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Importance of Direct Spin−Spin Coupling and Spin-Flip Excitations for the Zero-Field Splittings of Transition Metal Complexes: A Case Study

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Abstract: This work reports the evaluation of several theoretical approaches to the zero-field splitting (ZFS) in transition metal complexes. The experimentally well-known complex [Mn(acac)$_3$] is taken as an example. The direct spin−spin contributions to the ZFS have been calculated on the basis of density functional theory (DFT) or complete active space self-consistent field (CASSCF) wave functions and have been found to be much more important than previously assumed. The contributions of the direct term may exceed ∼1 cm^{-1} in magnitude and therefore cannot be neglected in any treatment that aims at a realistic quantitative modeling of the ZFS. In the DFT framework, two different variants to treat the spin−orbit coupling (SOC) term have been evaluated. The first approach is based on previous work by Pederson, Khanna, and Kortus, and the second is based on a "quasi-restricted" DFT treatment which is rooted in our previous work on ZFS. Both approaches provide very similar results and underestimate the SOC contribution to the ZFS by a factor of 2 or more. The SOC is represented by an accurate multicenter spin−orbit mean-field (SOMF) approximation which is compared to the popular effective DFT potential-derived SOC operator. In addition to the DFT results, direct "infinite order" ab initio calculations of the SOC contribution to the ZFS based on CASSCF wave functions, the spectroscopy-oriented configuration interaction (SORCI), and the difference-dedicated CI (DDCI) approach are reported. In general, the multireference ab initio results provide a more realistic description of the ZFS in [Mn(acac)$_3$]. The conclusions likely carry over to many other systems. This is attributed to the explicit treatment of the multiplet effects which are of dominant importance, since the calculations demonstrate that, even in the high-spin d^4 system Mn(III), the spin-flip excitations make the largest contribution to the SOC. It is demonstrated that the ab initio methods can be used even for somewhat larger molecules (the present calculations were done with more than 500 basis functions) in a reasonable time frame. Much more economical but still fairly reasonable results have been achieved with the INDO/S treatment based on CASSCF and SOC-CI wave functions.

1. Introduction

The zero-field splitting (ZFS) is typically the leading term in the spin Hamiltonian (SH) for transition metal complexes with a total ground-state spin $S > {}^1/_2$.[1−5] Its net effect is to introduce a splitting of the $2S + 1$ M_S levels (which are exactly degenerate at the level of the Born−Oppenheimer Hamiltonian), even in the absence of an external magnetic field.[4−6] Thus, an analysis and interpretation of the ZFS is imperative if the information content of the various physical methods which are sensitive to ZFS effects, such as electron paramagnetic resonance (EPR[1,7,8]), magnetic susceptibility measurements,[9] magnetic torque magnetometry,[10] magnetic circular dichroism (MCD[11]), and magnetic Mössbauer (MB) spectroscopy,[12] is to be developed. Renewed interest in ZFSs has recently arisen in the field of molecular magnetism. The ultimate goal there is to design single-molecule magnets for which is it known that a large negative, axial ZFS together with a high total ground-state spin are essential to achieve the desired magnetic characteristics.[13−15] Furthermore, ZFSs arise in magnetic interactions between remote paramagnetic centers.[16] In the EPR community, this is being used to increasing sophistication for the determination of distances.[17−20] (For recent developments and applications,

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(1) Pake, G. E.; Estle, T. L. *The Physical Principles of Electron Paramagnetic Resonance*; W.A. Benjamin Inc.: London, 1973.
(2) McGarvey, B. R. *Transition Met. Chem.* **1966**, *3*, 89.
(3) Boca, R. *Coord. Chem. Rev.* **2004**, *248*, 757.
(4) Neese, F. In *The Quantum Chemical Calculation of NMR and EPR Properties*; Kaupp, M., Bühl, M., Malkin, V., Eds.; Wiley-VCH: Heidelberg, 2004; p 541.
(5) Neese, F.; Solomon, E. I. In *Magnetoscience*−*From Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley VCH: Weinheim, 2003; Vol. IV, p 345.
(6) Neese, F.; Solomon, E. I. *Inorg. Chem.* **1998**, *37*, 6568.
(7) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*; Clarendon Press: Oxford, 1970.
(8) Atherton, N. M. *Principles of Electron Spin Resonance*, 2nd ed.; Ellis Horwood/Prentice Hall: New York, 1993.
(9) Girerd, J.-J.; Journeaux, Y. In *Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism*; Que, L., Jr., Ed.; University Science Books: Sausalito, CA, 2000; p 384.
(10) Cornia, A.; Gatteschi, D.; Sessoli, R. *Coord. Chem. Rev.* **2001**, *219*, 573.
(11) Neese, F.; Solomon, E. I. *Inorg. Chem.* **1999**, *38*, 1847.
(12) Gütlich, P.; Link, R.; Trautwein, A. *Mössbauer Spectroscopy and Transition Metal Chemistry*; Springer: Heidelberg/New York, 1978.
(13) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268.
(14) Gatteschi, D.; Sorace, L. *J. Solid State Chem.* **2001**, *159*, 253.
(15) Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054.

10.1021/ja061798a CCC: $33.50

see refs 21−26.) However, the analysis is always based on point dipole models which are certainly reasonable for large distances and well-localized spin densities but may become problematic otherwise. Consequently, the prediction of ZFSs from first physical principles is an important field of investigation. However, there has been surprisingly little activity in this field, and only in recent years have the modern electronic structure methods been adopted for the calculation of ZFSs.

It is well known that, to second order in perturbation theory, the ZFS has two contributions:[4,27] (a) a first-order term which involves the direct dipolar spin−spin interaction between pairs of electrons[28] and (b) a second-order term, arising from the spin−orbit coupling (SOC), that introduces some angular momentum into the ground state (assumed orbitally nondegenerate) and which is being picked up by the spin of a second electron.[6,27,29]

It is probably fair to state that transition metal chemistry is strongly dominated by the assumption that the second-order SOC contribution is the dominant source of the ZFS for all open-shell transition metal complexes. Hence, only a few semiempirical estimates of the spin−spin contributions have been made, all of which conclude that they are probably negligible[7,29] or at least small.[30] In 1964, Griffith wrote carefully in his groundbreaking book (ref 29, page 330): "The value of ρ in transition metal ions is uncertain, but at least it is probably not greater than 0.1 cm^{-1} in the ground terms of divalent or trivalent ions of the first transition series" (ρ is proportional to the spin−spin coupling energies). It appears that this estimate has ever since been taken for granted and was used as the main reason for neglecting the direct spin−spin coupling in the treatment of ZFSs of transition metal complexes. One important conclusion of the present work is that this assumption needs to be carefully reconsidered and that the first-order contributions may, in many cases, be much larger than previously assumed.

The SOC contribution to the ZFS is automatically obtained if all M_S multiplets are calculated in the presence of SOC. However, in a perturbative framework, the treatment of the SOC term is surprisingly difficult because the SOC mixes states of different multiplicity. This has been clearly recognized since the early days of ligand-field theory.[29] However, apparently, the first general second-order formulation of the ZFS tensor in standard **SDS** form has been derived in our previous work.[6] It has also been pointed out[4−6] that the ZFS and the **g**-tensor cannot be related to a common tensor $\mathbf{\Lambda}$ as is commonplace in many texts on ligand-field theory.[3,31,32] Finally, several sophisticated studies of SOC contributions to the ZFS by McGarvey and co-workers[2,33] and Solomon and co-workers[34,35] are noted which have given important insights into the geometric and electronic origins of the ZFS in transition metal complexes.

