

Calculation of ^{59}Co shielding tensor σ using LF-DFT

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^{59}Co NMR shielding tensor σ calculation using perturbation theory within the framework of Ligand Field-Density Functional Theory (LF-DFT) [1] is implemented for transition-metal complexes as an extension of the LF-DFT methodology. We give some first results for absolute and relative shielding tensors, which are in a good agreement with experimental results as well as with other theoretical calculations.

1. Introduction

It has already been noted, e.g. in Ref. [2], that ^{59}Co was one of the first nuclei, for which a dependency of the resonance frequency on the compound was observed [3] and therefore occupies a special place in NMR history [4]. ^{59}Co has a very large shielding tensor range of about 15,000 ppm [5]. The high sensitivity of the ^{59}Co nucleus permits experimental determination of not only the isotropic shift but also the components of the anisotropic shielding tensor [5]. And as there are absolute values extrapolated from experiment, the calculated absolute shielding can be compared with experimental findings [5]. For ^{59}Co a linear relation between shielding tensor and the wavelength of the first Metal Centred optical transition has been observed by Freeman et al. [6]. The residual paramagnetism of ^{59}Co complexes arises from distribution of electrons in orbitals being predominately cobalt 3d-orbitals [7] and can therefore be interpreted in terms of the behaviour of the metal 3d electrons [8]. Such a description in the framework of ligand field theory is reproducing successfully the above mentioned linear behaviour, that was 1st observed by Griffith and Orgel [8] and later generalized by Bramley et al. [2]. These authors also point out difficulties in cases with non-orthoaxial ligands.

Thus, ligand field theory should be able to reproduce ^{59}Co shielding tensors, but needs empirical parameters. Ligand Field-Density Functional Theory (LF-DFT) [1] is a Density Functional Theory (DFT) based ligand field (LF) model in which the ligand field parameters calculated in a non-empirical approach and therefore able to predict properties of transition-metal complexes. The calculation involves two steps. In the first place an Average Of Configuration (AOC) DFT electronic structure calculation, with equal

occupation of the d- or f-orbitals is carried out. Secondly, with these orbitals kept frozen, the energies of all single-determinants within the whole LF-monoifold is performed. These energies are then used to estimate all the Racah- and LF-parameters needed for a conventional LF-calculation in a least-squares sense. Its power has been demonstrated for the calculations of e.g. zero-field splitting [9], g- and A-tensor [10]. Hence introducing LF-DFT we are able to calculate the ^{59}Co shielding tensor without need of empirical data. Furthermore this approach allows us to evaluate further terms in our Hamiltonian. Even if there are already several methods for the calculation of σ for transition-metals, an overview is given e.g. by Helgaker et al. [11], we have herewith a method able to treat open-shell, medium-sized transition-metal complexes, which need multi-determinant interaction for a successful description.

Even if ^{59}Co shielding tensors are known since many years to have a temperature dependency [5], for which one finds different explanations (e.g. [8,5]), authors of Ref. [5] concluded in their study, that for reproducing main results, no low-temperature NMR data are necessary. So we calculate in this work like the authors of Ref. [8] the temperature independent paramagnetic and diamagnetic contribution of the ^{59}Co shielding tensor. We emphasize, that in order to obtain the electron-spin dependent terms we start our double-perturbation approach from a relativistic equation. There we add the magnetic perturbation, but take then the non-relativistic limit and thus our working equations are non-relativistic.

2. Theoretical part

We are working in a LF approach and therefore treat the complex as an 'ionic molecule'. i.e. the central atom, commonly a transition-metal (TM) ion, is subjected to a perturbation due to

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surrounding ligands. We interpret the residual paramagnetism of ^{59}Co complexes like the authors of Ref. [8] as arising from electrons in orbitals being predominantly cobalt 3d-orbitals and thus interpret it as behaviour of cobalt d electrons. Therefore we work in basis of the 10 cobalt 3d spinorbitals. The description of the multiplet structure and energies of states in this given basis are obtained with LF-DFT [1]. LF-DFT is a DFT based LF model – mapping the energies of the micro-states in LF-manifold from DFT single-determinant calculations to the corresponding LF micro-states, thus allowing us to estimate all Racah and LF-parameters in a least-square sense. It should be mentioned that we get the Racah parameter B and C as distinct parameters and therefore the constraint of ratio $\frac{C}{B} = 4$ is not necessary.

