

The calculation of ESR parameters by density functional theory: the g - and A -tensors of Co(acacen)

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Abstract

The new DFT based ligand field (LF) model is proposed to calculate the g - and A -tensors of [Co(acacen)] that is known to be a difficult case. The results obtained are compared with the ZORA approach implemented in ADF as well as with the experimental values. The calculations are in good agreement with the experimental data and demonstrate the ability of the method to reproduce the large anisotropy typical for this type of complexes. The ligand field – density functional theory method is therefore not simply a method to calculate multiplet structure, ligand field splittings and UV–Vis transitions, but is also appropriate to compute magnetic properties.

1. Introduction

A wealth of information is encoded in the electron paramagnetic resonance (EPR) spectra of a given molecule. The EPR spectroscopy provides unique insights into the structural and electronic features of both organic and inorganic paramagnetic compounds. In organic chemistry, the technique is mostly used to get access to information about free radicals, since it provides a direct experimental measure for the distribution of the unpaired spin density. In the field of inorganic, or bio-inorganic, chemistry, the method is applied to examine the splitting of orbital and spin levels and the molecular symmetry and environment.

Consequently, it is of great interest to compute and analyze the relevant quantities (g - and A -tensors) of an EPR spectrum from first principle calculations. Quan-

tum mechanical approaches can offer a valuable support to experiment, especially when competing interpretations are possible or quantitative relationships between observable and structure are sought. The area of theoretical and computational chemistry has in the last couple of years shown an increasing interest in the calculation of magnetic coupling parameters.

The application of density functional theory (DFT) to EPR spectroscopy is relatively recent excepting the pioneering work of Daul and Weber [1] based on multiple-scattering $X\alpha$. Schreckenbach and Ziegler [2] have presented energy derivative calculations for the g -tensor with the usage of gauge including atomic orbitals (GIAO). Baerends al. as well as Bruyndonckx [3] have published results of DFT calculations for the g - and A -tensors of TiF_3 by means of second order perturbation theory [4]. Furthermore, with the recent developments to include relativistic effects in modern DFT calculations, spin–orbit (SO) coupling can be taken into account variationally using the zeroth-order regular approximation (ZORA) to the Dirac equation [5–8].

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To obtain then the g -tensor, the effect of the external homogeneous magnetic field has only to be treated with first-order perturbation theory [9,10].

In this Letter, we present the result of calculations of the g - and A -tensors components for a transition metal complex: [Co(acacen)] or N,N' -ethylenebis(acetylacetonate)cobalt(II), as obtained from two methods: (i) the ligand field – density functional theory (LFDFT) i.e., a method proposed by Atanasov et al. [11,12] which is based on a DFT multi-determinants approach, (ii) directly, by calculating the Zeeman splitting of the ground Kramers doublet obtained by using ZORA calculation and second-order perturbation theory implemented in ADF for the hyperfine interaction [9,13]. The choice of this complex was motivated by two reasons: firstly, the [Co(acacen)] complex belongs to a series of complexes with tetradentate Schiff bases which received much attention during the last decades [14,15], largely because of their ability to reversibly absorb molecular oxygen under certain conditions. Secondly, it is a planar molecule (ligands are present only on a square planar environment) so it can be expected to show a large anisotropy of the ESR parameters.

In the following sections, a description of the methodological and computational details is given, including a brief outline of the LFDFT method. We show then, that with two methods, LFDFT and ZORA, this anisotropy is nicely reproduced. However, an analysis of the various contributions to the g - and A -tensors is only possible using the LFDFT method.

2. Methods

2.1. LFDFT: a new way to calculate ESR parameters

Let us assume that we know the complex geometry from X-ray data or from a geometry optimisation. The first step consists in a spin-restricted DFT SCF calculation of the average of configuration (AOC) of the d^n configuration. For [Co(acacen)], it means distributing the 7 electrons normally present in the d -shell over the five d -orbitals by occupying each of them by 1.4 electrons. The Kohn–Sham (KS) orbitals, which are constructed using this AOC are best suited for a treatment in which, interelectronic repulsion is approximated by atomic-like Racah parameters B and C , as it is done in LF theory. The next step consists in a spin-unrestricted calculation of the energies of all Slater determinants (SD) originating from the d^n shell, i.e., 120 SDs for d^7 TM ions. These SD energies and the KS eigenvectors with dominant d -character from the AOC calculation are used in a MATLAB program to determine the one-electron 5×5 LF matrix h_{ab} as well as the Racah parameters B and C [12]. Finally, we introduce these

parameters as input for a LF program which was originally dedicated to the calculation of multiplet energies but extended here to allow us to also calculate variationally the g - and A -tensors. The implementation of these two calculations is described in the two following sections.