In the ab initio framework, calculations of ZFSs have a relatively long history. It is not attempted here to review the considerable body of work that has been done (e.g., see refs 36−53). Owing to the possibility of an explicit representation of each M_S member of a given spatial multiplet with total spin S, configuration interaction (CI) methods have been used rather extensively to calculate zero-field splittings for atoms and small molecules with high sophistication. For larger molecules, rigorous multireference CI (MRCI) methods[54] are more difficult to apply, and consequently, related studies are rather scarce. Vahtras and co-workers have provided a concise description of a multiconfigurational self-consistent field (MCSCF) method for the prediction of ZFSs and have applied it with success to several small to medium sized organic molecules.[45,50,55−57] Applications to transition metal complexes have apparently not been reported. Rather successful studies along these lines on transition metal complexes have also been reported by Ribbing and co-workers.[47,48,58] In these works, MRCI as well as complete active space SCF (CASSCF) calculations together with second-order many-body perturbation theory (CASPT2) has been used to arrive at good predictions of the SOC contribution to the ZFS. DFT approaches to ZFS are even more scarce. As far as multiplet splittings in atoms are concerned, some studies using relativistic two-component DFT approaches which include the SOC have been reported.[59] A DFT-based perturbation theory

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(16) Berliner, L. J.; Eaton, S. S.; Eaton, G. R. *Distance Measurements in Biological Systems by EPR*; Kluwer Academic/Plenum Publishers: New York, 2000; Vol. 19.
(17) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *12*, 173.
(18) Eaton, G. R.; Eaton, S. S. *Acc. Chem. Res.* **1988**, *21*, 107.
(19) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1988**, *83*, 29.
(20) Bertrand, P.; More, C.; Guigliarelli, B.; Fournel, A.; Bennett, B.; Howes, B. *J. Am. Chem. Soc.* **1994**, *116*, 3078.
(21) Zanker, P. P.; Jeschke, G.; Goldfarb, D. *J. Chem. Phys.* **2005**, *122*, 024515.
(22) Denysenkov, V. P.; Prisner, T. F.; Stubbe, J.; Bennati, M. *Appl. Magn. Reson.* **2005**, *29*, 375.
(23) Hertel, M. M.; Denysenkov, V. P.; Bennati, M.; Prisner, T. F. *Magn. Reson. Chem.* **2005**, *43*, S248.
(24) Bennati, M.; Prisner, T. F. *Rep. Prog. Phys.* **2005**, *68*, 411.
(25) Schiemann, O.; Piton, N.; Mu, Y. G.; Stock, G.; Engels, J. W.; Prisner, T. F. *J Am. Chem. Soc.* **2004**, *126*, 5722.
(26) Biglino, D.; Schmidt, P. P.; Reijerse, E. J.; Lubitz, W. *Phys. Chem. Chem. Phys.* **2006**, *8*, 58.
(27) Harriman, J. E. *Theoretical Foundations of Electron Spin Resonance*; Academic Press: New York, 1978.
(28) McWeeny, R.; Mizuno, Y. *Proc. R. Soc. (London)* **1961**, *A259*, 554.
(29) Griffith, J. S. *The Theory of Transition Metal Ions*; Cambridge University Press: Cambridge, 1964.
(30) Vrjamasu, V. V.; Bominaar, E. L.; Meyer, J.; Münck, E. *Inorg. Chem.* **2002**, *41*, 6358.
(31) Bencini, A.; Benelli, C.; Gateschi, D. *Coord. Chem. Rev.* **1984**, *60*, 131.
(32) Benchini, A.; Gatteschi, D. *Transition Met. Chem.* **1979**, *8*, 1.
(33) McGarvey, B. R. *J. Chem. Phys.* **1964**, *41*, 3743.
(34) Deaton, J. C.; Gebhard, M. S.; Solomon, E. I. *Inorg. Chem.* **1989**, *28*, 877.
(35) Gebhard, M. S.; Deaton, J. C.; Koch, S. A.; Millar, M.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 2217.
(36) Hess, B. A.; Buenker, R. J.; Marian, C. M.; Peyerimhoff, S. D. *Chem. Phys.* **1982**, *71*, 79.
(37) Hess, B. A.; Marian, C. M.; Peyerimhoff, S. D. In *Modern Electronic Structure Theory*; Yarkony, D., Ed.; World Scientific Publishing Co.: Singapore, 1995.
(38) Hess, B. A.; Marian, C. M.; Wahlgren, U.; Gropen, O. *Chem. Phys. Lett.* **1996**, *251*, 365.
(39) Bomfleur, B.; Sironi, M.; Raimondi, M.; Voitländer, J. *J. Chem. Phys.* **2000**, *112*, 1066.
(40) Boorstein, S. A.; Gouterman, M. *J. Chem. Phys.* **1963**, *39*, 2443.
(41) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Chem. Phys.* **1992**, *96*, 10768.
(42) Koseki, S.; Gordon, M. S.; Schmidt, M. W.; Matsunaga, N. *J. Phys. Chem.* **1995**, *99*, 12764.
(43) Koseki, S.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **1998**, *102*, 10430.
(44) Kutzelnigg, W. *Einführung in die Theoretische Chemie*, Band 2; VCH: Weinheim, 1994.
(45) Loboda, O.; Minaev, B.; Vahtras, O.; Schimmelpfennig, B.; Agren, H.; Ruud, K.; Jonsson, D. *Chem. Phys.* **2003**, *286*, 127.
(46) Pritchard, R. P.; Kern, C. W.; Zamani-Khamiri, O.; Hameka, H. *J. Chem. Phys.* **1972**, *56*, 5744.
(47) Ribbing, C.; Odelius, M.; Laaksonen, A.; Kowaleski, J. *Int. J. Quantum Chem. Symp. Ser.* **1990**, *24*, 295.
(48) Ribbing, C.; Pierloot, K.; Ceulemans, A. *Inorg. Chem.* **1998**, *37*, 5227.
(49) Surjan, P. R.; Nemeth, K.; Bennati, M.; Grupp, A.; Mehring, M. *Chem. Phys. Lett.* **1996**, *251*, 115.
(50) Vahtras, O.; Loboda, O.; Minaev, B.; Agren, H.; Ruud, K. *Chem. Phys.* **2002**, *279*, 133.
(51) Zamani-Khamiri, O.; Hameka, H. *J. Chem. Phys.* **1971**, *61*, 1708.
(52) Yarkony, D. R. *Int. Rev. Phys. Chem.* **1992**, *11*, 195.
(53) Jensen, J. O.; Yarkony, D. R. *Chem. Phys. Lett.* **1987**, *141*, 391.
(54) Ganyushin, D.; Neese, F. *J. Chem. Phys.* **2006**, in press.
(55) Loboda, O.; Tunell, I.; Minaev, B.; Ågren, H. *Chem. Phys.* **2005**, *312*, 299.
(56) Minaev, B. F.; Khomenko, E. M.; Bilan, E. A.; Yashchuk, L. B. *Opt. Spectrosc.* **2005**, *98*, 209.
(57) Minaev, B.; Yaschuk, L.; Kukueva, V. *Spectrochim. Acta A* **2005**, *61*, 1105.
(58) Ribbing, C.; Odelius, M. *Mol. Phys.* **1993**, *78*, 1259.

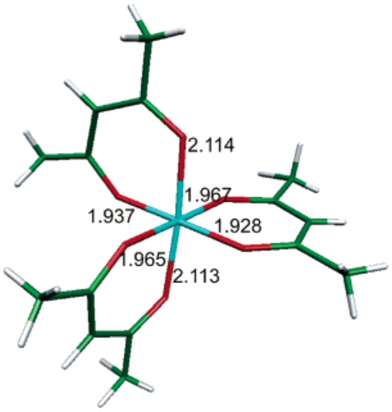

Figure 1. Structure of the [Mn(acac)$_3$] molecule used in the present study. Metal ligand bond distances are given in angstroms.

of the SOC contribution to the ZFS has been suggested by Pederson and Khanna[60] and has been applied with surprisingly high success by Kortus, Pederson, and co-workers (e.g., ref 61). While the results obtained for very large and extensively spin-coupled systems have been impressive, a validation study on mononuclear transition metal complexes is required and presently underway in an collaborative effort between the groups of Kortus, Ruiz, and the present author. The spin−spin coupling contribution to the ZFS was apparently first suggested by Petrenko et al.,[62] who adopted the general theory of McWeeny and Mizuno[28] on various second-order density matrices to the case of a single Kohn−Sham determinant and applied it to the CH$_2$ molecule.

The present work has the following purposes: (1) to provide a description of a quasi-restricted DFT method for the calculation of the SOC contribution to the ZFS which has been previously used with reasonable success; (2) to implement and evaluate a general method for the calculation of the spin−spin coupling contribution to the ZFS using an approach closely related to that pursued by Petrenko et al.;[28] (3) to compare the DFT results with those obtained via ab initio methods which include both static and dynamic correlation contributions and to demonstrate that such methods are readily applicable to medium-sized transition metal complexes; and (4) to expand on earlier semiempirical work on the ZFS at the intermediate neglect of the differential overlap/spectroscopic parametrization (INDO/S) level,[6] which is readily applied to very large molecules.

As a test case, the well-known [Mn(acac)$_3$] complex was chosen since it is well studied and has been used and will likely be widely used in the future for method comparisons.

