

Ab Initio and Coupled-Perturbed Density Functional Theory Estimation of Zero-Field Splittings in Mn^{II} Transition Metal Complexes

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The paper presents a method comparison for the prediction of zero-field splitting (ZFS) parameters in a series of Mn^{II} coordination complexes. The test set consists of Mn^{II} complexes that are experimentally well-characterized by X-ray diffraction and high-field electron paramagnetic resonance. Their ZFS parameters have been calculated using density functional theory (DFT) as well as complete active space self-consistent field (CASSCF) methods. It is shown that the recently introduced coupled-perturbed spin-orbit coupling (CP-SOC) approach [Neese, *F. J. Chem. Phys.* 2007, 127, 164112] together with hybrid-DFT functionals leads to a slope of the correlation line (plot of experimental vs calculated D values) that is essentially unity provided that the direct spin-spin interaction is properly included in the treatment. This is different from our previous DFT study on the same series of complexes where a severe overestimation of the D parameter has been found [Zein, S.; Duboc, C.; Lubitz, W.; Neese, F. *Inorg. Chem.* 2008, 47, 134]. CASSCF methods have been used to evaluate the ZFS in an “ab initio ligand-field” type treatment. The study demonstrates that a substantial part of the relevant physics is lost in such a treatment since only excitations within the manganese d-manifold are accounted for. Thus, a severe underestimation of the D parameter has been found. Because the CASSCF calculations in combination with quasidegenerate perturbation theory treats the SOC to all orders, we have nevertheless verified that second-order perturbation theory is an adequate approximation in the case of the high-spin d⁵ configuration.

Introduction

In the spin Hamiltonian (SH) formalism,¹ the zero-field splitting (ZFS, \mathbf{D} -) tensor describes the splitting of the magnetic sublevels of an orbitally nondegenerate state with total spin $S > 1/2$ in the absence of a magnetic field.^{2–5} The ZFS arises from the direct electron-electron magnetic dipole spin-spin (SS) interaction between unpaired electrons together with the spin-orbit coupling (SOC) of the ground state with electronically excited states.^{4,6–8} Accurate quantum chemical calculations of the ZFS parameters are of primary importance for interpreting a wide variety of magnetic data.^{5,9}

In quantum chemistry, the ZFS has only recently received detailed attention.^{10–15} From a fundamental point of view, the calculation of \mathbf{D} -matrix elements on the basis of multireference ab initio methods is perhaps the most satisfying approach since all magnetic sublevels can be explicitly considered in such a treatment. Numerous publications have shown that highly accurate predictions of ZFS parameters can be obtained.^{16–19} Density functional theory (DFT)-based calculations of ZFS parameters are, of course, more attractive from a computational point of view. In this case, the calculation of the \mathbf{D} -matrix proceeds by studying the linear response of the $M_S = S$ determinant with respect to an SS or spin-orbit perturbation.^{20,21} The general second-order perturbation theory of the ZFS tensor in terms of many-electron states has been known for quite a while.^{22,23} It is, however, unsuitable to be directly applied in the context of DFT. Straightforward arguments have been brought forward in the DFT context by Pederson and Khanna.¹⁴

The perturbational, Pederson and Khanna (SOC-PK), approach applied to mononuclear transition metal complexes typically leads to an underestimation by a factor of ~ 2 .⁶ This behavior can be partly corrected by accounting for the SS coupling.⁶ Mn^{II} coordination compounds are an exception to this general trend since a systematic overestimation of the ZFS was observed in a recent calibration study.¹⁰ It was concluded that this is probably inherent to the PK formula where the prefactors of different excitation classes that enter the perturbation sums are identical. However, both the general treatment^{22,23} and a recent theoretical study demonstrate that this should not be the case.^{10,21} In ref 21, a coupled-perturbed (CP) SOC approach was proposed where the prefactors of the SOC terms were corrected and the linear response equations for a SOC perturbation were derived and solved.²¹ Following these developments, Hartree-Fock (HF) exchange can be properly included in this method for the prediction of ZFSs. This opens the door for the application of hybrid functionals. An alternative route to treat the HF exchange is to proceed to localized HF methods as has been previously described by Reviakine et al.,²⁴ CP-SOC-based test calculations of the ZFS in diatomics led to a slope of the correlation line close to unity and with a standard error below 10%. This is to be compared to a slope of close to 0.5 obtained by other DFT approaches.^{24,21} However, this CP-SOC method has not yet been systematically tested in transition metal applications.