2.1.1. Calculation of g -tensor

Spin–orbit coupling cannot be ignored when ions or molecules contain heavy elements. The effect is not very large for 1st row transition metal (TM) elements but for the description of the g -tensor, spin–orbit coupling is essential since the neglect of this interaction would lead to an isotropic g -factor equal to 2.0023192.

The nature and origin of spin–orbit coupling have been discussed in many places [16]. Misetsich and Buch [17] have shown that the spin–orbit Hamiltonian of a molecule can be reasonably well approximated as

$$\hat{H}_{\text{so}} = \sum_{N,i} \zeta_N \vec{\ell}_{N,i} \cdot \vec{s}_i = \sum_i \vec{u}_{N,i} \cdot \vec{s}_i, \quad (1)$$

where ζ_N is the spin–orbit coupling constant of nucleus N , incorporated into the molecular operator $\vec{u}_{N,i}$ for electron i .

In order to carry out a spin–orbit calculation it is necessary to relate the resultant splitting of many electron states and also the interaction of different states through spin–orbit coupling to one-electron integrals. This can be done most conveniently in the basis of micro-states (Slater determinants) as shown in [18] for the calculation of multiplets, using Slater’s rules. Indeed the calculation of matrix elements of one- and two-electron operators between determinantal N -electron wave functions is straightforward. In the present case of spin–orbit interaction, only one-electron operators are involved. For TM complexes with light atoms such as carbon, nitrogen and oxygen, the spin–orbit coupling on the ligand can be completely neglected. The methodology we consider in the preceding section is based on LF theory, it is therefore justified to express the spin–orbit interaction of the whole d - or f -manifold by a single parameter ζ_{nl} , i.e.

$$\begin{aligned} \langle sm_s, \alpha | \hat{H}_{\text{so}} | sm'_s, b\beta \rangle \\ \approx \zeta_{nl} \langle sm_s, \ell m_\ell(a, \alpha) | \vec{l} \cdot \vec{s} | sm'_s, \ell m'_\ell(b, \beta) \rangle, \end{aligned} \quad (2)$$

where $\zeta_{nl} = \langle R_{nl} | \frac{1}{r} \frac{dV}{dr} | R_{nl} \rangle$ and $|lm\rangle$ are real spherical harmonics. In practice ζ_{nl} is evaluated either from the SO splitting obtained in ZORA or by solving the atomic Kohn–Sham equation numerically. In the second case the free ion value has to be reduced in multiplying it by the average metal population. The calculation of ζ_{nl} using LFDFT has been described in a recent publication [19].

The spin–orbit coupling constant was determined by DFT making a spin orbit calculation on the free ion

($\zeta = -598 \text{ cm}^{-1}$) and reduced further by the orbital reduction factor ($k = 0.77$, cf. Eq. (16)). The ground state Kramers doublet $|0 \pm\rangle$ is obtained by diagonalization of the full configuration interaction matrix: $\langle \text{SD}_\mu^d | \hat{h}_{\text{LF}} + \hat{g}_{\text{ER}} + \hat{h}_{\text{SO}} | \text{SD}_\nu^d \rangle$, where h_{LF} and h_{SO} have been defined previously [12] and where \hat{g}_{ER} represents the electrostatic inter-electronic repulsion [12]. The g -tensor can be calculated from the equation for the Zeeman matrix elements $\langle 0 \pm | k\hat{L}_\alpha + g_e\hat{S}_\alpha | 0 \pm \rangle$ equating them with those of the spin-hamiltonian $\langle \pm | g \cdot \vec{S}^{\text{eff}} | \pm \rangle$, i.e.