2. Materials and Methods

All calculations were performed with a development version of the ORCA program system[63] to which the functionality described in this paper was added. The structure of [Mn(acac)$_3$] used in the calculations is shown in Figure 1. All calculations were performed with the TZVP basis set,[64] which leads to a total of 558 basis functions. As described below, CASSCF calculations with four electrons in the five Mn 3d-based molecular orbitals (MOs) (CAS(4,5)), difference-dedicated configuration interaction (DDCI2),[65] and spectroscopy-oriented CI (SORCI)[66] on top of the CAS(4,5) reference states were carried out. In the individually selecting calculations, the selection threshold T_{sel} was 10^{-6} Eh, and the prediagonalization threshold T_{pre} was 10^{-4}. In the SORCI calculations, the natural orbital truncation threshold was set to 10^{-4} (see ref 66 for a detailed description of these thresholds). In the calculations, the orbitals were determined for the average of 5 $S = 2$ and 35 $S = 1$ roots, and the same number of roots was determined in the DDCI2 and SORCI calculations (SA-CASSCF(4,5)). Semiempirical INDO/S calculations were performed using the same SA-CASSCF-(4,5) procedure.

In addition, DFT calculations of the ZFS were carried out using the qausi-restricted theory outlined below as well as the method of Pederson and Khanna,[60] which was also implemented in the ORCA program. Since the method is, at the present stage of development, only valid for non-hybrid functionals, these calculations were carried out with the BP86 functional.[67,68] As expected, other functionals which are based on the generalized gradient approximation (GGA) yield very similar results and are therefore not reported. The SOC operator used was the recently described efficient implementation[69] of the SOMF concept.[38,70] The two-electron spin−spin coupling integrals were not approximated, and new code for their generation was incorporated into the ORCA program.

3. Results and Analysis

3.1. Theory. General Perturbation Theory of the ZFS. The first complete-to-second-order analytic form of the SOC contribution to the ZFS tensor for an orbitally nondegenerate electronic ground state in the standard **SDS** form has been given previously in terms of general *N*-electron wave functions of definite spin multiplicity. The following equations were derived for the elements of the **D**-tensor:[6]

$$D_{kl}^{\mathrm{SOC}-(0)} = -\frac{1}{S^2}\sum_{b(S_b=S)}\Delta_b^{-1}\langle 0SS|\sum_i h_k^{\mathrm{SO}}(i)s_{i,z}|bSS\rangle \times \langle bSS|\sum_i h_l^{\mathrm{SO}}(i)s_{i,z}|0SS\rangle \quad (1)$$

$$D_{kl}^{\mathrm{SOC}-(-1)} = -\frac{1}{S(2S-1)}\sum_{b(S_b=S-1)}\Delta_b^{-1} \times \langle 0SS|\sum_i h_k^{\mathrm{SO}}(i)s_{i,+1}|bS-1S-1\rangle \times \langle bS-1S-1|\sum_i h_l^{\mathrm{SO}}(i)s_{i,-1}|0SS\rangle \quad (2)$$

$$D_{kl}^{\mathrm{SOC}-(+1)} = -\frac{1}{(S+1)(2S+1)}\sum_{b(S_b=S+1)}\Delta_b^{-1} \times \langle 0SS|\sum_i h_k^{\mathrm{SO}}(i)s_{i,-1}|bS+1S+1\rangle \times \langle bS+1S+1|\sum_i h_l^{\mathrm{SO}}(i)s_{i,+1}|0SS\rangle \quad (3)$$

where $\Delta_b = E_b - E_0$ is the energy difference between multiplet "*b*" and the ground-state multiplet in the absence of SOC. To

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(59) Mayer, M.; Krüger, S.; Rösch, N. *J. Chem. Phys.* **2001**, *115*, 4411.
(60) Pederson, M. R.; Khanna, S. N. *Phys. Rev. B* **1999**, *60*, 9566.
(61) Kortus, J. *Phys. Rev. B* **2002**, *66*, 092403.
(62) Petrenko, T. T.; Petrenko, T. L.; Bratus, V. Y. *J. Phys: Condens. Matter* **2002**, *14*, 12433.
(63) Neese, F. *ORCA—an ab initio, density functional and semiempirical program package*, Version 2.4.45; Max-Planck institute for bioinorganic chemistry: Mülheim an der Ruhr, Germany, 2005.
(64) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.
(65) Miralles, J.; Castell, O.; Caballol, R.; Malrieu, J. P. *Chem. Phys. Lett.* **1993**, *172*, 33.
(66) Neese, F. *J. Chem. Phys.* **2003**, *119*, 9428.
(67) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
(68) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(69) Neese, F. *J. Chem. Phys.* **2005**, *122*, 034107/1.
(70) Berning, A.; Schweizer, M.; Werner, H. J.; Knowles, P. J.; Palmieri, P. *Mol. Phys.* **2000**, *98*, 1823.

arrive at the complete ZFS tensor, the direct electron−electron spin−spin coupling which arises in first-order in perturbation theory must be added:

$$D_{kl}^{(\mathrm{SS})} = \frac{g_{\mathrm{e}}^2}{4}\frac{\alpha^2}{S(2S-1)}\left\langle 0SS\left|\sum_i\sum_{j\neq i}\frac{r_{ij}^2\,\delta_{kl} - 3(\mathbf{r}_{ij})_k(\mathbf{r}_{ij})_l}{r_{ij}^5}\times \{2s_{iz}s_{jz} - s_{ix}s_{jx} - s_{iy}s_{jy}\}\right|0SS\right\rangle \quad (4)$$

In eqs 1−4, α is the fine-structure constant (∼1/137 in atomic units), g_{e} the free-electron g-value ($g_{\mathrm{e}} = 2.002319...$), and $|aSM\rangle$ is a member of an, in general, infinite set of N-electron states with energies E_a. All quantum numbers that are necessary to unambiguously identify the given state, except for the total spin S and the projection quantum number M, have been included in the compound index "a" ($a = 0$ for the electron ground-state multiplet). The operators $s_{i,m}$ are the components of the spin-vector operator of the ith electron with spherical components $m = 0,\pm1$, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the distance vector between electrons i and j, with r_{ij} being its magnitude. It is apparent from eqs 1−4 that the calculation of ZFSs is very challenging, since (a) the spin−spin and the spin−orbit operators are complicated spin-dependent operators, (b) the SOC contribution arises in second order in perturbation theory, thus requiring the response of the ground state to the SOC perturbation to be determined, and (c) the SOC requires the treatment of excited states of different spin multiplicity than the ground state, which is an added complication compared to the case of the **g**-tensor.[6]

Treatment of Spin−Orbit Coupling. For convenience, an effective reduced one-electron SOC operator, $h_\mu^{\mathrm{SO}}(i)$, with three spatial components $\mu = x,y,z$ is assumed. Previously, the parameterization by Koseki et al.[41−43] was used in the ORCA program, where

$$h_k^{\mathrm{SO}}(i) = \sum_A \xi(r_{iA})l_k^A(i) \quad (5)$$

where $l_k^A(i)$ is the kth component of the orbital angular momentum operator relative to center A, and $\xi(r_{iA})$ is a suitable radial operator, i.e.,

$$\xi(r_{iA}) = \frac{\alpha^2}{2}\frac{Z_A^{\mathrm{eff}}}{|\mathbf{r}_i - \mathbf{R}_A|^3} \quad (6)$$

where Z_A^{eff} is a semiempirical nuclear charge for atom A at position $\mathbf{R}_A$. However, while this operator gives reasonable results for 2p- and 3d-elements, in the present work the operator $\hat{h}_k^{\mathrm{SO}}$ is treated by an accurate mean-field (SOMF) approximation to the full Breit−Pauli SOC operator. The SOMF approach has been developed by Hess et al.[38] It is widely used within Schimmelpfennig's AMFI program in a number of quantum chemistry codes.[71] However, it introduces two further approximations: (a) the neglect of multicenter SOC terms and (b) the use of atomic self-consistent field orbitals and their averaged occupation numbers in place of the molecular charge densities. Both approximations were introduced in the interest of computational efficiency, and their justification is through the successful molecular test calculations.[45,72−82]

An efficient implementation of the SOMF concept was discussed, which is based on the following formulation of the effective one-electron operator:[69,70]

$$\langle\varphi_\mu|h_k^{\mathrm{SO}}|\varphi_\nu\rangle = \langle\varphi_\mu|\hat{h}_k^{\mathrm{1el-SO}}|\varphi_\nu\rangle + \sum_{\kappa\tau}P_{\kappa\tau}\Big[(\varphi_\mu\varphi_\nu|\hat{g}_k^{\mathrm{SO}}|\varphi_\kappa\varphi_\tau) - \frac{3}{2}(\varphi_\mu\varphi_\kappa|\hat{g}_k^{\mathrm{SO}}|\varphi_\tau\varphi_\nu) - \frac{3}{2}(\varphi_\tau\varphi_\nu|\hat{g}_k^{\mathrm{SO}}|\varphi_\mu\varphi_\kappa)\Big] \quad (7)$$

with the one- and two-electron SOC operators,

$$\hat{h}_k^{\mathrm{1el-SO}}(\mathbf{r}_i) = \frac{\alpha^2}{2}\sum_i\sum_A Z_A r_{iA}^{-3}\,\hat{\mathbf{l}}_{iA;k} \quad (8)$$

$$\hat{g}_k^{\mathrm{SO}}(\mathbf{r}_i,\mathbf{r}_j) = -\frac{\alpha^2}{2}\hat{\mathbf{l}}_{ij;k}\,r_{ij}^{-3} \quad (9)$$