Thus, the aim of this paper is to evaluate the performance of the CP-SOC approach to the ZFS for the series of Mn^{II} complexes that have previously been studied.^{11,12} This allows for an unambiguous comparison between different methods to treat the SOC contribution to the ZFS. Furthermore, because CASSCF calculations have proven to be surprisingly successful

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for the prediction of the ZFSs of Mn^{III} complexes,^{6,25} we have extended our investigation of Mn^{II} ZFSs to this multiconfigurational entry level. The potential benefit of this method is that it treats the spin-flips within the metal d-shell correctly and uses proper spin-eigenfunctions in the evaluation of SOC matrix elements.

Theory

Orbitally nondegenerate magnetic compounds with a ground-state total spin $S \geq 1$ are subject to the ZFS that describes the lifting of the degeneracy of the $2S + 1$ magnetic sublevels $M_S = S, S - 1, \dots, -S$ in the absence of an external magnetic field. From perturbation theoretical arguments, it follows that the ZFS arises from two contributions: (i) to first order, the direct SS interaction; and (ii) to second order, the SOC.^{4,6,22,26} These effects can be phenomenologically collected in a SH of the form:

$$\hat{H}_{\text{ZFS}} = \hat{\mathbf{S}}\mathbf{D}\hat{\mathbf{S}} \quad (1)$$

In a coordinate system that diagonalizes the \mathbf{D} -tensor, the ZFS Hamiltonian can be written as

$$\hat{H}_{\text{ZFS}} = D\left[\hat{S}_z^2 - \frac{1}{3}S(S+1)\right] + E[\hat{S}_y^2 - \hat{S}_x^2] \quad (2)$$

where D and E are the axial and rhombic ZFS parameters, respectively:

$$D = D_{zz} - \frac{1}{2}(D_{xx} + D_{yy}) \quad (3)$$

and

$$E = \frac{1}{2}(D_{xx} - D_{yy}) \quad (4)$$

The convention $0 \leq E/D \leq 1/3$ uniquely determines the choice of axes.²⁷

SOC. In this paper, the SOC operator is represented by an effective reduced one-electron operator [$h_p^{\text{SO}}(i)$] that is chosen to be the spin-orbit mean-field (SOMF) approximation.^{28–30} In this case, the general sum-overstates (SOS) treatment shows that for a system with ground-state spin S to the second order, only excited states with total spin $\Delta S = S' - S = 0, \pm 1$ contribute to the \mathbf{D} -tensor (excited states with $\Delta S = 0$ are referred to as “same-spin” and those with $\Delta S = \pm 1$ are denoted as “spin-flip” states).²²

In the spin-unrestricted Kohn and Sham (UKS) formalism, the PK equations for the same-spin and spin-flip contributions can be written as follows:^{6,14}

Same-spin:

$$D_{K,L}^{(0)} = D_{K,L}^{\alpha\alpha} + D_{K,L}^{\beta\beta} = \frac{1}{4S^2} \sum_{i\alpha, a\alpha} (\psi_i^\alpha | h^{K;\text{SOC}} | \psi_a^\alpha) U_{a\alpha}^{L;(0)} + \frac{1}{4S^2} \sum_{i\beta, a\beta} (\psi_i^\beta | h^{K;\text{SOC}} | \psi_a^\beta) U_{a\beta}^{L;(0)} \quad (5)$$

