed, as rhodium has a very low magnetogyric ratio; consequently, its chemical shifts are typically measured relative to frequency standards [93], which is beyond the scope of this study.

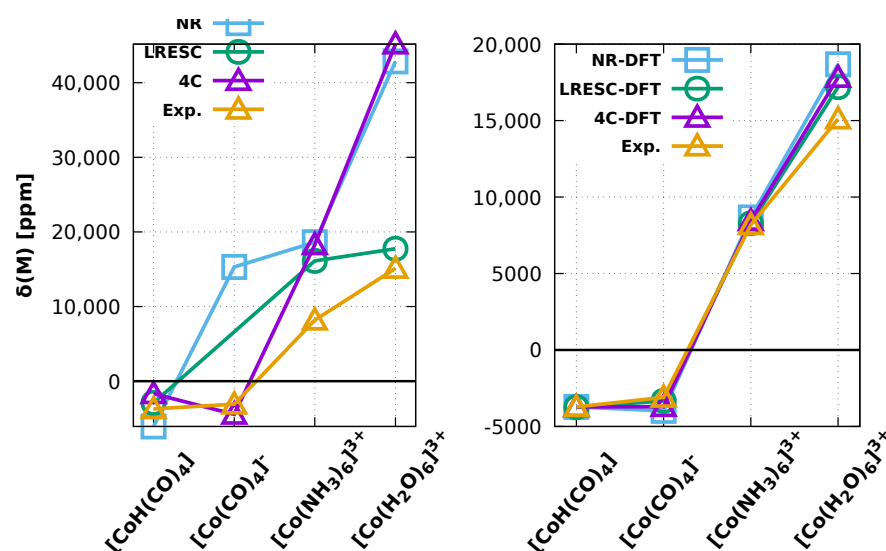


Figure 8. (left) HF or DHF; (right) BHandHLYP. Chemical shifts in ppm on transition metal atoms in $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, and $[\text{Co}(\text{NH}_3)_6]^{3+}$ systems, using $[\text{Co}(\text{CN})_6]^{3-}$ system as reference, calculated with NR, LRESC, and 4C methodologies, along with experimental results.

The overestimation of the shielding effect for $\sigma^{LD}(\text{Co})$ in $[\text{Co}(\text{CO})_4]^-$, when electron correlation is not included, causes $\delta^{LRESC}(\text{Co})$ to deviate from $\delta^{Exp.}(\text{Co})$. In contrast, this same behavior is necessary to reproduce the experimental chemical shift in the cobalt atom in the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ system. All methodologies yield results closer to the experimental values when electron correlation is included, regardless of the system.

4.3. Set III of Molecules with Atoms Belonging to Group VIB

In this section, we analyze the shielding and chemical shifts in the nuclei of transition metals that belong to set III of molecules (Figure 1). All these nuclei belong to group VIB of the periodic table. The values for $\sigma^{NR}(M)$, $\sigma^{LRESC}(M)$, and $\sigma^{4C}(M)$ are presented in Table 11. It can be observed that the difference between $\sigma^{LRESC}(M)$ and $\sigma^{4C}(M)$ increases with Z_M . Such a difference in the systems $[\text{WO}_4]^{2-}$ and $\text{W}(\text{CO})_6$ exceeds 20%, as was also demonstrated for other atoms in the 6th row of the periodic table [16,21].

Table 11. Shielding, in ppm, of nuclei of transition metals in the $[\text{MO}_4]^{2-}$ and $\text{M}(\text{CO})_6$ molecular systems, where $M = \text{Cr}, \text{Mo}, \text{W}$. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

	HF/DHF			BHandHLYP		
	$\sigma^{NR}(M)$	$\sigma^{LRESC}(M)$	$\sigma^{4C}(M)$	$\sigma^{NR}(M)$	$\sigma^{LRESC}(M)$	$\sigma^{4C}(M)$
$[\text{CrO}_4]^{2-}$	−5736.55	−6003.32	−5910.87	−3823.28	−3673.76	−3646.89
$\text{Cr}(\text{CO})_6$	−2816.26	−3260.47	−2919.70	−1621.02	−1522.83	−1489.431
$[\text{MoO}_4]^{2-}$	−208.81	260.00	386.97	−379.20	56.29	182.21
$\text{Mo}(\text{CO})_6$	854.41	1362.18	1500.53	964.02	1450.65	1579.51
$[\text{WO}_4]^{2-}$	1020.02	3650.73	5777.88	643.72	3037.34	5014.75
$\text{W}(\text{CO})_6$	4165.40	6763.55	8612.05	4130.55	6641.15	8605.53

The shielding constant, regardless of the method used to calculate it, is primarily influenced by the increase in Z_M . However, a significant variation is observed when the four oxygen atoms are replaced by six CO groups.