Here, $\mathbf{P}$ is the total charge density matrix, Z_A is the nuclear charge of atom A, r_{iA} is the position of electron i relative to nucleus A, and $\hat{\mathbf{l}}_{iA;k}$ is the kth component of the angular momentum of the ith electron relative to atom A. Likewise, $\hat{\mathbf{l}}_{ij;k}$ is the kth component of the angular momentum of electron i relative to electron j. The one-electron term of the SOMF approximation (the first term in eq 7) is treated exactly. The two-electron part of the SOMF Hamiltonian features a Coulomb term (the first term in the summation in eq 7), which is efficiently and accurately represented by the resolution of the identity (RI) approximation,[69] while the much smaller exchange terms (the last two terms in eq 7) are sufficiently well treated within a one-center approximation. This is referred to as the RI-SOMF(1X) operator.[69] It should be noted that, in the SOMF approach, the spin−same orbit and spin−other orbit contributions as well as exchange effects are all treated to a good approximation. This is not the case for the widely used SOC operators, which are derived from the local DFT potential, since they do not consider the important spin−other orbit contributions[74] and introduce an exchange part of the wrong sign.[69]

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(71) Schimmelpfennig, B. *AMFI − an atomic mean field integral program*; University of Stockholm: Stockholm, Sweden, 1996.

(72) Gagliardi, L.; Schimmelpfennig, B.; Maron, L.; Wahlgren, U.; Willets, A. *Chem. Phys. Lett.* **2001**, *344*, 207.

(73) Kaupp, M.; Reviakine, R.; Malkina, O. L.; Arbuznikov, A.; Schimmelpfennig, B.; Malkin, V. *J. Comput. Chem.* **2001**, *23*, 794.

(74) Malkina, O. L.; Schimmelpfennig, B.; Kaupp, M.; Hess, B. A.; Chandra, P.; Wahlgren, U.; Malkin, V. G. *Chem. Phys. Lett.* **1998**, *296*, 93.

(75) Launilla, O.; Schimmelpfennig, B.; Fagerli, H.; Gropen, O.; Taklif, A. G.; Wahlgren, U. *J. Mol. Spectrosc.* **1997**, *186*, 131.

(76) Malmqvist, P. Å.; Roos, B. O.; Schimmelpfennig, B. *Chem. Phys. Lett.* **2002**, *357*, 230.

(77) Rubio-Pons, O.; Loboda, O.; Minaev, B.; Schimmelpfennig, B.; Vahtras, O.; Ågren, H. *Mol. Phys.* **2003**, *101*, 2103.

(78) Ruud, K.; Schimmelpfennig, B.; Ågren, H. *Chem. Phys. Lett.* **1999**, *310*, 215.

(79) Schimmelpfennig, B.; Maron, L.; Wahlgren, U.; Teichteil, C.; Fagerli, H.; Gropen, O. *Chem. Phys. Lett.* **1998**, *286*, 261.

(80) Schimmelpfennig, B.; Maron, L.; Wahlgren, U.; Teichteil, C.; Fagerli, H.; Gropen, O. *Chem. Phys. Lett.* **1998**, *286*, 267.

(81) Vahtras, O.; Engström, M.; Schimmelpfennig, B. *Chem. Phys. Lett.* **2002**, *351*, 424.

(82) Wahlgren, U.; Sjøvoll, M.; Fagerli, H.; Gropen, O.; Schimmelpfennig, B. *Theor. Chem. Acc.* **1997**, *97*, 324.

A “Quasi-restricted” DFT Approach to the ZFS. To apply the general theory (eqs 1−4) within a DFT framework, a simple approach was developed which was used with some success in previous studies.[83,84] Below, the motivation for the working equations is provided. A key aspect of the ZFS in the formulation of eqs 1−4 is the presence of N-electron spin eigenfunctions. Genuine excited-state wave functions are generally not available in DFT treatments, which are valid only for the electronic ground state. However, it is well known that, in the absence of nonlocal exchange potentials, the magnetic linear response equations reduce to sum-over-orbital pairs equations which crudely resemble sum-over-states equations. However, even though these two approaches are radically different in their philosophy, there is a connection between them. Pragmatic sum-over-states-like arguments have been used for a long time in NMR computations with DFT where effective shifts have been incorporated in the denominators of the sum-over-orbital pair equations in order to compensate for a lack of agreement between DFT orbital energy differences and excitation energies.[85]

Consequently, the first task is to construct a spin eigenfunction for the ground state from the spin-unrestricted DFT solution which does not have this property. It would, of course, be possible to start the development from an open-shell spin-restricted DFT treatment, but this was avoided since the major effects of spin polarization should be retained in the treatment. In the following, it is assumed that the system under investigation is well described by a spin-polarized treatment, which means that the spin-polarized determinant is close to the open-shell spin-restricted solution and $\langle \hat{S}^2\rangle \approx S(S+1)$. This assumption does not hold for spin-coupled systems where broken-symmetry solutions exist. In constructing a spin eigenfunction from a spin-polarized DFT calculation, use was made of the fact that the spin-unrestricted natural orbitals (obtained from the diagonalization of the density matrix) fall into three categories: (1) Orbitals with occupation number exactly equal to 1.0. These $2M_S$ MOs are taken as SOMOs (ψ_p,ψ_q), and they are all occupied by a single spin-up electron. (2) MOs with occupation number close to 2.0. These $(N_{el} - 2M_S)/2$ MOs (ψ_i,ψ_j) are taken as doubly occupied MOs (DOMOs). (3) Weakly occupied MOs with occupation numbers close to 0. These orbitals (ψ_a,ψ_b) span the virtual space. The ground-state determinant is then simply the one constructed from the DOMO and SOMO sets. Its energy is slightly higher than that of the spin-polarized determinant, but it is a spin eigenfunction with total spin $S = M_S$ and is very close to the open-shell spin-restricted ground-state DFT solution. Therefore, this set of orbitals is referred to as “quasi-restricted orbitals” (QROs). To canonicalize the invariant subspaces, the following procedure was chosen: the DOMOs diagonalize the spin-down Fock operator $\hat{F}^{\beta}$, the virtual MOs diagonalize the spin-up Fock operator $\hat{F}^{\alpha}$, and the open-shell orbitals diagonalize their average, $(\hat{F}^{\alpha} + \hat{F}^{\beta})/2$. This choice was made since excitations from the DOMO to the SOMO subspace involve a spin-down electron and excitations from the SOMO to the virtual space involve a spin-up electron. Therefore, a compromise choice was made for the open-shell orbitals. However, while each DOMO is associated with a unique orbital energy, ϵ_i^{β} and ϵ_a^{α}, each open-shell orbital is assigned two orbital energies, $\epsilon_p^{\alpha} \equiv \langle\psi_p|\hat{F}^{\alpha}|\psi_p\rangle$ and $\epsilon_p^{\beta} \equiv \langle\psi_p|\hat{F}^{\beta}|\psi_p\rangle$. Small off-diagonal Fock matrix elements between the sub-blocks are ignored in the present treatment.