Spin-flip:

$$D_{K,L}^{(-1)} = D_{K,L}^{\alpha\beta} = -\frac{1}{4S^2} \sum_{i\alpha, a\beta} (\psi_i^\alpha | h^{K;\text{SOC}} | \psi_a^\beta) U_{a\beta}^{L;(-1)} \quad (6)$$

and

$$D_{K,L}^{(+1)} = D_{K,L}^{\beta\alpha} = -\frac{1}{4S^2} \sum_{i\beta, a\alpha} (\psi_i^\beta | h^{K;\text{SOC}} | \psi_a^\alpha) U_{a\alpha}^{L;(0)} \quad (7)$$

where $K, L = x, y, z$. Here, $\psi_p^\sigma = \sum_\mu c_{\mu p} \phi_\mu$ is the p -th spin-UKS molecular orbital with spin $\sigma = \alpha, \beta$, expanded in a basis set

$\{\phi\}$ and with orbital energy $\varepsilon_{p\sigma}$. As usual, the labels i, j denote doubly occupied molecular orbitals (MOs) and a, b denote virtual MOs. In the absence of HF exchange—the only case considered by PK—the first-order perturbed orbital coefficients are given by ($m = 0, \pm 1$):

$$U_{a\sigma}^{L;(m)} = -\frac{(\psi_a^\sigma | h^{L;\text{SOC}} | \psi_i^{\sigma'})}{\varepsilon_{a\sigma} - \varepsilon_{i\sigma'}} \quad (8)$$

A more general approach for the determination of the first-order wave function coefficients was recently derived in a linear response framework.²¹ In the CP-SOC formalism, the perturbed orbitals in the presence of a SOC perturbation are expanded as:

$$\psi_i^{\alpha[L;(m)]}(\mathbf{r}) = \sum_{a\alpha} U_{a\alpha}^{L;(m)} \psi_a^\alpha(\mathbf{r}) + \sum_{a\beta} U_{a\beta}^{L;(m)} \psi_a^\beta(\mathbf{r}) \quad (9)$$

$$\psi_i^{\beta[L;(m)]}(\mathbf{r}) = \sum_{a\alpha} U_{a\alpha}^{L;(m)} \psi_a^\alpha(\mathbf{r}) + \sum_{a\beta} U_{a\beta}^{L;(m)} \psi_a^\beta(\mathbf{r}) \quad (10)$$

$U_{a\alpha}^{L;(m)}$ are the components of the mixing coefficients of spin-up and spin-down orbitals. The three contributions to the \mathbf{D} -tensor are then conveniently written in the $\{\phi\}$ basis:

$$D_{K,L}^{(0)} = \frac{1}{4S^2} \sum_{\mu\nu} (\mu | h^{K;\text{SOC}} | \nu) \left(\sum_{i\alpha, a\alpha} U_{a\alpha}^{L;(0)} c_{\mu i}^\alpha c_{\nu a}^\alpha + \sum_{i\beta, a\beta} U_{a\beta}^{L;(0)} c_{\mu i}^\beta c_{\nu a}^\beta \right) \quad (11)$$

$$D_{K,L}^{(-1)} = \frac{1}{2S(2S-1)} \sum_{\mu\nu} (\mu | h^{K;\text{SOC}} | \nu) \left(\sum_{i\alpha, a\beta} U_{a\beta}^{L;(-1)} c_{\mu i}^\alpha c_{\nu a}^\beta + \sum_{i\beta, a\alpha} U_{a\alpha}^{L;(-1)} c_{\mu i}^\beta c_{\nu a}^\alpha \right) \quad (12)$$

$$D_{K,L}^{(+1)} = \frac{1}{2(S+1)(2S+1)} \sum_{\mu\nu} (\mu | h^{K;\text{SOC}} | \nu) \left(\sum_{i\alpha, a\beta} U_{a\beta}^{L;(0)} c_{\mu i}^\alpha c_{\nu a}^\beta + \sum_{i\beta, a\alpha} U_{a\alpha}^{L;(0)} c_{\mu i}^\beta c_{\nu a}^\alpha \right) \quad (13)$$

The unknown $U_{a\alpha}^{L;(m)}$ coefficients are obtained by solving a set of linear response equations as explained in detail in ref 21.