In Figure 9, we show results of σ_p^X and σ_d^X ($X = \text{NR, LRESC, 4C}$) for molecules with the nuclei of transition metals belonging to row VI of the periodic table. It is important to highlight that, regardless of the atom of transition metals, the difference between $\sigma_p^{\text{LRESC}}(M)$ and $\sigma_p^{4C}(M)$ is vanishingly small. However, in other molecules, the paramagnetic components are the main source of the differences among $\sigma^{\text{LRESC}}(M)$ and $\sigma^{4C}(M)$, especially when the atom of interest belongs to the 6th row of the periodic table [16,21] or is the mercury atom in the HgX_2 systems (Section 4.1).

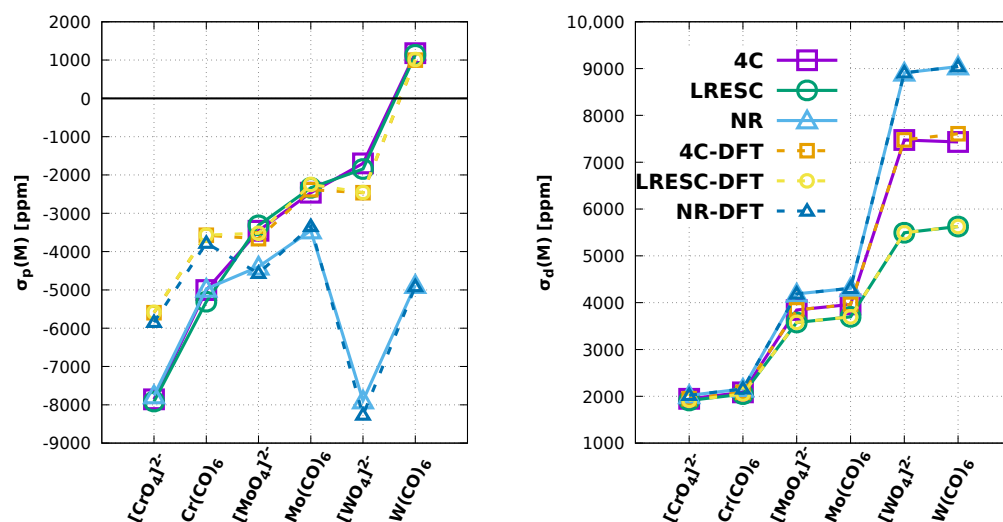


Figure 9. The paramagnetic and diamagnetic components of the shielding of the nuclei of transition metals belonging to group VI of the periodic table in $[\text{MO}_4]^{2-}$ and $\text{M}(\text{CO})_6$ molecules. These quantities were calculated using the HF and DHF methodologies, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

The difference between $\sigma_d^{\text{LRESC}}(M)$ and $\sigma_d^{4C}(M)$ is primarily due to the fact that the LRESC model overestimates the relativistic correction as Z_M increases. The overestimation of the relativistic correction by LRESC in the $[\text{WO}_4]^{2-}$ and $\text{W}(\text{CO})_6$ systems exceeds 1000 ppm.

Isotropic values, in ppm, of the LRESC model with LMOs on the $[\text{WO}_4]^{2-}$ and $\text{W}(\text{CO})_6$ molecules are presented in Tables 12 and 13. The effect of electron correlation is negligibly small for $\sigma_d^{\text{NR}}(\text{W})$, $\sigma_d^{\text{NLD}}(\text{W})$, $\sigma^{\text{OZK}}(\text{W})$, and $\sigma_p^{\text{NLD}}(\text{W})$ mechanisms.

The $\sigma_p^{\text{LRESC}}(\text{W})$ in the $[\text{WO}_4]^{2-}$ and $\text{W}(\text{CO})_6$ molecular systems is primarily due to the difference between the contributions of the core(W) to $\sigma_p^{\text{NLD}}(\text{W})$ and $\sigma_p^{\text{NR}}(\text{W})$. The orbitals that most contribute to the NR paramagnetic component are the 4d(W) atomic orbitals. The differences between the contributions of the core and valence MOs is responsible for the small magnitude of $\sigma^{\text{LD}}(\text{W})$. In the case of the total NLD contribution, it is observed that only the NR diamagnetic component has an increment in the shielding when the oxygen atoms are replaced by CO groups.