$$\begin{pmatrix} |+\rangle & |-\rangle \\ \frac{1}{2}g_{zz} & \frac{1}{2}(g_{zz} + ig_{zy}) \\ \frac{1}{2}(g_{zx} - ig_{zy}) & -\frac{1}{2}g_{yy} \end{pmatrix} \begin{pmatrix} |0+\rangle & |0-\rangle \\ \langle 0+ | k\hat{L}_\alpha + g_e\hat{S}_\alpha | 0+\rangle & \langle 0+ | k\hat{L}_\alpha + g_e\hat{S}_\alpha | 0-\rangle \\ \langle 0- | k\hat{L}_\alpha + g_e\hat{S}_\alpha | 0+\rangle & \langle 0- | k\hat{L}_\alpha + g_e\hat{S}_\alpha | 0-\rangle \end{pmatrix}, \quad (3)$$

or

$$\begin{aligned} g_{zz} &= \langle 0+ | k\hat{L}_z + g_e\hat{S}_z | 0+ \rangle - \langle 0- | k\hat{L}_z + g_e\hat{S}_z | 0- \rangle, \\ g_{xx} &= \langle 0+ | k\hat{L}_x + g_e\hat{S}_x | 0- \rangle + \langle 0- | k\hat{L}_x + g_e\hat{S}_x | 0+ \rangle, \\ g_{xy} &= i(\langle 0- | k\hat{L}_x + g_e\hat{S}_x | 0+ \rangle - \langle 0+ | k\hat{L}_x + g_e\hat{S}_x | 0- \rangle), \end{aligned} \quad (4)$$

where k is the orbital reduction factor used to scale the spin-orbit coupling constant of the free ion, $\alpha = x, y, z$ and \vec{L}_α and \vec{S}_α are the orbital and spin-angular momentum operators. For n -electrons, we have

$$\hat{L}_\alpha = \sum_{i=1}^n l_{i\alpha}, \quad (5)$$

$$\hat{S}_\alpha = \sum_{i=1}^n s_{i\alpha}. \quad (6)$$

2.1.2. Calculation of A -tensor

The ligand field description of the hyperfine interaction is already well described in the literature [20,21], but we summarize it briefly here. The interaction between the nuclear and electrons angular momenta of a many-electron system is described by the hyperfine coupling Hamiltonian

$$H_{\text{HF}} = \hat{A}_{\text{HF}} \cdot \vec{I}, \quad (7)$$

where \hat{A}_{HF} , the hyperfine coupling operator is given by Eqs. (8) and (9), summation being carried out over all electrons (see [20] for more details)

$$\vec{H}_{\text{HF}} = P \sum_{i=1}^n (\vec{l}_i + \frac{1}{\gamma} \vec{a}_i - \kappa \vec{s}_i) \cdot \vec{I} \quad (8)$$

and

$$\vec{a}_i = 4\vec{s}_i - (\vec{l}_i \cdot \vec{s}_i)\vec{l}_i - \vec{l}_i(\vec{l}_i \cdot \vec{s}_i). \quad (9)$$

The first term corresponds to the interaction of the nuclear spin with the orbital angular momentum of the electron, the second term to the interaction of the nuclear spin with the electronic spin and the last term is the Fermi contact term. P in Eq. (8) is the electron-nuclear dipolar coupling constant defined as

$$P = g_e \beta \gamma_N \hbar \langle r^{-3} \rangle_{3d}, \quad (10)$$

where γ_N is the giromagnetic ratio of the nucleus N (for Co: $\gamma_N = 0.63171 \times 10^4 \text{ G}^{-1}$) [22], β the bohr magneton and $\langle r^{-3} \rangle_{3d}$ the expectation value of the $1/r^3$ operator over the 3d wavefunction. The parameter κ is related with the Fermi hyperfine coupling constant a_F ($g_e = 2.0023$)

$$a_F = \frac{8\pi}{3} g_e \beta \gamma_N \hbar \sum_i [\rho_{i\uparrow}(0) - \rho_{i\downarrow}(0)] \quad (11)$$

as

$$\kappa = -\frac{a_F}{P}. \quad (12)$$

Direct substitution yields

$$\kappa = -\frac{8\pi}{3} \sum_i [\rho_{i\uparrow}(0) - \rho_{i\downarrow}(0)] \frac{1}{\langle r^{-3} \rangle_{3d}} \quad (13)$$

with γ_N in G^{-1} , P in cm^{-1} and $\langle r^{-1} \rangle_{3d}$ in atomic units, we have explicitly

$$P = g_e \gamma_N \times 332.5258 \times 10^{-9} \times \langle r^{-3} \rangle_{3d}. \quad (14)$$