SS Coupling. On the basis of the ground-state Slater determinant, the SS part of the \mathbf{D} -tensor can be estimated according to the McWeeny and Mizuno formula:³¹

$$D_{K,L} = -\frac{g_e^2 \alpha^2}{16S(2S-1)} \sum_{\mu\nu\kappa\tau} \{P_{\mu\nu} P_{\kappa\tau} - P_{\mu\kappa} P_{\nu\tau}\} \langle \mu\nu | r_{12}^{-5} \{3r_{12,K} r_{12,L} - \delta_{KL} r_{12}^2\} | \kappa\tau \rangle \quad (14)$$

where $\mathbf{P}^{\alpha-\beta} = \mathbf{P}^\alpha - \mathbf{P}^\beta$ is the spin density matrix with $P_{\mu\nu}^\sigma = \sum_{p\sigma} c_{\mu p}^\sigma c_{\nu p}^\sigma$ and \mathbf{c}^σ is the MO coefficient matrix for spin σ ; α is the fine structure constant ($\sim 1/137$ in atomic units).

Test Set

A set of 11 experimentally well-characterized coordination compounds for which high-field electron paramagnetic resonance (HF-EPR) data as well as X-ray structures are available form the test set for the present study.^{32–35} These compounds cover tetra-, penta-, and hexa-coordinated manganese ions, with N, O, and Cl in the first coordination sphere. Complexes containing heavier ligands were not considered in this study since they require a careful treatment of scalar relativistic effects that will be presented elsewhere. The following table summarizes the experimental data.

TABLE 1: Experimental Data of the Studied Mn^{II} Complexes^a

complex ^b	<i>D</i> (cm ⁻¹)	<i>E/D</i>	no.	coord. no.
[Mn(OPPh ₃) ₂ Cl ₂] ^{32,33}	0.165	0.027	1	4
[Mn(terpy)Cl ₂] ³⁴	-0.260	0.290	2	5
[Mn(Me ₂ N-terpy)Cl ₂] ³⁵	+0.270	0.222	3	5
[Mn(phenyl-terpy)Cl ₂] ³⁵	-0.319	0.223	4	5
[Mn(mesityl-terpy)Cl ₂] ³⁵	-0.295	0.271	5	5
[Mn(tolyl-terpy)Cl ₂] ³⁵	-0.250	0.320	6	5
[Mn(EtO-terpy)Cl ₂] ³⁵	-0.295	0.322	7	5
[Mn(terpy)(NCS) ₂] ³⁵	-0.300	0.170	8	5
[Mn(dpva)Cl ₂] ³⁴	-0.315	0.222	9	5
[Mn(tpa)Cl ₂] ¹¹	+0.118	0.200	10	6
[Mn(<i>t</i> Buterpy) (N ₃) ₂] ³⁵	-0.315	0.254	11	5

^a Where available, the sign of *D* is indicated. ^b OPPh₃ = triphenylphosphine oxide; terpy = 2,2':6'',2''-terpyridine; tpa = tris-2-picolylamine; dpva = dipyrido[4,3-b;5,6-b]acridine; Me₂N-terpy = 4'-(*N,N*-dimethylamino)-terpy; *t*Buterpy = 4,4',4''-triter-butyl-terpy; tolyl-terpy = 4'-(4-methylphenyl)-terpy; mesityl-terpy = 4'-mesityl-terpy; and EtO-terpy = 4'-ethoxy-terpy.

TABLE 2: Calculated vs Experimental *D* Parameters for the Series of 11 Mn^{II} Complexes^a

	correlation coefficients	slope	standard error (cm ⁻¹)
CP(BP)	0.988	1.735	0.078
CP(B3LYP)	0.977	0.997	0.062
PK(BP)	0.989	1.571	0.067
PK(B3LYP)	0.975	0.874	0.057

^a Linear regression results (SS contributions are included).