A nucleus with a non-zero magnetic moment $\vec{\mu}$ interacts with an external magnetic field \vec{H} as

$$-\vec{\mu} \cdot \vec{H} \quad (1)$$

The application of the external field induces a secondary field $\vec{H}' = \int \frac{\vec{r}_{ij}(r)}{r_{ij}^3} d\nu$ where \vec{j} is the electric current density due to the action of the applied external magnetic field onto the motion of the electrons around the nucleus. The induced electronic system change leads in 1st order to

$$E = \mu_0 \vec{\mu} \cdot (1 - \sigma) \cdot \vec{H} \quad (2)$$

with μ_0 : vacuum permeability constant and σ : shielding tensor, which is also known e.g. as chemical shift [12] or as screening constant [13]. This, in general anisotropic, shielding tensor can be split into a so called paramagnetic and a diamagnetic part [13]:

$$\sigma = \sigma^d + \sigma^p \quad (3)$$

As we use ^{59}Co as origin of our coordinate frame, σ^d gives rise to a lowering of the magnetic field H^{nucl} as compared with the external field H^{obs} while the opposite is true for σ^p [2].

For calculating σ , defined in (2), we evaluate the expectation value of the corresponding operator over the ground-state $\langle 0|0\rangle$. Therefore we use a double-perturbation approach as e.g. vide infra [14], and so perturb the ground state wave function and the operator.

For a molecule in an external field, the corresponding LF-Hamiltonian can be written as

$$\mathcal{H} = \underbrace{\sum h_{\text{core}} + \sum_{i>j} \frac{1}{r_{ij}} + \sum_i \zeta_{\text{nd}} \vec{l}_i \cdot \vec{s}_i + V_{\text{LF}}}_{\mathcal{H}_0} + \underbrace{\frac{\mu_0 \beta_e}{\hbar} (k_{\text{orf}} \vec{L} + g_e \vec{S}) \cdot \vec{H}}_{\equiv \vec{Z} \cdot \vec{H} = \mathcal{H}_1, \text{Zeeman term}} \quad (4)$$

where h_{core} : one-particle core Hamiltonian, ζ_{nd} : spinorbit coupling constant, simplified as constant for all electrons in the n d-orbital, V_{LF} : potential derived by the ligands, β_e : bohr magneton, k_{orf} : orbital reduction factor, g_e : electron-spin g-factor, \vec{L} : total electron angular momentum, \vec{S} : total electron-spin momentum.

For fields used in NMR spectroscopy $E(\mathcal{H}_1) \ll E(\mathcal{H}_0)$. Hence we can use perturbation theory. Thus to 1st order perturbation theory, ground-state wavefunction $|0\rangle$ can be written as a function of wavefunctions of unperturbed states $|\psi\rangle$ with energies ε

$$|0\rangle = |\psi_0\rangle + \frac{\mu_0 \beta_e}{\hbar} \sum_x H_x \frac{\langle \psi_n | k_{\text{orf}} L_x + g_e S_x | \psi_0 \rangle}{\varepsilon_0 - \varepsilon_n} |\psi_n\rangle \quad (5)$$

We start from Dirac's relativistic equation where we eliminate the small component (esc). As we finally want to calculate (3) we are just interested in terms containing $\vec{\mu}$ and so looking for the operator-part coming up by introducing a vectorpotential \vec{A} . The difference of the operator with and without vectorpotential \vec{A} , we call it Δ , can be formulated as:

$$\frac{2m_e c \Delta}{e} = 2f \vec{A} \cdot \vec{p} + f \hbar \vec{\sigma} \cdot \nabla \times \vec{A} + \vec{\sigma} \cdot (\vec{p} f) (\vec{\sigma} \cdot \vec{A}) + \frac{e}{c} f \vec{A}^2 \quad (6)$$