Next, excited determinants of definite total spin are constructed by performing excitations between the invariant orbital subspaces. Four types of excitations must be considered: (1) DOMO → SOMO excitations $\psi_i \rightarrow \psi_p$, with energy $\Delta E(\psi_i \rightarrow \psi_p) = \epsilon_p^{\beta} - \epsilon_i^{\beta}$. The objective for replacing excitation energies with orbital energy differences is that, in DFT, the orbital energy difference is a well-defined zeroth-order approximation to the excitation energies. This no longer holds if exact exchange is present, and consequently, the present treatment applies only to non-hybrid functionals. The $\psi_i \rightarrow \psi_p$ excitation leads to a single determinant of the same spin S as the ground state. (2) SOMO → VIRTUAL excitations $\psi_p \rightarrow \psi_a$, with energy $\Delta E(\psi_p \rightarrow \psi_a) = \epsilon_a^{\alpha} - \epsilon_p^{\alpha}$. These excitations lead to single determinants of the same total spin as the ground state. (3) SOMO → SOMO excitations $\psi_p \rightarrow \psi_q$, with energy $\Delta E(\psi_p \rightarrow \psi_q) = \epsilon_q^{\beta} - \epsilon_p^{\alpha}$. These excitations lead to single determinants with total spin $S' = S - 1$. (4) DOMO → VIRTUAL excitations $\psi_i \rightarrow \psi_a$. While there are several possible spin couplings of various total spins S', the only ones that are kept are the most important excitations, in which the spin of the excited electron is flipped such that the excited determinant is a spin eigenfunction with spin $S' = S + 1$, and consequently the excitation energy $\Delta E(\psi_i \rightarrow \psi_a) = \epsilon_a^{\alpha} - \epsilon_i^{\beta}$. By this construction, the major part of the spin polarization is still contained in the orbital energies, while the treatment is based on spin eigenfunctions, as desired. After inserting the four classes of excitations in eqs 1−3, one obtains the SOC contribution to the ZFS as

$$
\begin{aligned}
D_{kl}^{(\mathrm{SOC})} = & -\frac{1}{4S^2}\sum_{i,p}\frac{\langle\psi_i|h_k^{\mathrm{SOC}}|\psi_p\rangle\,\langle\psi_p|h_l^{\mathrm{SOC}}|\psi_i\rangle}{\epsilon_p^{\beta}-\epsilon_i^{\beta}} \\
& -\frac{1}{4S^2}\sum_{p,a}\frac{\langle\psi_p|h_k^{\mathrm{SOC}}|\psi_a\rangle\,\langle\psi_a|h_l^{\mathrm{SOC}}|\psi_p\rangle}{\epsilon_a^{\alpha}-\epsilon_p^{\alpha}} \\
& +\frac{1}{4}\frac{1}{S(2S-1)}\sum_{p\neq q}\frac{\langle\psi_p|h_k^{\mathrm{SOC}}|\psi_q\rangle\,\langle\psi_q|h_l^{\mathrm{SOC}}|\psi_p\rangle}{\epsilon_q^{\beta}-\epsilon_p^{\alpha}} \\
& +\frac{1}{2}\frac{1}{(S+1)(2S+1)}\sum_{i,a}\frac{\langle\psi_i|h_k^{\mathrm{SOC}}|\psi_a\rangle\,\langle\psi_a|h_l^{\mathrm{SOC}}|\psi_i\rangle}{\epsilon_a^{\alpha}-\epsilon_i^{\beta}}
\end{aligned}
\qquad (10)
$$

It is interesting to compare this equation to the model presented by Pederson and Khanna, which was derived from a completely different line of reasoning.[60] In the present notation, their treatment, which holds for the case of a spin-unrestricted ground-state determinant and in the absence of exact exchange, reads

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(83) Ray, K.; Begum, A.; Weyhermüller, T.; Piligkos, S.; van Slageren, J.; Neese, F.; Wieghardt, K. *J. Am. Chem. Soc.* **2005**, *127*, 4403.
(84) Schöneboom, J.; Neese, F.; Thiel, W. *J. Am. Chem. Soc.* **2005**, *127*, 5840.
(85) Malkin, V. G.; Malkina, O. L.; Casida, M. E.; Salahub, D. R. *J. Am. Chem. Soc.* **1994**, *116*, 5898.

$$
\begin{aligned}
D_{kl}^{(\mathrm{SOC})} = &-\frac{1}{4S^2}\sum_{i_\beta,a_\beta}\frac{\langle\psi_i^\beta|h_k^{\mathrm{SOC}}|\psi_a^\beta\rangle\,\langle\psi_a^\beta|h_l^{\mathrm{SOC}}|\psi_i^\beta\rangle}{\epsilon_a^\beta-\epsilon_i^\beta}\\
&-\frac{1}{4S^2}\sum_{i_\alpha,a_\alpha}\frac{\langle\psi_i^\alpha|h_k^{\mathrm{SOC}}|\psi_a^\alpha\rangle\,\langle\psi_a^\alpha|h_l^{\mathrm{SOC}}|\psi_i^\alpha\rangle}{\epsilon_a^\alpha-\epsilon_i^\alpha}\\
&+\frac{1}{4S^2}\sum_{i_\alpha,a_\beta}\frac{\langle\psi_i^\alpha|h_k^{\mathrm{SOC}}|\psi_a^\beta\rangle\,\langle\psi_a^\beta|h_l^{\mathrm{SOC}}|\psi_i^\alpha\rangle}{\epsilon_a^\beta-\epsilon_i^\alpha}\\
&+\frac{1}{4S^2}\sum_{i_\beta,a_\alpha}\frac{\langle\psi_i^\alpha|h_k^{\mathrm{SOC}}|\psi_a^\alpha\rangle\,\langle\psi_a^\alpha|h_l^{\mathrm{SOC}}|\psi_i^\alpha\rangle}{\epsilon_a^\alpha-\epsilon_i^\beta}
\end{aligned}
\qquad (11)
$$

Comparison of eqs 10 and 11 shows that the basic ingredients of the two methods are essentially identical. Apart from using quasi-restricted versus spin-unrestricted MOs, the main difference concerns the prefactors in front of the spin-flip contributions. As will be shown below, the two formulations provide essentially identical results if the same SOC operator is used. (It was verified in the course of this work that **g**-tensor calculations with the quasi-restricted method provide results very similar to those of the spin-unrestricted linear response treatment, provided that the spin contamination of the spin-unrestricted determinant is small.)

Spin−Spin Contributions to the ZFS. For the spin−spin part of the ZFS, McWeeny and Mizuno have shown that, in the case that $|0SS\rangle$ is approximated by a single determinant, the second-order spin density matrix is readily factorized into one-electron contributions[28] and eq 4 can be rewritten as

$$
D_{kl}^{(\mathrm{SS})} = \frac{g_e^2}{4}\frac{\alpha^2}{S(2S-1)}\sum_{\mu\nu}\sum_{\kappa\tau}\{P_{\mu\nu}^{\alpha-\beta}P_{\kappa\tau}^{\alpha-\beta}-P_{\mu\kappa}^{\alpha-\beta}P_{\nu\tau}^{\alpha-\beta}\}\times \langle\mu\nu|r_{12}^{-5}\{3r_{12,k}r_{12,l}-\delta_{kl}r_{12}^2\}|\kappa\tau\rangle \qquad (12)
$$

Here, $\mathbf{P}^{\alpha-\beta} = \mathbf{P}^\alpha - \mathbf{P}^\beta$ is the spin density matrix in the atomic orbital basis, with $P_{\mu\nu}^\sigma = \sum_{k_\sigma} c_{\mu k}^\sigma c_{\nu k}^\sigma$ and $\mathbf{c}^\sigma$ being the MO coefficient matrix of spin σ. This equation was implemented without further approximations. The two-electron spin−spin integrals appearing in eq 12 look complicated on first glance but are readily evaluated over Gaussian functions using the same techniques as those established for the electron−electron repulsion integrals.[86] The same approximation has been previously suggested by Petrenko et al. and shown to work well for CH_2.[62] In terms of rigorous DFT theory, the treatment of two-electron observables is problematic since, in principle, only the diagonal elements of the first-order density matrix are known. If one evaluates the spin−spin contribution by eq 12, it is tacitly assumed that the second-order density matrix of the non-interacting reference state and the exact second-order density coincide, which is certainly not the case. It is unknown what kind of error is introduced by this approximation. Its main justification may remain for some time to come that, at least to the best of the author's knowledge, it is without practical alternative at the present level of sophistication of DFT.