The structures of all considered complexes are shown in the following figure.

Computational Details

All results presented in this paper have been obtained using the ORCA electronic structure package³⁶ and are based on the X-ray structures. The rationale for this choice is discussed at length in ref 10.

In the CASSCF-based ab initio calculations, the SOC contribution to the ZFS was obtained within a quasi-degenerate perturbation theory (QDPT) formalism where the SOC operator is diagonalized in a basis of multiconfigurational wave functions obtained from a full CI calculation in a limited set of active electrons and orbitals that were obtained from a preceding CASSCF calculation.⁷ The active space was chosen to consist of the five metal d-based molecular orbitals since this allows for a clean connection to ligand field theory. The CASSCF calculations were usually started from the natural orbitals of a BP^{37,38}/TZVP³⁹ DFT calculation, which led to reliable convergence to the correct solution. All sextet (1) and quartet (24) roots were included in the SOC calculation. The SS contribution is calculated from (eq 14) on the basis of single root CASSCF(5,5) wave function, which amounts to a mean-field approximation.⁷

DFT calculations have been performed using the BP^{37,38} and B3LYP⁴⁰ density functionals and the TZVP basis set. Further basis set extensions have a minor effect on the results.¹⁰ The calculations were converged to 10⁻⁷ Eh.

Results

To elucidate the relative merits of the theoretical methods used for the calculation of the ZFS parameters, we performed several sets of calculations on the complexes included in our test set. Here, we present the result of the linear regression obtained from plotting calculated vs experimental values. All results account for the SOC together with SS contributions unless mentioned otherwise. The quality of the theoretical result is best judged from the standard error of the linear regression analysis since this parameter directly documents the correlation between theory and experiment. Deviations of the slope from unity indicate systematic errors of the theoretical method for the particular test set. In the linear regression, the intercept was forced to zero since both calculated and experimental *D* and *E* are equal to zero in cubic symmetry.

CP vs PK and BP vs B3LYP. The CP-SOC approach²¹ for the calculation of the SOC contribution to the ZFS allows for

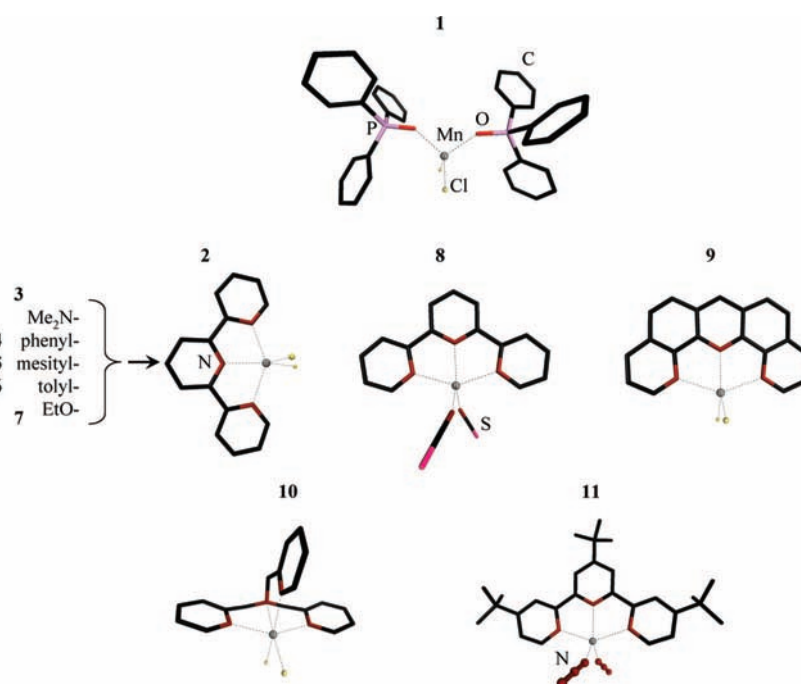


Figure 1. Molecular structures of Mn^{II} complexes considered in this paper.