Finally, the A -tensor can be calculated, similarly to the g -tensor, from the aforementioned ground Kramers doublet $|0 \pm\rangle$ evaluating the hyperfine matrix elements $\langle 0 \pm | A_\alpha^{\text{hf}} | 0 \pm \rangle$ as

$$\begin{aligned} A_{zz} &= \langle 0+ | A_\alpha^{\text{hf}} | 0+ \rangle - \langle 0- | A_\alpha^{\text{hf}} | 0- \rangle, \\ A_{xx} &= \langle 0+ | A_\alpha^{\text{hf}} | 0- \rangle + \langle 0- | A_\alpha^{\text{hf}} | 0+ \rangle, \\ A_{xy} &= i(\langle 0- | A_\alpha^{\text{hf}} | 0+ \rangle - \langle 0+ | A_\alpha^{\text{hf}} | 0- \rangle), \end{aligned} \quad (15)$$

where $\alpha = x, y, z$ and k is the orbital reduction factor used to scale the spin-orbit coupling constant of the free ion. k is determined by

$$k = \frac{\sum_{i=1}^{2l+1} \sum_{\mu=1}^{2l+1} c(i, \mu)^2}{2l+1} = 0.77, \quad (16)$$

where $l = 2$, i and μ are running, respectively, over the d-AO's and MO's with dominant d-character, $c(i, \mu)$ being the contribution of the i th AO to the μ th MO considered.

We now consider the numerical evaluations of P and κ which are used in the calculation of the A -tensor components.

The value of P has been calculated using TZP exponents given by the ADF data base and a numerical

integration resulting to $\langle r^{-3} \rangle_{3d} = 5.83 \text{ cm}^{-3}$ for the free ion: Co^{2+} . The corresponding value: $P = 245 \times 10^{-4} \text{ cm}^{-1}$ has been further reduced according to Eq. (16) to $P = 188 \times 10^{-4} \text{ cm}^{-1}$.

The value of α_F needed to obtain κ (Eq. (12)) is more subtle to evaluate and deserves a bit of explanation. In fact there is no Fermi interaction within d^n configuration. However, the analysis of the hyperfine structure of supposedly d -electrons clearly requires an isotropic contribution denoted here as a_F . This term has two well-known contributions: (i) the spin polarization of the closed $|ns\rangle$ shells through the unpaired electron occupying the ground Kramers-doublet and (ii) the direct admixture of $|4s\rangle$ into the ground Kramers doublet through spin-orbit coupling with the low-lying $|d_{z^2}, A_1\rangle$ excited state that is contaminated by orbital interaction with $|4s\rangle$ of Co because of the low symmetry of $[\text{Co}(\text{acacen})]$. Indeed, this mixing amounts to 4%.

The first contribution to a_F is easily obtained using the DENSF utility program of ADF to compute $\rho_{i\uparrow}(0) - \rho_{i\downarrow}(0)$ (Eq. (11)) from an all-electron spin-polarized KS-calculation of $[\text{Co}(\text{acacen})]$. The second contribution to a_F is obtained from the weight of all SD that contain d_{z^2} present in the ground Kramers doublet. The resulting parameters $a_F = -28 \times 10^{-4}$ and $P = 188 \times 10^{-4} \text{ cm}^{-1}$ lead to $\kappa = 0.147$, which was used in the calculation of the A -tensor. Table 1 summarizes all non-empirically determined parameters used in the calculation of the ESR and multiplet fine structure.