Direct ab Initio Calculation of the ZFS. In several instances, it is advisable to step outside the domain of perturbation theory. In particular, in the cases of near orbital degeneracy or very large SOC, the perturbation treatment breaks down and an infinite order treatment is imperative. In the present work, this was done in the ab initio domain in the framework of quasi-degenerate perturbation theory. The calculations consist basically of the following steps: (1) Calculation of state-averaged CASSCF wave functions for a given set of target states. In the case of transition metal complexes, these are the various multiplets which arise from the given d^N configuration of the metal. Either these wave functions are used directly as $|aSS\rangle$, or an approximate dynamic correlation treatment on top of the SA-CASSCF calculation will be performed. In the present calculations, the dynamic correlation methods were taken as DDCI2[65] and SORCI,[66] which also heavily leans on the concepts of DDCI. In any case, the first step produces a set of many-electron multiconfigurational and multideterminantal orthogonal and non-interacting (through the Hamiltonian) spin eigenfunctions $|aSS\rangle$. (2) In the next step, the set of states $|aSS\rangle$ is enhanced to include all M_S components for each state, to give the larger set $|aSM\rangle$. (3) Inside the $|aSM\rangle$ set, the Born−Oppenheimer plus SOC operators are simultaneously diagonalized to yield N-electron "relativistic" states and their energies (quasi-degenerate perturbation theory). The matrix to be diagonalized is

$$
\langle aSM|\hat{H}_{\mathrm{BO}}+\hat{H}_{\mathrm{SOC}}|bS'M'\rangle = \delta_{ab}\delta_{SS'}\delta_{MM'}E_a^{(\mathrm{S})} + \langle aSM|\hat{H}_{\mathrm{SOC}}|bS'M'\rangle \qquad (13)
$$

The Wigner−Eckart theorem can be used to write the SOC matrix elements in the following form, in which the M,M' dependence is factored out:[6]

$$
\left\langle aSM\left|\sum_{m=0,\pm1}(-1)^m\sum_i \hat{h}_{-m}^{\mathrm{SOC}}(i)\hat{s}_m(i)\right|bS'M'\right\rangle = \begin{pmatrix} S' & 1 & S \\ M' & m & M\end{pmatrix} Y_{IJ}^{SS'}(-m) \qquad (14)
$$

Here, $\left(\begin{smallmatrix} S' & 1 & S \\ M' & \mathrm{m} & M\end{smallmatrix}\right)$ is a Clebsch−Gordon coefficient, and the reduced matrix elements $Y_{IJ}^{SS'}(-m)$ were explained previously.[5,6] Their calculation involves considerable effort, since each state $|aSS\rangle$ is a linear combination of a potentially large set of N-electron configuration state functions (CSFs). An efficient methodology was implemented in the ORCA program, and the technical details of the implementation are described elsewhere.[54] Nevertheless, from the lowest $2S + 1$ eigenvalues of the matrix in eq 13, the SOC contribution to the ZFS is readily extracted (vide infra).

The rigorous spin−spin contribution to the ZFS has not yet been implemented into the ORCA program. However, an interesting possibility is to use eq 12 also in the context of correlated ab initio methods. In this case, the SCF spin density matrix is simply replaced by the correlated spin density matrix. This is then termed the "mean-field" approximation to the spin−spin coupling. As will be developed in detail elsewhere, it may be regarded as the first term in a cumulant expansion of the second-order density. In preliminary calculations, it was found that this approximation is quite accurate (similarly to the mean-field approximation to the SOC). The full implementation of the CASSCF-level spin−spin coupling has been previously

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(86) Helgaker, T.; Taylor, P. R. In *Modern Electronic Structure Theory*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; p 725.

Table 1. Comparison of Contributions to the Calculated Zero-Field Splitting between the Quasi-restricted DFT Method and the Perderson−Khanna−Kortus Approach, as Well as Comparison of the Results Obtained with the SOMF and V^{eff} SOC Operators[a]

method		*D*	*E*
BP86-QR-SOMF[b]	$\alpha \rightarrow \alpha$	−0.42	−0.03
	$\beta \rightarrow \beta$	−0.03	−0.00
	$\alpha \rightarrow \beta$	−1.07	−0.10
	$\beta \rightarrow \alpha$	+0.00	+0.00
	spin−spin	−0.99	−0.17
	total	−2.51	−0.316
BP86-PKK-SOMF[c]	$\alpha \rightarrow \alpha$	−0.32	−0.04
	$\beta \rightarrow \beta$	+0.02	−0.01
	$\alpha \rightarrow \beta$	−1.29	−0.14
	$\beta \rightarrow \alpha$	−0.01	+0.01
	spin−spin	−0.99	−0.18
	total	−2.59	−0.36
BP86-PKK-V^{eff} [c]	$\alpha \rightarrow \alpha$	−0.45	−0.05
	$\beta \rightarrow \beta$	+0.01	−0.01
	$\alpha \rightarrow \beta$	−1.69	−0.19
	$\beta \rightarrow \alpha$	+0.01	+0.01
	spin−spin	−0.99	−0.18
	total	−3.12	−0.42
expt		−4.52	−0.25

[a] BP86/TZVP, all numbers are in cm^{-1}. [b] With quasi-restricted method (eq 10). [c] With Pederson−Khanna−Kortus method (eq 11).

reported by Vahtras and co-workers[50] and is also in progress in this laboratory.

3.2 Results for [Mn(acac)$_3$]. In this section, the various methods discussed above are tested on a popular and well-studied complex, namely [Mn(acac)$_3$], a high-spin d^4 system with tetragonal distortion. Its ZFS has been measured to high precision by Barra et al. and by Krzystek et al.,[87,88] who arrived at values of $D = -4.52$ cm^{-1} and $E/D = 0.05$ cm^{-1}. Krzystek et al. also provided a concise ligand-field explanation of the origin of the ZFS: due to the Jahn−Teller active d^4 ion, the complex distorts in the direction of tetragonal elongation, which leaves the d$_{z^2}$-based MO empty, and according to the standard ligand-field analysis, this leads to a negative *D* value.[87,88] (For further ligand-field arguments, see ref 5.) The main intention of the present work is to compare the different computational methods discussed above for this well-understood case. The DFT-optimized structure of the complex used in all calculations clearly shows the tetragonal distortion. It was kindly provided by Prof. Kortus and is shown in Figure 1. Coordinates are available in the Supporting Information.

Comparison of DFT Methods. The comparison of the results of the two different approximations to the SOC part of the ZFS in second-order perturbation theory-based DFT calculations is shown in Table 1. It is evident that the two approximations produce similar predictions for the ZFS. The small differences come partly from the prefactor in front of the individual terms in eqs 10 and 11, and partly from the different approximations made in setting up the working equations. However, the experience gained so far indicates that both methods tend to give similar predictions.

The DFT calculations predict the correct sign and an overall reasonable rhombicity. However, the absolute value of *D* is considerably underestimated. As expected, the SOC part contains two significant contributions: The first contribution comes from the $\alpha \rightarrow \alpha$ excitations. These correspond primarily to the spin-allowed (quintet → quintet) ligand-field excitations and have usually been solely held responsible for the ZFS. However, compared to the final value, they contribute only ~ -0.4 cm^{-1} (∼16%), which renders arguments based on spin-allowed ligand-field excitations alone in high-spin d^4 systems unreliable. As anticipated, a second and even larger SOC contribution arises from the $\alpha \rightarrow \beta$ (quintet → triplet) excitations. These excitations contribute ∼40−50% of the final *D* value. Perhaps the most surprising number in Table 1 is the large contribution of the direct spin−spin coupling term. It contributes as much as −1 cm^{-1} to the final *D* value and, therefore, significantly improves the agreement with the experimental values. The final predicted *D* is then still underestimated, but since all terms have been treated with a minimum number of approximations (SOC and spin−spin integrals), it is believed that this number properly reflects the intrinsic accuracy of the DFT-based procedures for the prediction of ZFSs. It is possible that hybrid DFT procedures, once properly implemented, give slightly better predictions. However, it is considered to be unlikely that they resolve the remaining disagreement with experiment.

To provide a fair comparison to other DFT implementations, in particular to the program of Pederson, Khanna, and Kortus (PKK), where the DFT ZFS methodology was first derived and implemented, the results of calculations with the PKK method for the treatment of the SOC term and the effective potential DFT method for the treatment of the SOC operator were compared. As is evident from Table 1, the results of these latter computations agree somewhat better with the experimental values than the ones with the SOMF operator. However, this apparent improvement is treacherous, since the V^{eff} treatment of the SOC operator intrinsically overestimates SOC matrix elements.[69] Thus, the apparently better ZFS values result from a certain degree of error cancellation in the DFT calculations.

Comparison of ab Initio Results. All ab initio calculations reported in this work are based on the smallest reasonable complete active space self-consistent field (CASSCF) treatment in which four active electrons occupy the five metal d-based orbitals. In the calculations, the 5 possible quintet states as well as 35 triplet states were calculated and included in the “infinite-order” SOC calculation. Up to 100 singlet states were also included but provided negligible contributions to the *D* and *E* values (<0.01 cm^{-1}). Thus, the set of quintet and triplet states provides a converged set of ligand-field excited states which are presumed to dominate the SOC contribution to the ZFS in transition metal complexes. Since the diagonalization of the SOC matrix introduces some higher order spin-Hamiltonian terms into the final energies, it is not possible to present the results in terms of a **D**-tensor in the same way as in perturbation theoretical treatments. Instead, one can use the closed form solutions of the spin-Hamiltonian problem for $S = 2$ provided by Hendrich and Debrunner.[89] The eigenfunctions and eigenvalues are

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(87) Krzystek, J.; Yeagle, G. J.; Park, J.-H.; Britt, R. D.; Meisel, M. W.; Brunel, L.-C.; Telser, J. *Inorg. Chem.* **2003**, *42*, 4610.