We set $f = 1$ and $\vec{A} = \vec{A}_1 + \vec{A}_2$, where $\vec{A}_1 = k_1 \frac{1}{2} \vec{B} \times \vec{r}$: i.e. the interaction due to an external static magnetic field (in SI $k_1 = c$) and $\vec{A}_2 = k_2 \frac{\vec{\mu} \times \vec{r}}{r^3}$: interaction due to nuclear spin (more general $\vec{A}_2 = \sum_Q \left(\frac{1}{r_Q^3} (\vec{\mu}_Q \times \vec{r}_Q) \right)$ with $\vec{\mu}_Q$: nuclear magnetic moment of nucleus Q , $\vec{r}_Q = \vec{r} - \vec{R}_Q$, but here because of the LF-theory approximation just one nucleus is needed. In SI: $k_2 = ck_u = c \frac{\mu_0}{4\pi}$). Following Griffith [13], we use (6) to 1st order in $\vec{\mu}$, like e.g. [15,14].

Terms 1-3 of the right-hand side in (6) will give a contribution

$$\tilde{\Delta} = \frac{1}{\hbar} k_u 2g_p \beta_e \beta_N \langle \vec{r}^{-3} \rangle [\vec{I} \cdot \vec{I}] \quad (7)$$

$$+ \xi \left[l(l+1) \vec{s} \cdot \vec{I} - \frac{3}{2} (\vec{I} \cdot \vec{s}) (\vec{I} \cdot \vec{I}) - \frac{3}{2} (\vec{I} \cdot \vec{I}) (\vec{I} \cdot \vec{s}) \right] \quad (8)$$

$$+ \frac{8\pi}{3} \frac{1}{\langle \vec{r}^{-3} \rangle} \delta(r_k) \vec{s} \cdot \vec{I} \quad (9)$$

where g_p : proton g-factor, β_N : nuclear magneton, \vec{I} : nuclear angular momentum, ξ : dimensionless constant, for d-electrons $\xi = \frac{2}{(2l-1)(2l+3)}$, $\delta(\cdot)$: 'Dirac's delta function'. Thereby (7) describes the interaction of the nuclear spin with the orbital angular momentum of the electron, (8) describes the interaction of the nuclear spin with the electron-spin (a dipole interaction) and (9) describes the so-called Fermi-contact term, a term which contributes only if spin density is present at the nucleus [15]. The importance of this term for other nuclei has already been shown, e.g. in [15].

The terms (8) and (9) can be reformulated, see e.g. Griffith [13], and so we get for a d^n system

$$\mathcal{H}_{\text{Hf}} = P \left(\vec{L} \cdot \vec{I} - \kappa \vec{S} \cdot \vec{I} + \frac{1}{7} \sum_{k=1}^n \vec{a}_k \cdot \vec{I} \right) = P \vec{Q} \cdot \vec{I} \quad (10)$$

where the system specific constant $P = \frac{1}{\hbar} k_u g_e g_p \beta_e \beta_N \langle \vec{r}^{-3} \rangle$. This expression is known as the hyperfine Hamiltonian. It leads to a paramagnetic shielding tensor

$$\sigma_{\alpha\alpha'} = -2k_u g_e \frac{\beta_e^2}{\hbar^2} \langle \vec{r}^{-3} \rangle \sum_{n \neq 0} \frac{\langle \psi_0 | \Omega_\alpha | \psi_n \rangle \langle \psi_n | Z_{\alpha'} | \psi_0 \rangle}{\varepsilon_n - \varepsilon_0} \quad (11)$$