Considering electron correlation effects, the contributions to $\sigma^{(Mv+Dw)/p}(\text{W})$ and $\sigma^{\text{SO}}(\text{W})$ of the double bonds $\text{W}=\text{O}$ and $\text{LP}_\pi(\text{O})$ orbitals tend toward positive values, while the contribution of single bonds $\text{W}-\text{O}$ becomes more negative. This is responsible for the increment in $\sigma^{\text{LD}}(\text{W})$ in the WO_4 molecular system, and a similar behavior is observed in the molecule $\text{W}(\text{CO})_6$. The molecules MO_4 and $\text{M}(\text{CO})_6$ ($M = \text{Cr, Mo}$) exhibit behaviors that are similar to those in the tungsten-containing systems (see the Supporting Information).

Table 12. Isotropic values of the LRESC model with LMOs on the atom of W in the $[\text{WO}_4]^{2-}$ system. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

HF						
	Core (W)	4 × Core (O)	4 × WO	4 × LP _σ (O)	8 × (W = O, LP _π (O))	Σ
σ_d^{NLD}	−3416.10	−0.11	−0.30	1.02	0.32	−3415.17
σ_d^{NR}	8672.22	41.98	53.70	49.78	91.41	8909.09
σ^{PSOK}	−47.01	2.61	403.05	70.58	287.56	716.79
$\sigma^{Mv/p+Dw/p}$	385.07	0.24	−211.60	−103.68	−555.27	−485.24
σ^{SO}	57.33	−0.51	−62.05	−12.93	−205.92	−224.08
σ^{LD}	395.39	2.34	129.40	−46.03	−473.63	7.47
σ^{OZK}	438.69	0.12	1.72	1.80	2.12	444.45
σ_p^{NLD}	5592.12	0.00	0.72	0.48	0.63	5593.95
σ_p^{NR}	158.65	−51.45	−5203.23	−286.33	−2506.72	−7889.08
BHandHLYP						
	Core (W)	4 × Core (O)	4 × WO	4 × LP _σ (O)	8 × (W = O, LP _π (O))	Σ
σ_d^{NLD}	−3414.49	−0.11	−0.57	−0.06	−0.35	−3415.58
σ_d^{NR}	8679.49	41.98	59.79	37.00	91.74	8910.01
σ^{PSOK}	172.40	1.46	680.88	44.76	−174.07	725.42
$\sigma^{Mv/p+Dw/p}$	−492.20	0.06	−360.67	116.53	113.56	−622.72
σ^{SO}	−57.48	−0.21	−147.72	−36.48	−92.61	−334.51
σ^{LD}	−377.29	1.31	172.49	124.81	−153.13	−231.81
σ^{OZK}	441.95	0.11	2.58	−0.36	1.56	445.84
σ_p^{NLD}	5594.57	0.00	0.34	−0.02	0.27	5595.16
σ_p^{NR}	−705.46	−38.32	−5795.11	−806.26	−921.15	−8266.29

Table 13. Isotropic values, in ppm, of the LRESC model with LMOs on the atom W in the $\text{W}(\text{CO})_6$ system. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