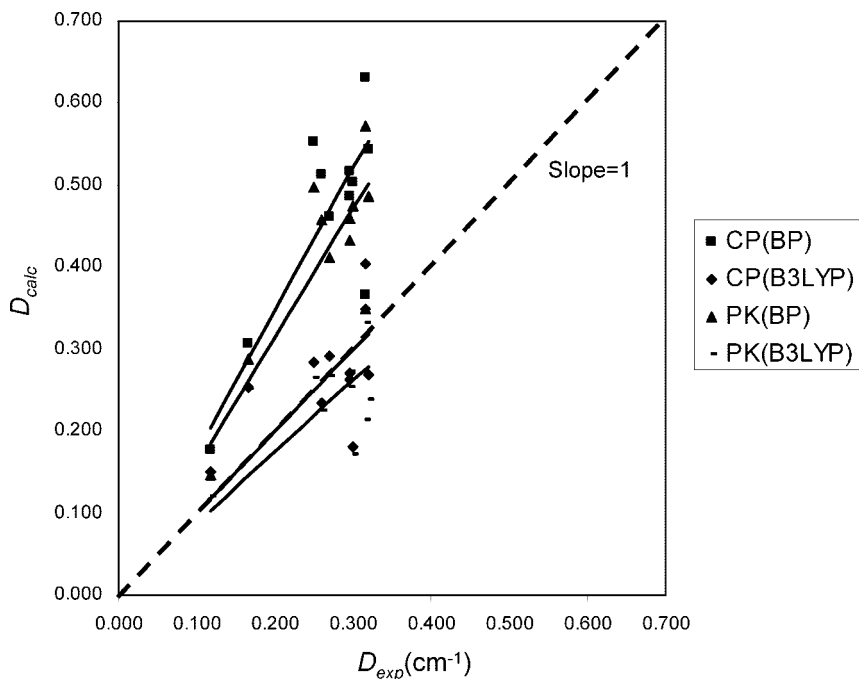


Figure 2. Comparison of correlations between calculated and measured D parameters from several theoretical approaches.

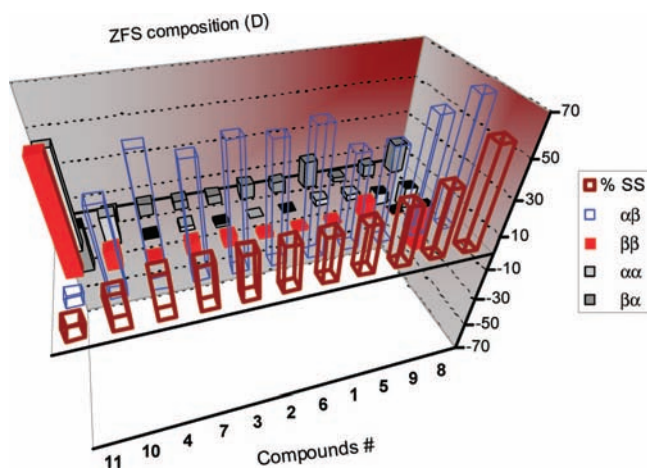


Figure 3. Percentage of the D components as calculated by the CP(B3LYP) method.

the introduction of the HF exact-exchange in DFT calculations through the a_x coefficient in eqs 33–38 of ref 21. The choice $a_x = 0$ leads to “pure” DFT functionals and $a_x = 0.20$ corresponds to the amount of the nonlocal exchange in the B3LYP⁴⁰ functional. We first compare the CP-SOC method with the PK approach for GGA (BP) and hybrid (B3LYP) density functionals. In this way, we are able to deconvolute the corrections coming from the SOC method and those caused by the specific choice of the DFT potential (Table 2) and (Figure 2) summarize the results obtained from CP(BP), CP(B3LYP), PK(BP), and PK(B3LYP) methods for the estimation of the axial D parameters. The individual values can be found in the Supporting Information.