where

$$\vec{Z} = k_{\text{orf}} L_x + g_e S_x \quad (12)$$

$$\vec{Q} = \vec{L} - \kappa \vec{S} + \frac{1}{7} \sum_{k=1}^n \vec{a}_k \quad (13)$$

$$\vec{a}_k = 4\vec{s}_k - (\vec{l}_k \cdot \vec{s}_k) \vec{l}_k - \vec{l}_k (\vec{l}_k \cdot \vec{s}_k) \quad (14)$$

$$\kappa = -\frac{8\pi}{3} \frac{1}{\langle \vec{r}^{-3} \rangle} \sum_i [\langle \rho_{i1}(0) - \rho_{i0}(0) \rangle] w_i \quad (15)$$

The summation runs in (15) over all the micro-states of the LF manifold, i.e. the $\binom{10}{n}$ single-determinants where ρ_1 and ρ_0 are respectively the up and down spin densities. We weight them according to their contribution to the ground-state w_i . Notation (11) relates to use of ligand field theory, that is why we have no sum over different nuclei. We like to note, that compared to the formula used in [8] and [2] we have two additional terms: $-\kappa \vec{S}$ and $\frac{1}{7} \sum_{k=1}^n \vec{a}_k$ in our Hamiltonian. Applying Slaters rules of integration, (12) and (13) are easy to evaluate. Working in the framework of LF-DFT the wavefunction of unperturbed states $|\psi_i\rangle$ ($i = 0, n$) are known and (11) can directly be implemented.

On the other hand, the last term in (6) also contributes to σ as $\langle \psi_0 | \mathcal{O} | \psi_0 \rangle$. For reason of symmetry it can be reformulated as

$$k_1 k_2 \mu_0 \frac{e^2}{2mc^2 r^3} \left[r^2 \vec{H} \cdot \vec{\mu} - \frac{1}{3} r^2 \vec{H} \cdot \vec{\mu} \right] = \frac{e^2}{3mc^2 r} k_1 k_2 \mu_0 \vec{H} \cdot \vec{\mu} \quad (16)$$

and therefore gives a contribution

$$\sigma_{1e}^d = k_1 k_2 \frac{e^2}{3mc^2} \langle r^{-1} \rangle_e \quad (17)$$

which is called diamagnetic part of the shielding tensor. The authors of [14] found σ^d to be independent from the molecule geometry and so confirm our result. As (17) originates from Dirac's equation, it is a one electron expression. Unlike (11), (17) is independent of the basis in which the expression has been worked out – in our case the one of LF-DFT – and all metal electrons contribute. Therefore, for many electron systems, we obtain

$$\sigma^d = k_1 k_2 \frac{e^2}{3mc^2} \sum_e \langle r^{-1} \rangle_e \quad (18)$$

The sum in (18) corresponds to $\int \frac{\rho(r)}{r} r^2 dr$ in Lamb's formula [16] if one expresses the density as $\rho(r) = \sum_{n\lambda} \omega_{n\lambda} [P_{n\lambda}(r)]^2$ where $\omega_{n\lambda}$: the occupation number of orbital of type λ (i.e. s, p, d, f, ...) and quantum number n (both spins), $P_{n\lambda}$: the radial part of the atomic wavefunction times r .

3. Computational details

All DFT calculations were performed using the Amsterdam density functional (ADF) program package (release 2007.01 or, if COSMO model is used, release 2004.01) [17]. If not mentioned specially, the generalized gradient approximation (GGA) in form of Perdew–Wang 91 (PW 91) [18] for exchange-correlation functionals has been used with an all electron ZORA triple- ζ Slater type orbital (STO) plus one polarization function (TZP) basis set. Relativistic effects have been taken into account through ZORA, implemented in ADF.