HF								
	Core (W)	6 × Core (C)	6 × Core (O)	3 × 4d (W)	6 × WC	6 × CO	12 × C=O	6 × LP _σ (O)
σ_d^{NLD}	−3415.32	−0.08	−0.09	−2.17	0.86	0.76	0.24	0.42
σ_d^{NR}	8672.45	54.76	35.16	50.61	54.71	47.97	81.39	44.98
σ^{PSOK}	−35.70	−1.10	−0.17	37.73	47.02	182.40	135.32	99.87
$\sigma^{Mv/p+Dw/p}$	198.23	−0.32	0.03	319.36	−101.32	−253.17	−195.77	−145.73
σ^{SO}	34.14	0.24	0.05	−277.30	12.81	−35.50	−25.41	−21.75
σ^{LD}	196.67	−1.18	−0.08	79.79	−41.50	−106.28	−85.86	−67.62
σ^{OZK}	439.07	0.09	0.10	3.51	0.47	0.87	0.31	0.61
σ_p^{NLD}	5592.90	0.00	0.00	0.30	1.03	0.20	0.04	0.09
σ_p^{NR}	116.95	−77.52	−40.03	−2927.84	−632.75	−644.01	−585.51	−85.92
BHandHLYP								
	Core (W)	6 × Core (C)	6 × Core (O)	3 × 4d (W)	6 × WC	6 × CO	12 × C=O	6 × LP _σ (O)
σ_d^{NLD}	−3414.39	−0.08	−0.09	−1.89	0.77	0.06	−0.10	0.00
σ_d^{NR}	8677.30	54.77	35.16	51.05	71.37	42.22	77.90	32.10
σ^{PSOK}	74.37	−0.25	0.59	86.81	347.36	20.19	3.87	−17.37
$\sigma^{Mv/p+Dw/p}$	−178.67	0.07	0.08	195.90	−381.11	−35.23	3.24	3.58
σ^{SO}	−11.46	0.04	0.08	−165.53	−31.53	−9.39	−15.37	−5.69
σ^{LD}	−115.76	−0.15	0.75	117.18	−65.28	−24.44	−8.26	−19.48
σ^{OZK}	441.41	0.09	0.09	3.38	0.99	0.19	0.25	−0.07
σ_p^{NLD}	5594.70	0.00	0.00	0.28	0.42	0.02	0.01	0.01
σ_p^{NR}	−252.92	−68.52	−31.89	−3024.01	−988.78	−525.58	123.08	−142.70

The chemical shifts, in ppm, in the nuclei of atoms of transition metals in $M(\text{CO})_6$ molecules, using $[\text{MO}_4]^{2-}$ systems as reference, calculated at NR, LRESC, and 4C levels of theory, along with experimental results, are shown in Tables S46 and S47 and Figure 10.

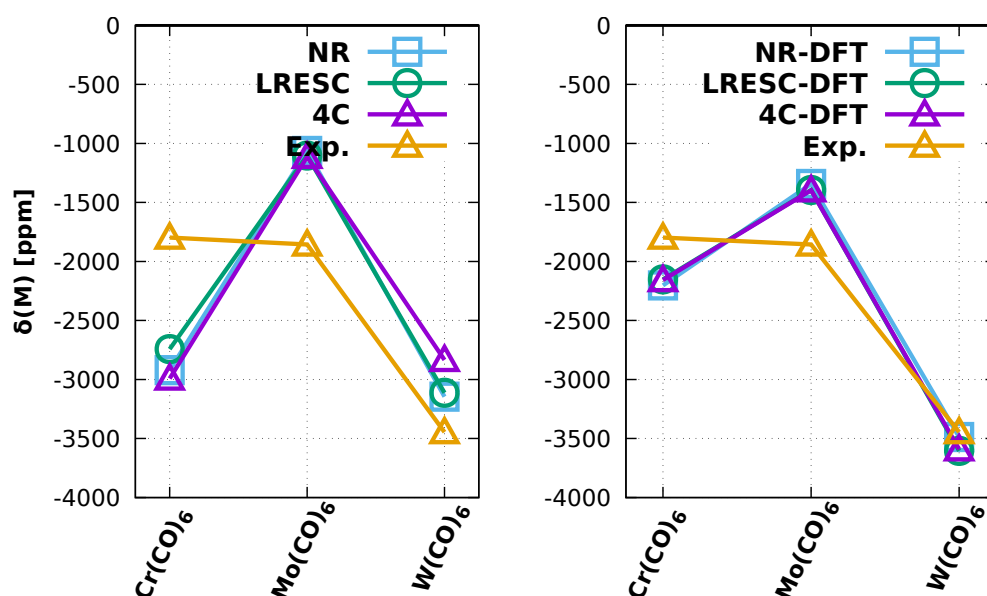


Figure 10. Chemical shifts, in ppm, in atoms of transition metals in $M(\text{CO})_6$ molecules, using $[\text{MO}_4]^{2-}$ systems as reference, calculated with NR, LRESC, and 4C levels of theory, along with experimental results. These quantities were calculated at the HF and DHF levels of theory, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study.

The high values of the paramagnetic component of the chromium atom, regardless of the methodology, are responsible for the difference between the calculated and experimental chemical shifts, which decreases when considering the electron correlation. In contrast, the calculated chemical shifts in molybdenum and tungsten atoms reproduce the experimental trend, and the differences decrease as Z_M increases. These improvements in the calculation of $\delta(M)$ as Z_M increases are due to an increased deshielding effect in both the paramagnetic and diamagnetic components. Furthermore, $\delta(M)$ is primarily determined by the core(M) LMOs, as the influence of the LD correction is negligible.