2.2. Spin-orbit ZORA approach

We use the ZORA implementation available in the ADF code to calculate g - and A -tensors in order to com-

Table 1
All non-empirically determined parameters used in the calculation of the ESR parameters and multiplet fine structure

Racah's parameters	B	$512 \pm 53 \text{ cm}^{-1}$
	C	$3118 \pm 225 \text{ cm}^{-1}$
Ligand field matrix elements	$\langle x'y' h_{LF} x'y' \rangle$	$-1071 \pm 407 \text{ cm}^{-1}$
	$\langle y'z' h_{LF} y'z' \rangle$	$6308 \pm 407 \text{ cm}^{-1}$
	$\langle z'^2 h_{LF} z'^2 \rangle$	$5052 \pm 407 \text{ cm}^{-1}$
	$\langle x'^2 - y'^2 h_{LF} x'^2 - y'^2 \rangle$	$3731 \pm 407 \text{ cm}^{-1}$
	$\langle z'^2 h_{LF} x'^2 - y'^2 \rangle$	$2771 \pm 407 \text{ cm}^{-1}$
	$\langle x'z' h_{LF} x'z' \rangle$	$-24003 \pm 407 \text{ cm}^{-1}$
Spin-orbit coupling constant	ζ	460 cm^{-1}
Orbital reduction factor	k	0.77
Electron-nuclear dipolar coupling constant	P	$188 \times 10^{-4} \text{ cm}^{-1}$
	κ	0.147

The mean square deviation between fitted and calculated (DFT) SD-energies is equal to 246 cm^{-1} .

pare the results with those from LFDFT and with experiment. This method, developed by van Lenthe et al. [9,13], uses GIAO, where the g - and A -tensors are calculated in a spin-orbit relativistic calculation using ZORA Hamiltonian with a spin restricted wavefunction.

3. Computational details

The DFT calculations were performed with the Amsterdam density functional (ADF) program package (release 2003.01) [23]. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) for exchange-correlation functionals were used. The LDA was applied with the Vosko, Wilk, and Nusair functional [24] and the GGA by using the exchange-correlation Perdew-Wang 91 functional [25]. The atoms were described by a triple- ζ Slater type orbital (STO) basis sets plus one polarization function and the frozen core (FC) approximation was used up to 3p for cobalt and up to 1s for carbon, nitrogen and oxygen for the g -tensor calculation and the LFDFT calculations. For the calculation of A -tensor, we used all electrons basis sets.

The geometry of the complex has been adopted from X-ray crystallographic data determined by Cariati et al. [26]. Since the deviation from C_{2v} symmetry is not significant we have chosen to impose this symmetry in our calculations. The coordinate system of $\text{Co}(\text{acacen})$ which by convention, has always been used to discuss this type of complexes is shown in Fig. 1. In this way the molecule belongs actually to the point group $C_{2v}(x)$, with x as the principal symmetry axis instead of the more conventional z -axis. The d -orbitals have hereby the following symmetry labels: d_{z^2} and $d_{x^2-y^2}$, a_1 ; d_{xy}, b_2 ; d_{xz}, b_1 ; d_{yz}, a_2 . In the ADF calculations another orientation has been adopted (x', y', z' : Fig. 1) with twofold axis along z . However, results have been always converted back to the traditional one (x, y, z).

4. Results and discussion

The $\text{Co}(\text{acacen})$ with a d^7 -configuration for Co^{II} has low-spin $S = 1/2$ ground state. It shows a large anisotropy of both the g - and A -tensors (Tables 3 and 4) related to the low (C_{2v}) symmetry of the Co^{2+} coordination centers. A MO-diagram comprising MO's dominated by the 3d-atomic orbitals (Fig. 2) shows the typical splitting for square planar coordination with the σ -antibonding $d_{xy}(b_2)$ -orbital, separated by about 27.4 kK from the weaker $\sigma - d_{z^2}$, the in-plane $\pi - d_{x^2-y^2}$ (both of a_1 symmetry) and the π out-of-plane yz (a_2) and xz (b_1) orbitals. The latter ones are much less separated in energy, covering a narrow range of energies (7.4 kK), as shown in Fig. 2. The d_{xz} and d_{yz} π -orbitals