LF-DFT calculations were used to obtain the energies and wave functions of the ^{59}Co 3d spinorbitals using Matlab [19] scripts ([1,20]). Quantities as $[\langle \rho_\uparrow(0) - \rho_\downarrow(0) \rangle]$, the difference between the up- and downspin-density at the ^{59}Co nucleus in (15) can be computed with ADF. According to Ref. [20] we have

$$\langle r^{-3} \rangle \simeq \langle r_{3d}^{-3} \rangle \simeq k_{\text{off}} \langle r(\text{atom})_{3d}^{-3} \rangle \quad (19)$$

where $\langle r(\text{atom})_{3d}^{-3} \rangle$ has been calculated with XATOM [21], a numerical solver of the atomic Kohn–Sham equation and the orbital reduction factor k_{off} is set equal to the average population of TM d-orbitals in the molecular orbitals with main-TM d-orbital character in the DFT calculation. Also the constant $\langle r^{-1} \rangle$ used in (17) has been calculated with [21] according to the same method as (19).

$\text{Co}(\text{CN})_6^{3-}$: as reference value of ^{59}Co shielding tensor, aqueous $\text{Co}(\text{CN})_6^{3-}$ is used. We calculated its σ -value using the optimized octahedral geometry.¹ GGA/PW 91 is known to overestimate bond lengths in geometry optimizations, hence geometry has been optimized with LDA/VWN [23]. To mimic water effects and to deal with the high negative charge, COSMO model (with water as solvent, Van der Waal radii out of [24]) has been used for all calculations.

$\text{Co}(\text{acac})_3$ (acac: acetylacetonate), $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$: the geometry was taken from published crystal structure [25]. The DFT calculations correspond to a single molecule in vacuum. Since surrounding molecules have a non-negligible influence we replace all surrounding atoms in a sphere of radius 10 Å by their point charges. The values of the point charges are Mulliken point charges

¹ octahedral since it is observed in [22] that the deviation from O_h symmetry is marginable and there is no reason, why the aqueous complex in average should have a reduced geometry.

of the corresponding atom of a $\text{Co}(\text{acac})_3$ calculation in vacuum, also using GGA/PW 91 with a TZP basis set.

$\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_4\text{H}_6)$: published crystal structure [26] has been used for the geometry of the molecule.

4. Results and discussion

We obtain $\sum_e \langle r^{-1} \rangle_e = 121a_0^{-1}$ for atomic Co(III) as $[\text{Ar}]3d^6$ and $= 122a_0^{-1}$ for atomic Co(I) as $[\text{Ar}]3d^8$, thus we get for the unreduced diamagnetic contributions to the shielding tensor of $\sigma_{\text{Co(III)}}^d = 2144$ ppm and $\sigma_{\text{Co(I)}}^d = 2168$ ppm. For a free Co(0) as $[\text{Ar}]3d^7 4s^2$ we obtain $\sum_e \langle r^{-1} \rangle_e = 122a_0^{-1}$ and $\sigma_{\text{Co(0)}}^d = 2171$ ppm, which is in a good agreement with previous calculation for the free atom yielding 2166 ppm given in Ref. [27], 2100 ppm given in Ref. [13], respectively.

We use the following notation:

$$\sigma_{ii} = \sigma_{ii}^p + \sigma^d \quad (20)$$

$$\delta_{ii} = \sigma_{ii}^{\text{ref}} - \sigma_{ii} \quad (21)$$

$$\delta_{\text{iso}} = \frac{1}{3} \text{Tr}(\delta) \quad (22)$$

As reference we use the values calculated for aqueous $\text{K}_3\text{Co}(\text{CN})_6$.

As seen from inspection of Table 1, the values for absolute chemical σ_{iso} shift are in good agreement with experimental and theoretical work as well as the relative shielding tensors δ_{iso} . This is especially noteworthy in case of the complex $\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_4\text{H}_6)$, which is not a typical candidate for ligand field theory. The very large Ω for this special complex compared to experimental result and other calculations given in [26] clearly demonstrates the limitation of the theory.