5. Conclusions

In this work, we analyze the magnetic shielding constants and chemical shifts in the atoms of transition metals in the molecular systems shown in Figure 1. Relativistic effects on these response properties are studied at LRESC and 4C levels of approach, and the chemical shifts are compared with available experimental results. Additionally, the LRESC results are expressed as contributions due to localized molecular orbitals; in particular, the contributions due to each ligand-dependent (LD) mechanism, which are behind the trends of relativistic effects, are analyzed.

The main findings are as follows:

1. Calculations with the LRESC model mainly reproduce the trends and magnitude of the 4C shielding constant values for many molecules—especially those with atoms up to the fifth row of the periodic table. This behavior is also observed with respect to the experimental chemical shift, though, in contrast to the 4C shielding, the LRESC model could give closer values to the experimental ones for some molecules, like $\text{W}(\text{CO})_6$.

2. In the cases of $[\text{Co}(\text{CO})_4]^-$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ complexes, which have five and three d -AOs filled, respectively, the LRESC/HF calculations show a too large contribution from their occupied d -AOs associated with the $\sigma^{SO(SD)}$ term. This wrong behavior is overcome when the LRESC/BHandHLYP level of theory is applied.
3. The occupied d -AOs show the highest sensitivity to changes in the chemical environment surrounding the transition metal in set II, as well as in the $M(\text{CO})_6$ systems ($M = \text{Cr}, \text{Mo}, \text{W}$). Consequently, these orbitals generally determine the trend in the LD mechanism associated with the paramagnetic component, which experiences stronger relativistic corrections than the diamagnetic component. Furthermore, it is also observed that the non-relativistic paramagnetic component in those systems is determined mainly by the occupied d -AOs. In set I of molecules and the $[\text{MO}_4]^{2-}$ systems ($M = \text{Cr}, \text{Mo}, \text{W}$), the magnitudes of $\sigma^{LD}(M)$ and $\sigma_p^{NR}(M)$ are determined by bonding and/or LP_π molecular orbitals.
4. For the family of compounds MX_2 ($M = \text{Zn}, \text{Cd}, \text{Hg}$; $X = \text{Cl}, \text{Br}, \text{I}$), when $M = \text{Zn}$, the highest relativistic effects arise from the $\sigma^{SO(FC)}$ mechanism, but, for $M = \text{Cd}$ and especially for $M = \text{Hg}$, the contributions of the $\sigma^{SO(FC)}$ mechanism become smaller, in percentage, compared with the σ^{PSOK} and the $\sigma^{Mv/p}$ mechanisms when $M = \text{Hg}$.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/magnetochemistry12080092/s1>, Table S1: Chemical shifts (δ) of transition metal atoms in MX_2 ($M = \text{Zn}, \text{Cd}, \text{Hg}$; $X = \text{Cl}, \text{Br}, \text{I}$) systems at NR ($\delta^{NR}(M)$), LRESC ($\delta^{LRESC}(M)$), and 4C ($\delta^{4C}(M)$) levels. The reference systems for ZnX_2 , CdX_2 , and HgX_2 are $\text{Zn}(\text{NO}_3)_2$, $\text{Cd}(\text{ClO}_4)_2$, and HgMe_2 , respectively. These quantities were calculated using the HF and DHF methodologies, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study. Experimental chemical shifts ($\delta^{Exp.}(M)$) are also shown. Table S2: Chemical shifts at HF/cv3z and BHandHLYP/cv3z levels of the theory in ppm on transition metal atoms in the $[\text{Co}(\text{CO})_4]^-$, $[\text{CoH}(\text{CO})_4]$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, and $[\text{Co}(\text{NH}_3)_6]^{3+}$ systems calculated with NR, LRESC, and 4C methodologies. The experimental chemical shifts for Co are taken from references [42,43]. The reference is $[\text{Co}(\text{CN})_6]^{3-}$ for Co-containing systems. Table S3: Chemical shifts, in ppm, of transition metal atoms in $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) molecules calculated at NR, LRESC, and 4C levels of theory. The experimental chemical shifts for the Cr nuclei were taken from reference [69], while those for Mo and W nuclei were taken from [70] and [71], respectively. The molecules of reference are $[\text{MO}_4]^{2-}$. These quantities were calculated using the HF and DHF methodologies, as well as the BHandHLYP functional, with the dyall.cv3z basis set. The gauge origin was placed at the site of the atom under study. Table S4: Isotropic values, in ppm, of the LRESC mechanisms with LMOs on the Zn atom in the $\text{Zn}(\text{NO}_3)_2$. The theory level is HF/cv3z and the gauge origin is in the site of the nucleus of Zn. Table S5: Isotropic values, in ppm, of the LRESC mechanisms with LMO on the Zn atom in the $\text{Zn}(\text{NO}_3)_2$. The theory level is BHandHLYP/cv3z and the gauge origin is in the site of the nucleus of Zn. Table S6: Isotropic values in ppm of the LRESC mechanisms with LMO on the Zn in the ZnCl_2 . The theory level is HF/cv3z and the gauge is in the site of the nucleus of Zn. Table S7: Isotropic values in ppm of the LRESC mechanisms with LMO on the Zn atom in the ZnCl_2 . The theory level is BHandHLYP/cv3z and the gauge origin is in the site of the nucleus of Zn. Table S8: Isotropic values in ppm of the LRESC mechanisms with LMO on the Zn atom in the ZnBr_2 . The theory level is HF/cv3z and the gauge origin is in the site of the nucleus of Zn. Table S9: Isotropic values in ppm of the LRESC mechanisms with LMO on the Zn atom in the ZnBr_2 . The theory level is BHandHLYP/cv3z and the gauge origin is in the site of the nucleus of Zn. Table S10: Isotropic values in ppm of the LRESC mechanisms with LMO on the Zn atom in the ZnI_2 . The theory level is HF/cv3z and the gauge origin is in the site of the nucleus of atom of Zn. Table S11: Isotropic values in ppm of the LRESC mechanisms with LMO on the Zn atom in the ZnI_2 . The theory level is BHandHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Zn. Table S12: Isotropic values in ppm of the LRESC mechanisms with LMO on the Cd atom in the $\text{Cd}(\text{ClO}_4)_2$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom

of Cd. Table S13: Isotropic values in ppm of the LRESP mechanisms with LMO on the Cd atom in the $\text{Cd}(\text{ClO}_4)_2$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S14: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Cd in the CdCl_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S15: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Cd in the CdCl_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S16: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Cd in the CdBr_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S17: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Cd in the CdBr_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S18: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Cd in the CdI_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S19: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Cd in the CdI_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Cd. Table S20: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgMe_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S21: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgMe_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S22: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgCl_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S23: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgCl_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S24: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgBr_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S25: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgBr_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S26: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgI_2 . The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S27: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Hg in the HgI_2 . The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Hg. Table S28: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{CN})_6]^{3-}$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S29: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{CN})_6]^{3-}$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S30: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{CoH}(\text{CO})_4]$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S31: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{CoH}(\text{CO})_4]$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S32: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{CO})_4]^-$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S33: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{CO})_4]^-$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S34: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{NH}_3)_6]^{3+}$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S35: Isotropic values in ppm of the LRESP mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{NH}_3)_6]^{3+}$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S36: Isotropic values in ppm of the LRESP mechanisms

with localized molecular orbital over the Co in the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S37: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Co in the $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Co. Table S38: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Rh in the $[\text{Rh}(\text{Cp})(\text{CO})_2]$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Rh. Table S39: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Rh in the $[\text{Rh}(\text{Cp})(\text{CO})_2]$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Rh. Table S40: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Rh in the $[\text{Rh}(\text{CO})_4]^-$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Rh. Table S41: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Rh in the $[\text{Rh}(\text{CO})_4]^-$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Rh. Table S42: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Rh in the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Rh. Table S43: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Rh in the $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Rh. Table S44: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Cr in the $[\text{CrO}_4]^{2-}$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Cr. Table S45: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Cr in the $[\text{CrO}_4]^{2-}$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Cr. Table S46: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Cr in the $\text{Cr}(\text{CO})_6$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Cr. Table S47: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Cr in the $\text{Cr}(\text{CO})_6$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Cr. Table S48: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Mo in the $[\text{MoO}_4]^{2-}$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Mo. Table S49: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Mo in the $[\text{MoO}_4]^{2-}$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Mo. Table S50: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Mo in the $\text{Mo}(\text{CO})_6$. The theory level is HF/cv3z and the gauge origin is in the site of nucleus of the atom of Mo. Table S51: Isotropic values in ppm of the LRESC mechanisms with localized molecular orbital over the Mo in the $\text{Mo}(\text{CO})_6$. The theory level is BHANDHLYP/cv3z and the gauge origin is in the site of nucleus of the atom of Mo.

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