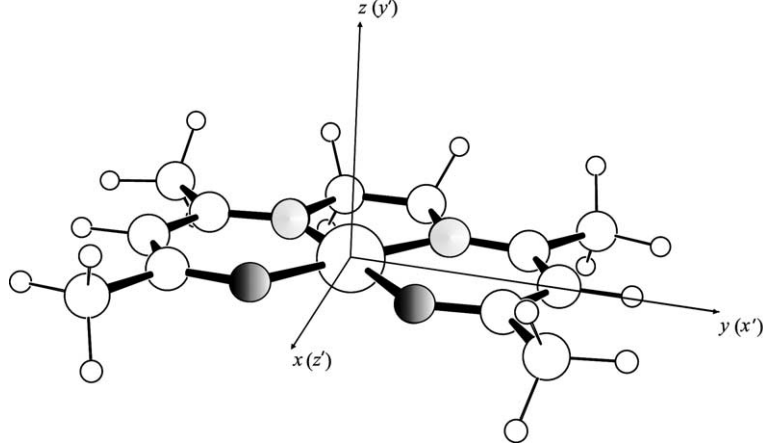


Fig. 1. The axial coordinates of the system in the discussion (x, y, z) and in the ADF calculations (x', y', z') are represented above.

which are degenerate in a square planar complex (e.g., D_{4h} symmetry) are found in [Co(acacen)] to be considerably split (7.0 kK), this being responsible for large in-plane anisotropy of the main values of the g - and A -tensors. The underlying cause of this large splitting can be understood in the context of the molecular orbital model. Restricting to the highest occupied π (a_2) (HOMO) and lowest unoccupied π^* (b_1) (LUMO) ligand orbitals, we notice that the corresponding 3d-orbitals with the same symmetry, d_{yz} (d_{xz}) become destabilized (stabilized) by the interplay of π -donation (π -back donation). The consequences of this anisotropic π -bonding effects have been accounted for in refined LF models,

such as the phase coupling concept of Ceulemans et al. [27–29], quantifying an early idea of Orgel [30]. However, quantitatively, a large number of ill defined model parameters had to be introduced in order to account for this effect. Our LFDFT results lend full support of the π -anisotropy, as reflected by the calculated LF transitions (Table 2) and the calculated g - and A -tensors (Tables 3 and 4). With 7 electrons on the closely spaced a_2 , a_1, b_1 and a_1 -orbitals we have a $|d_{yz}^1, {}^2A_2\rangle$ ground state. Mixing with excited states via spin–orbit coupling then leads to the observed anisotropic g - and A -tensors. These are given in Tables 3 and 4, where we also include results of ZORA spin–orbit calculations. Both the ZORA and the LFDFT show largest values for g_{xx} and A_{xx} . However, finer details in the g -tensor anisotropy, in particular the $g_{zz} > g_{yy}$ relationship are better reproduced by the LFDFT method. As far as the overall agreement between theoretical and experimental A -tensor components goes, both the ZORA and the LFDFT calculations are of comparable moderate quality. However, we must keep in mind that experimental values of A_{xx} , A_{yy} and A_{zz} are less accurately determined. Thus, coordination to more distant atoms in the solid seems to make important contributions [15]. However, this is beyond the scope of the present study. Finally, we should mention that models of g and A -tensors,

Table 2

Multiplet splitting energies determined by the LFDFT method using GGA functional and frozen core approximation and compared to experiment (in cm^{-1})

	LFDFT	Exp.
2A_2	0.0	–
2A_1	4665	–
2B_1	7036	4000
2A_1	10885	8000
4B_1	13021	–
4A_1	12835	–
4B_1	14694	–

Table 3

g -Tensor values of [Co(acacen)] determined by spin–orbit restricted spin–orbit ZORA calculation and the LFDFT approaches and compared to a set of experimental data

	ZORA		LFDFT	GGA	EXP [15]
	LDA	GGA	A	B	
g_{xx}	2.85	2.76	3.21	2.80	2.92/3.26
g_{yy}	1.89	1.93	1.87	1.94	1.90(\pm 0.03)
g_{zz}	1.91	1.92	1.87	2.11	2.00(\pm 0.02)
g_{iso}	2.22	2.20	2.28	2.32	

LFDFT column A corresponds to the two states model: 97% $|d_{yz}^1 d_{xy}^2, {}^2A_2\rangle + 3\% |d_{yz}^1 d_{xy}^2, {}^2A_1\rangle$, and column B to the full calculation. For the experimental data, we give a range of values because of a strong dependency upon the host lattice. g_{iso} represents the isotropic g -value, $g_{iso} = (g_{xx} + g_{yy} + g_{zz})/3$.