(88) Barra, A. L.; Gatteschi, D.; Sessoli, R.; Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Uytterhoeven, M. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2329.

(89) Hendrich, M. P.; Debrunner, P. G. *Biophys. J.* **1989**, *56*, 489.

$$|2^s\rangle = a^+(|+2\rangle + |-2\rangle)/2^{1/2} + a^-|0\rangle \qquad E_{2s} = 2\sqrt{D^2 + 3E^2} \tag{15}$$

$$|2^a\rangle = (|+2\rangle - |-2\rangle)/2^{1/2} \qquad E_{2a} = 2D \tag{16}$$

$$|1^s\rangle = (|+1\rangle + |-1\rangle)/2^{1/2} \qquad E_{1s} = -D + 3E \tag{17}$$

$$|1^a\rangle = (|+1\rangle - |-1\rangle)/2^{1/2} \qquad E_{1a} = -D - 3E \tag{18}$$

$$|0'\rangle = a^-(|+2\rangle + |-2\rangle)/2^{1/2} - a^+|0\rangle \qquad E_{0'} = -2\sqrt{D^2 + 3E^2} \tag{19}$$

where

$$a^{\pm} = \frac{1}{4}\sqrt{1 \pm D/\sqrt{D^2 + 3E^2}}$$

Thus, given the eigenvalues from the diagonalization of the SOC-CI matrix, D and E can determined as

$$D = \pm\frac{1}{4}\sqrt{\Delta^2 - \frac{4}{3}\delta^2} \tag{20}$$

$$E = \frac{\delta}{6} \tag{21}$$

with $\Delta = |E_0 - E_{2s}|$ and $\delta = |E_{1s} - E_{1a}|$. The drawback of this procedure is that higher order terms are included in some average way into the values of D and E, which is generally not satisfactory. However, in the case of [Mn(acac)$_3$], the higher order spin Hamiltonian terms account for splittings on the order of ~0.1 cm,[87,88] which is negligible with respect to the remaining errors of the calculations.

Judging from Table 2, the SOC contributions to the ZFS predicted by the ab initio methods are considerably larger than those predicted by the DFT methods and bring the computed D value closer to the experimental value. The effects of dynamic correlation brought in by the SORCI and DDCI2 calculations are significant and further increase the ZFS over its CASSCF value. If additivity of triplet and quintet contributions is assumed (this should be a good approximation since perturbation theory is valid for [Mn(acac)$_3$] due to the lack of near-degeneracy effects), then the CASSCF results indicate that ~38% of the D value (-1.38 cm^{-1}) comes from the quintets and 62% (-2.28 cm^{-1}) from the triplets, again confirming that these contributions dominate over the quintet contributions. Comparing to the DFT numbers, it becomes evident that both contributions are underestimated by a factor of 2−3 in the DFT treatments. Thus, neither type of excitation is solely responsible for the underestimation of the ZFS by DFT methods.

However, there is a caveat in the ab initio numbers insofar as they do not contain any spin−spin contribution. To do this rigorously is presently not possible, since the spin−spin tensor alone has a different orientation than the complete **D**-tensor, and consequently, one cannot simply add the calculated spin−spin value (-1.65 cm^{-1} at the CASSCF(4,5) level in the mean-field approximation) to the D value deduced from the spin−orbit CI calculation. The most consistent procedure would be to introduce the spin−spin coupling at the same time as the spin−orbit coupling into the CI procedure. Alternatively, one could try to deduce a complete **D**-tensor from the spin−orbit CI procedure and combine it with the mean-field spin−spin tensor. Both alternatives are presently being tested. Taking the ~−1 cm^{-1} spin−spin contribution from the DFT calculation as a rough guide, it is likely that, after including the direct spin−spin terms, the final D values from the ab initio procedures will turn out to slightly overestimate the magnitude of the D value in [Mn(acac)$_3$] but probably not nearly as much as the DFT methods underestimate them. In this case, the CASSCF value would turn out to be the best. This is largely parallel to what was observed in calculations on atoms and diatomic molecules.[54]

Table 2. Results of ab Initio Calculations of the ZFS Parameters for [Mn(acac)$_3$]^a

method		D	E
CASSCF(4,5)	SOC ($S = 1 + S = 2$)	−3.67	−0.36
SORCI(4,5)	SOC ($S = 1 + S = 2$)	−4.13	−0.44
DDCI2(4,5)	SOC ($S = 1 + S = 2$)	−4.21	−0.44

^{a} The TZVP basis set and the SOMF operator were used in all calculations.

Semiempirical Calculations. While the ab initio results are still quite manageable for the size of molecule treated in this work, it may be desirable to use a related approach based on an explicit treatment of the transition metal multiplets but with a lower computational cost. The ORCA program was therefore enhanced by the capability to perform CASSCF and spin−orbit CI calculations based on semiempirical methods. The favorite choice of semiempirical method for transition metal spectroscopy is Zerner's INDO/S method, since it has proven to give fairly good results for the optical[90−95] and magnetic[6,96] spectra of open-shell transition metal ions. In the present work, the standard parametrization in the ORCA program has been adopted without any change. Based on a CASSCF(4,5) treatment and using the same 5 quintet and 35 triplet roots, the INDO/S method predicts a SOC contribution to the D value of -4.68 cm^{-1} and $E/D = 0.13$. Thus, compared to the ab initio results, the INDO/S method slightly overestimates the D value and gives a somewhat exaggerated rhombicity. The results are nevertheless in fairly pleasing agreement, given that these calculations are about 3−4 orders of magnitude faster than the corresponding ab initio or DFT calculations while being not inferior to the latter.

Excitation Energies. Krzystek et al.[87] have remeasured and assigned the absorption spectrum of [Mn(acac)$_3$] in their ligand-field analysis of the D value. Using ligand-field calculations, they assigned the three bands observed at 9520, 17 900, and 21 500 cm^{-1} to the $^5A_{1g}$, $^5B_{2g}$, and ^5E_g spin-allowed ligand-field transitions arising from the expected $^5B_{1g}$ ground state of a tetragonally elongated distorted octahedral ligand field. The symmetry was idealized to axial, despite the fact that $E/D \approx 0.05$, which therefore introduces a slight approximation. After adjustment of several ligand-field parameters, the D value was

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(90) Zerner, M. C.; Loew, G. H.; Kirchner, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589.
(91) Anderson, W. P.; Edwards, W. D.; Zerner, M. C. *Inorg. Chem.* **1986**, *25*, 272.
(92) Zerner, M. C. In *Metal−Ligand Interactions: from Atoms, to Clusters, to Surfaces*; Salahub, D. R., Russo, N., Eds.; Kluwer Academic Publishers: Amsterdam, 1992; p 101.
(93) Zerner, M. C. In *Metal Ligand Interactions*; Russo, N., Salahub, D. R., Eds.; Kluwer Academic: Amsterdam, 1996; p 493.
(94) Zerner, M. C. In *Reviews in Computational Chemistry, Vol. 2*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: Heidelberg, 1990; p 315.
(95) Manne, R.; Zerner, M. C. *Int. J. Quantum Chem. Symp.* **1986**, *19*, 165.
(96) Neese, F. *Int. J. Quantum Chem.* **2001**, *83*, 104.

Table 3. Transition Energies (in cm^{-1}) for Some Ligand-Field Excited States Calculated by the Various Quantum Chemical Methods Used in This Study

	SA-CASSCF	SORCI	DDCI2	QRO-BP86	INDO/S	exp[a]
$^5E_g \rightarrow {}^5E_g$	6690	7040	6950	7903	7670	9520
$^5E_g \rightarrow {}^5T_{2g}$	16310	18310	18120	23540	20730	17900
	17650	19770	19510	23560	22010	21500
	18060	20570	20210	26330	22710	21500
$^5E_g \rightarrow {}^3T_{1g}$	13690	11190	11810	11960	5570	
	13930	11340	12080	13511	5930	
	14800	12250	13130	14100	6830	

[a] Experimental values are quoted from ref 87.

very well reproduced. However, the spin−spin coupling was not included in the analysis, and according to the present results, the good agreement of the ligand-field calculations may therefore be somewhat fortuitous.

Below the parent, O_h symmetry labels were kept since the structure used was of C_1 symmetry, and therefore an assignment to D_{4h} terms would have been ambiguous. The ligand-field transition energies are important since they enter the denominators of the perturbation treatment and are, of course, equally important in determining the amount of state mixing upon diagonalization of the SOC-CI matrix. In addition to the quintet → quintet excitations, the first low-symmetry split $^3T_{1g}$ ($e_g \rightarrow t_{2g}$ de-excitation) ligand-field excited state is listed since it makes a major contribution to the D value and serves as a guide for the position of the spin-flip excitations relative to the quintets.