Concerning the DFT functionals, our numerical results show that the inclusion of HF exchange improves the quality of the calculations since CP(B3LYP) gives a slope that is essentially unity for the correlation of calculated values with experimental ones, while the BP functional leads to a pronounced overestimation of the calculated parameters. In addition, the standard error is smaller in the case of CP(B3LYP) as compared to CP(BP). The superiority of B3LYP over BP was also found for the series

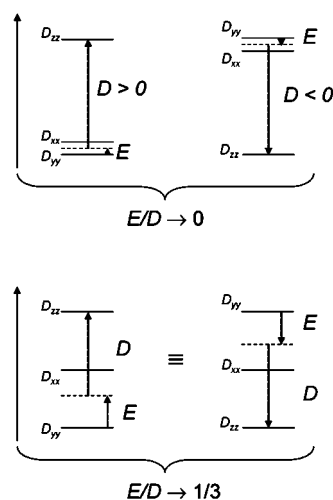


Figure 4. Sign of D for different cases of E/D . Top: straightforward prediction of the sign of D in the near axial case. Bottom: Ambiguous prediction of the sign of D in the near rhombic case.

of diatomic molecules studied in ref 21, but there, the BP approach led to a systematic underestimation of the D value.

It is interesting to compare the CP-SOC method to the PK approach (that was the most successful method in our earlier study¹⁰) for identical DFT functionals. The PK(B3LYP) approach leads to a systematic underestimation of the D parameters. This result would have been expected (and has been found by the Yamaguchi group⁴¹) from a SOC treatment where the nonlocal exchange is not considered in the response of the orbitals to the SOC perturbation.

Individual Contributions to D . Upon analyzing the individual contributions to the \mathbf{D} -tensor, it becomes apparent that the CP-SOC approach diminishes all SOC contributions to the ZFS. Figure 3 presents the individual contributions in graphical form (to be compared with Figure 4 in ref 10).

The individual ZFS contributions are seen to be confined to a range $\pm 70\%$ of the final D value unlike the previous PK(BP) results, where the individual contributions exceeded in some

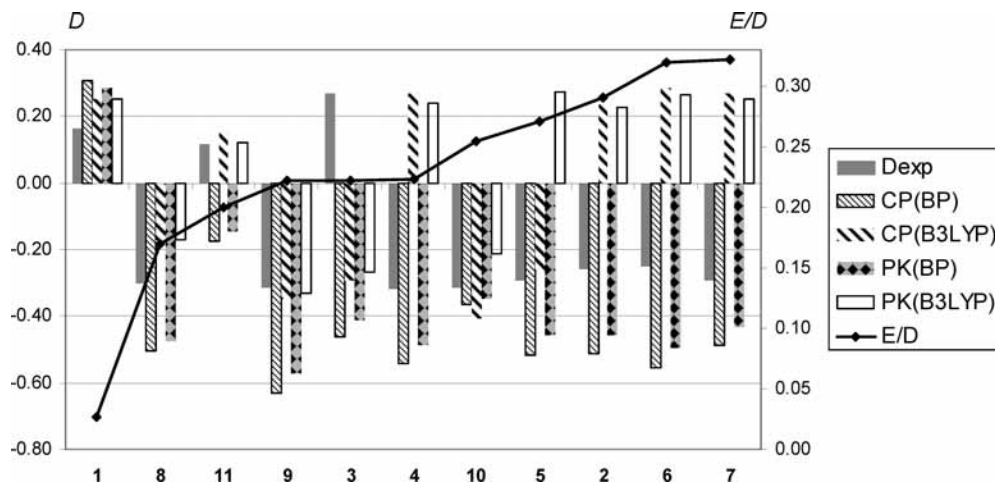


Figure 5. Prediction of the sign of D as function of the rhombicity E/D as predicted by different computational strategies (in all cases, SS contributions are included and are of the same sign of the total).