Table 4

A -tensor values of [Co(acacen)] determined by spin-orbit restricted spin-orbit ZORA calculation and the LFDFT approaches and compared to a set of experimental data

	ZORA		LFDFT	GGA	EXP [15]
	LDA	GGA	A	B	
A_{xx}	151	108	95	55	100/128
A_{yy}	25	28	12	14	32/40
A_{zz}	66	71	39	19	29/34

LFDFT column A corresponds to the two states model: $97\% [d_{yz}^1 d_{xy}^2, ^2A_2] + 3\% [d_{xz}^2 d_{xy}^2, ^2A_1]$, and column B to the full calculation. For the experimental data, we give a range of values because of a strong dependency upon the host lattice.

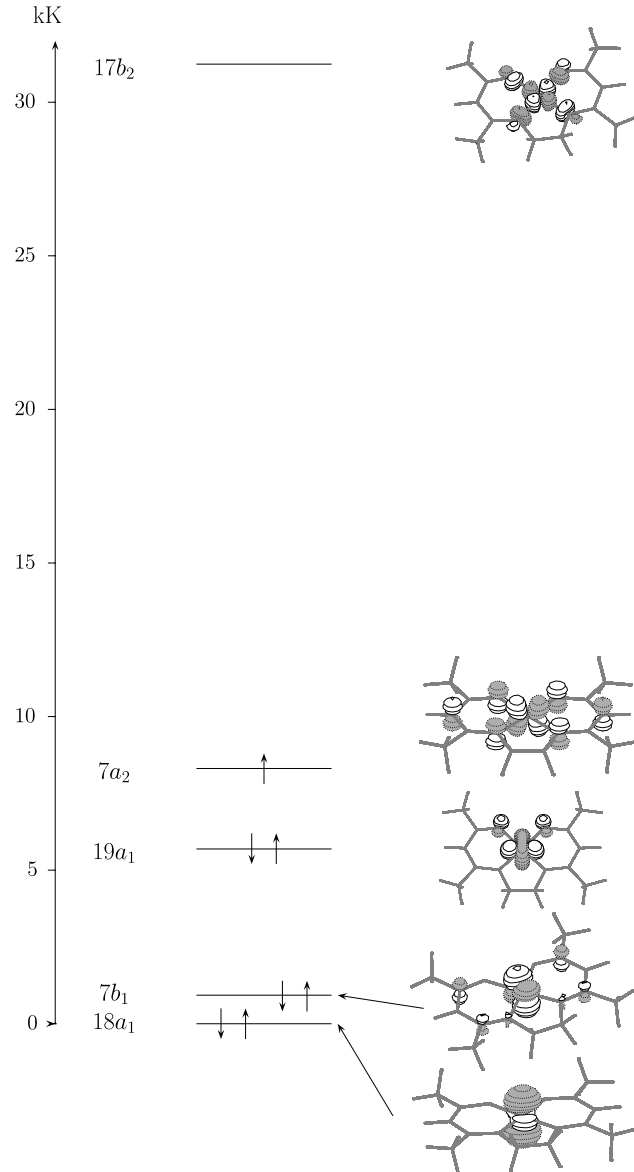


Fig. 2. MO diagram for the ground state configuration of Co(acacen) determined by DFT.

confined to one or two excited states (resulting in two-state model $|d_{yz}^1, ^2A_2\rangle - |d_{z^2}^1, ^2A_1\rangle$ [15], or three state model $|d_{yz}^1, ^2A_2\rangle - |d_{z^2}^1, ^2A_1\rangle - |d_{xz}^1, ^2B_1\rangle$ [28,29], respectively), reflect essential features of the physical ori-

gin of the anisotropy. In Tables 3 and 4 we list the results from a consideration using a two-state model. The overall features are reasonably reproduced using this simplified approach. However, our present calculation enables a more detailed description of the experimental findings, particularly the difference between g_{yy} and g_{zz} for the g -tensor, and important contributions to A_{xx} from other excited states, ignored by the two or three states models are taken into account.