It is evident from Table 3 that the ab initio methods provide a fairly consistent set of excitation energies which agree well with the experimental findings. The deviations from experiment are only 1000−2000 cm^{-1}. Note that the position of the first ligand-field excited state, while being low in energy (as expected for an "intra-E_g" transition), is not important for the D value since it has an almost vanishing SOC interaction with the $^5B_{1g}$ ground state. All other states listed contribute strongly to the D value. However, they still do not dominate the D value, as many of the other triplet excited ligand-field states also have large SOC matrix elements with the ground state. The INDO/S calculations lead to good agreement with the ab initio results for the quintets but significantly underestimate the transition energies (~6000 cm^{-1}) to the triplets. This is likely the cause of the exaggerated SOC contribution to D in this method. The behavior of the DFT results is somewhat surprising in that the denominators of the QRO calculation agree well with the ab initio results for the triplets but less so for the quintets. In any case, the denominators are certainly of acceptable quality, given the approximations that were made, and support the underlying idea of the QRO-based ZFS method. Since the DFT calculations also give somewhat larger T-state splittings upon symmetry lowering, which, if anything, should *increase* the calculated ZFS, a substantial part of the deviation between the ab initio and the DFT results must also arise from the SOC matrix elements in the numerator.

4. Conclusions

To the best of the author's knowledge, the present work provides the first complete implementation of the spin−spin and spin−orbit parts of the ZFS in a DFT framework. While the DFT results are qualitatively reasonable, much work remains to be done before DFT becomes an accurate tool in the prediction of ZFSs in transition metal complexes. Consequently, several efficient ab initio methods for the calculations of the ZFSs were implemented and were shown to be substantially more accurate than DFT for the prediction of ZFSs. Already at the state-averaged CASSCF (SA-CASSCF) level with only the metal d-orbitals in the active space, a level of theory which is readily extended to larger molecules, the results are surprisingly good. However, upon recovering at least differential dynamic correlation as in the SORCI and DDCI2 procedures, significant changes in the computed ZFSs were observed. In our opinion, the successful prediction of the ZFS requires a careful treatment of the low-lying multiplets of the transition metal ions, and in this respect, it is believed that multideterminantal, multiconfigurational ab initio methods have presently more to offer than DFT procedures since they readily give access to an explicit representation of all members of all multiplets. This is particularly true for the spin-flip excitations which lead to lower total spin than that of the ground state and frequently provide the dominant contributions to the ZFS. Indeed, it was shown here that even the simple semiempirical INDO/S method is capable of giving reasonable predictions of the SOC contributions to the ZFS if it is combined with CASSCF and SOC-CI techniques. Since such calculations are computationally very cheap, it is anticipated that similar calculations have a considerable potential for studies on large molecules − at least for obtaining an initial evaluation of the behavior of the system.

A third finding of the present work is the important role of the direct spin−spin coupling contributions to the ZFS. While the mean-field method used in this paper is certainly associated with some uncertainties, it appears evident that the direct spin−spin contributions are much larger than previously assumed and need to be taken into account if a realistic modeling of the ZFS in transition metal complexes is to be achieved. This is particularly true if the second-order SOC contributions are not exceedingly large, as is often the case. The SOC contributions become certainly dominant if there are very low-lying multiplets. This situation has recently been met in studies on high-valent $(FeO)^{2+}$ sites[84,97] as well as transition metal dithiolenes of iron and cobalt.[83] However, there are many situations in which this is not the case. For example, the ZFSs of Fe(III), Mn(II), and Cr(III) complexes are typically $|D| \leq 1-2$ cm^{-1}, and in this case the spin−spin terms should not be neglected. In retrospect, the important role of direct spin−spin coupling probably should have been anticipated, since spin−spin coupling contributions have been calculated previously to be up to ~1 cm^{-1} for small molecules and organic molecules.[36,37,39,40,45,49−51,53,77,81,98−101] In our opinion, there is no a priori electronic structure reason why these contributions should be an order of magnitude smaller in transition metal complexes. The unpaired electrons reside in relatively compact d-orbitals, which means that the average electron−electron distance is rather short. Apart from that, the spin−spin part is, like the SOC contribution to the ZFS, zero for cubic and higher symmetries. Thus, geometric distortions should be expected to induce significant spin−spin contributions in a similar way as they induce significant SOC contributions to the ZFS. It is considered unlikely that the error in the computed numbers is as large as an order of magnitude. Thus, even if the calculated direct spin−spin couplings in this work

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(97) Neese, F. *J. Inorg. Biochem.* **2006**, *100*, 716−726.

would turn out to be too high by a factor of 2−3, the conclusion about their importance would still remain.

It should be noted that, concerning the SOC part, calculations similar to the ones reported in this paper have been performed previously. In particular, highly sophisticated studies on small molecules were reported by the Bonn group,[36−38,102,103] by Gordon, Fedorov, and co-workers[104−108] and by Vathras, Minaev, and co-workers.[45,50,55−57,77] Some applications to larger molecules have been reported[47,48,58] by means of the RASSI program in the MOLCAS package, which also allows SOC calculations.[76] However, in this case, the many electron states are, in general, individual CASSCF wave functions rather than fully correlated states. The diagonal energies can be replaced by more accurate CASPT2 values, which, together with the treatment of the SOC on the basis of individual CASSCF states, appears to provide good results. From a methodological point of view, we believe that the DDCI2 and SORCI approaches have the advantages that (a) the SOC matrix elements are treated using the entire (partially) correlated wave function rather than only the CASSCF reference wave function, (b) the reference coefficients are “relaxed” in the field of dominant perturbing configurations rather than being held fixed at their CASSCF values, and (c) the “infinite-order” treatment of the perturbing CSFs avoids any intruder state problem which may occasionally complicate the application of the CASPT2 method. The obvious drawback is that neither the DDCI2 nor the SORCI approach is rigorously size-consistent. This may potentially deteriorate the results for larger molecules. However, both methods are only moderately size-inconsistent. While we do regard this disadvantage as significant and hope to solve it in revised versions of these methods, the results assembled over the past three years do not indicate grave size-inconsistency problems in DDCI2 or SORCI, which is in line with the conjectures of Malrieu and co-workers.[65,109−111] Furthermore, the calculated excitation energies in this work compare well with the experimentally deduced transition energies.

The present work was performed on an isolated example, and a larger test set needs to be studied in order to arrive at a fair assessment of the relative merits of the different approaches. The results of this study, however, have been encouraging and demonstrate the important roles of spin-flip excitations and direct spin−spin coupling for the ZFSs of transition metal complexes. Further work along these lines is in progress.

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Supporting Information Available: Coordinates of [Mn(acac)$_3$] used in the calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(98) Davidson, E. R.; Ellenbogen, J. C.; Langhoff, S. R. *J. Chem. Phys.* **1980**, *73*, 865.
(99) Hameka, H. *J. Chem. Phys.* **1959**, *31*, 315.
(100) Langhoff, S. R. *J. Chem. Phys.* **1974**, *61*, 1708.
(101) Takeda, R.; Mitsuo, S.; Yamanaka, S.; Yamaguchi, K. *Polyhedron* **2005**, *24*, 2238.
(102) Hess, B. A.; Marian, C. M. In *Computational Molecular Spectroscopy*; Jensen, P., Bunker, P. R., Eds.; John Wiley & Sons: New York, 2000; p 169ff.
(103) Marian, C. M. In *Reviews in Computational Chemistry, Vol 17*; Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2001.
(104) Fedorov, D. G.; Gordon, M. S. *J. Chem. Phys.* **1999**, *112*, 5611.
(105) Fedorov, D. G.; Gordon, M. S. *J. Chem. Phys.* **2000**, *112*, 5611.
(106) Fedorov, D. G.; Finley, J. P. *Phys. Rev. A* **2001**, *6404*, 4.
(107) Fedorov, D. G.; Koseki, S.; Schmidt, M. W.; Gordon, M. S. *Int. Rev. Phys. Chem.* **2003**, *22*, 551.
(108) Koseki, S.; Fedorov, D. G.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2001**, *105*, 8262.
(109) Cabrero, J.; Caballol, R.; Malrieu, J. P. *Mol. Phys.* **2002**, *100*, 919.
(110) Cabrero, J.; Calzado, C. J.; Maynau, D.; Caballol, R.; Malrieu, J. P. *J. Phys. Chem. A* **2002**, *106*, 8146.
(111) Garcia, V. M.; Castell, O.; Caballol, R.; Malrieu, J. P. *Chem. Phys. Lett.* **1995**, *238*, 222.