The form of \mathcal{H}_{HF} as well as the LF-DFT implementation allows to analyse the different contributions. As the perturbation of the ground-state wavefunction (5) depends on the magnetic field \vec{H} and its value is not needed neither for the calculation of the paramagnetic (11) nor diamagnetic part shielding tensor (17), we just can say something about contributions of different single-determinants to the unperturbed ground-state wavefunction $|\psi_0\rangle$. The $[\text{Co}(\text{CN})_6]^{3-}$ ground-state wavefunction $|\psi_0\rangle$ is in our formalism very well represented by the single-determinant with holes in $x^2 - y^2$ and z^2 and contributes with a coefficient $|c|^2 = 0.99$. Looking at the different contributions of \mathcal{H}_{HF} to σ_{ij}^p we find, that the terms involving electron-spin ($-\kappa \vec{S} + \frac{1}{7} \sum_{k=1}^n \vec{a}_k$ in (13)) bring just a very small contribution to the diagonal elements of $\leq 0.5\%$ or $\simeq 24$ ppm, respectively. For $\text{Co}(\text{acac})_3$ we find a totally different behaviour of the ground-state wavefunction $|\psi_0\rangle$, where we need at most 14 contributing single-determinants for $\sum_i |c_i|^2 \geq 0.9$. Even if the terms involving electron-spin interaction in \mathcal{H}_{HF} yields a contribution till $\simeq 200$ ppm this corresponds just to $\simeq 1\%$. The ground-state wavefunction $|\psi_0\rangle$ can be built up to ≥ 0.9 by 7 single-determinants and there is not a clearly dominating micro-state. As for the off-diagonal elements in σ_{ij}^p they get a contribution of electron-spin terms in (13) of as much as $\simeq 11\%$, but in absolute terms they are all ≤ 70 ppm. Therefore we can conclude that σ_{ij}^p is clearly dominated by the term of \mathcal{H}_{HF} stemming from the interaction of the nuclear spin with the orbital angular momentum of the electron (7). This agrees very well with previous calculations from ligand field approaches like e.g. [8] and [2] who obtained already good results without the interaction of the nuclear spin with the electron spin (8) and the so-called Fermi-contact term (9) in their Hamiltonian. This also does not contradict to ref [15] as we are here calculating the chemical shielding σ for the transition-metal atom itself.

Our calculations of the paramagnetic shielding tensors σ^p are very sensitive to geometries, what is very useful for confirming

Table 1
Calculated absolute and relative shielding tensors.

Molecule	σ^p	σ_{iso}	δ_{iso}
$\text{K}_3\text{Co}(\text{CN})_6$			
This work	$\begin{pmatrix} -6892 & 0 & 0 \\ 0 & -6892 & 0 \\ 0 & 0 & -6893 \end{pmatrix}$	-5504	
Reference ^a		-5378 to -5170	
$\text{Co}(\text{acac})_3$			
This work	$\begin{pmatrix} -18,241 & -492 & 214 \\ -493 & -17,683 & 356 \\ 214 & 356 & -21,298 \end{pmatrix}$	-17,487	11,983
Reference ^b		-17,700	12,500
$\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_4\text{H}_6)$			
This work	$\begin{pmatrix} -9961 & 986 & -3088 \\ 987 & -2013 & 101 \\ -3094 & 114 & -4113 \end{pmatrix}$	-3899	-1605
Reference ^c		-4624 to -3179	-807

^a Out of [5], calculations for $\text{K}_3\text{Co}(\text{CN})_6$ crystal, where they calculated the shift for all three crystallographically distinct sites.

^b Out of [5], cited values out of experiments.

^c Out of [26], σ_{iso} : calculated value, δ_{iso} : cited experimental value.

shielding tensors for given geometry but makes a prediction for unknown geometry more difficult.

5. Conclusions

We have shown that in the framework of LF-DFT, calculation of shielding tensors σ for ^{59}Co can be implemented according to the procedure presented above and gives good agreement. Thus, our method and algorithm is validated. Furthermore it allows us an insight to different contributions to σ . From a theoretical point of view there should be no restriction to ^{59}Co and therefore the method should work general for d-systems.

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