5. Conclusions

In this work, we have extended our LFDFT approach with ESR fine structures, demonstrating that the model works, even in such complicated situations as the Co(acacen) complex. No doubt, the method can be refined including anisotropic covalent reduction factors and anisotropic spin-orbit coupling and inter-electronic repulsion. A practicable scheme for anisotropic spin-orbit coupling has been published [19]. However we have found that calculating all these quantities using an average-of-configuration concept, thus introducing non-empirical atomic like B , C and ζ parameters and further, a single overall parameter k -in order to account for covalent reduction is a reasonable approximation, capable of describing electronic transitions and multiplet fine structures.

References

- [1] C.A. Daul, J. Weber, *Helv. Chim. Acta* 65 (1982) 2486.
- [2] G. Schreckenbach, T. Ziegler, *J. Phys. Chem. A* 101 (1997) 3388.
- [3] R. Bruyndonckx, *Density Functional Theory as a Practical Tool to Calculate Molecular Properties: EPR and Jahn-Teller parameters*. Ph.D. Thesis, University of Fribourg, Switzerland, 1999.
- [4] P. Belanzoni, E.J. Baerends, S. van Asselt, P.B. Langewen, *J. Chem. Phys.* 99 (1995) 13094.
- [5] E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 99 (1993) 4597.
- [6] R. van Leeuwen, E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 101 (1994) 1272.
- [7] E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.* 101 (1994) 9783.
- [8] E. van Lenthe, J.G. Snijders, E.J. Baerends, *J. Chem. Phys.* 105 (1996) 6505.

- [9] E. van Lenthe, P.E.S. Wormer, A. van der Avoird, J. Chem. Phys. 107 (1997) 2488.
- [10] P. Belanzoni, E. Van Lenthe, E.J. Baerends, J. Chem. Phys. 114 (2001) 4421.
- [11] M. Atanasov, C.A. Daul, C. Rauzy, Chem. Phys. Lett. 367 (2003) 737.
- [12] M. Atanasov, C.A. Daul, C. Rauzy, Struct. Bond. 106 (2004) 97.
- [13] E. van Lenthe, A. van der Avoird, P.E.S. Wormer, J. Chem. Phys. 108 (1998) 4783.
- [14] M. Calvin, C.H. Barkelew, J. Am. Chem. Soc. 68 (1946) 2267.
- [15] C. Daul, C.W. Schlaepfer, A. von Zelewsky, Struct. Bond. 36 (1978) 128.
- [16] J.C. Slater, Quantum Theory of Atomic Structure, vol. 2, McGraw-Hill, London, 1960.
- [17] A.A. Missetich, T. Buch, J. Chem. Phys. 41 (1964) 2524.
- [18] C.A. Daul, Int. J. Quantum Chem. 52 (1994) 867.
- [19] M. Atanasov, C. Rauzy, P. Baettig, C.A. Daul, Int. J. Quantum Chem., in press.
- [20] J.S. Griffith, The Theory of Transition-Metal Ions, University Press, Cambridge, 1971.
- [21] A. Bencini, D. Gatteschi, J. Magn. Reson. 34 (1979) 653.
- [22] J.E. Wertz, J.R. Bolton, Electron Spin Resonance, Elementary Theory and Practical Applications, McGraw-Hill, New York, 1972.
- [23] G. te Velde, F.M. Bickelhaupt, E.J. Baerends, C. Fonseca Guerra, S.J.A. van Gisbergen, J.G. Snijders, T. Ziegler, J. Comput. Chem. 22 (2001) 931.
- [24] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Chem. 58 (1980) 1200.
- [25] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
- [26] F. Cariati, F. Morazzoni, C. Busetto, G. Del Piero, A. Zazzetta, J. Chem. Soc., Dalton Trans. (1976) 342.
- [27] A. Ceulemans, M. Dendooven, L.G. Vanquickenborne, Inorg. Chem. 24 (1985) 1153.
- [28] A. Ceulemans, M. Dendooven, L.G. Vanquickenborne, Inorg. Chem. 24 (1985) 1159.
- [29] A. Ceulemans, R. Debuyst, F. Dejeheh, G.S.D. King, M. Vanhecke, J. Phys. Chem. 94 (1990) 105.
- [30] L.E. Orgel, J. Chem. Soc. (A) 6 (1961) 3683.