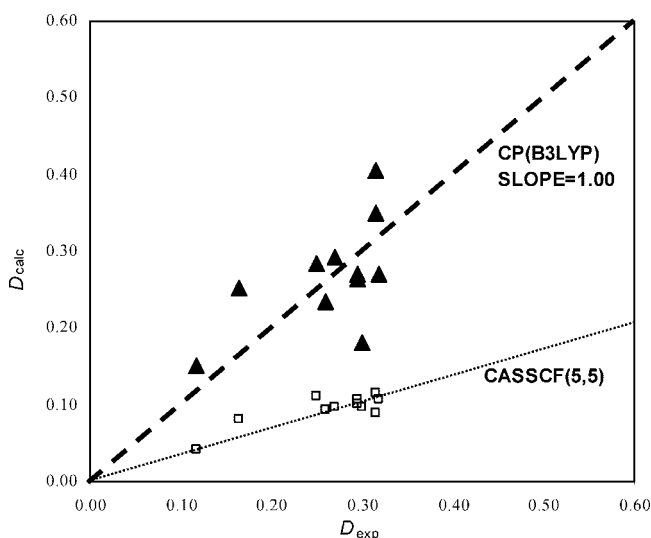


Figure 6. Comparison of CP and CASSCF(5,5) with experiment (SS contributions are included in both cases).

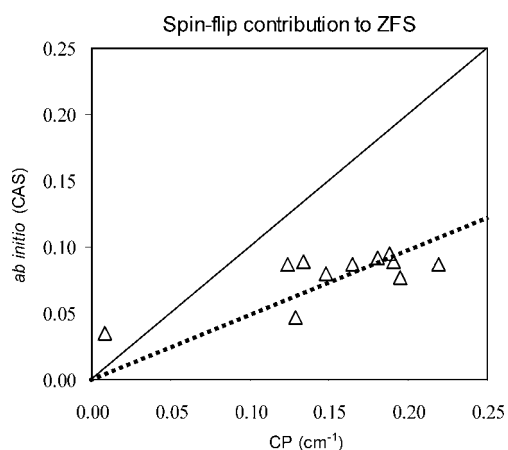


Figure 7. Spin-flip ($S' = S - 1$) excited states contribution to the ZFS from CP(B3LYP) and CAS(5,5) methods.

cases 150% of the calculate $|D|$ values.¹⁰ Unlike found and explained earlier in the PK case,¹⁰ the CP-SOC approach leads to $D^{\alpha\alpha} + D^{\beta\beta} \neq 0$, and thus, the cancellation of the same-spin and opposite spin contributions does not occur. This is a direct consequence of the different prefactors of the spin-flip contributions in the CP-SOC method. In PK(B3LYP), the CP wave

function is used but with the prefactors suggested by the PK approach.¹⁰ Consequently, the residual contribution from the difference between the $\alpha\alpha$ and the $\beta\beta$ parts of the \mathbf{D} -tensor was missing in the PK treatment. The CP-SOC formalism corrects this deficiency and leads to a slope of the correlation line that is essentially unity.

Sign of D as a Function of Rhombicity. The prediction of the sign of D is more challenging since it becomes ambiguous for E/D values close to the rhombic limit. This well-known difficulty is illustrated in the Figure 4.

It is obvious that the sign of D becomes highly sensitive to small errors in the relative values of D_{xx} and D_{yy} if E/D approaches 1/3. With this limitation in mind, it is not surprising that the likeliness of predicting the correct sign of D decreases as E/D increases. Figure 5 compares the results of CP(BP), CP(B3LYP), PK(BP), and PK(B3LYP) calculations with signs of D deduced from HF-EPR measurements.

For E/D below 0.2, all theoretical methods correctly predict the sign of D . However, as E/D increases, the first methods to give a wrong sign of D are those based on the BP functional, that is, PK(BP) and CP(BP). At about $E/D \approx 0.22$, the calculated sign of D starts to be ambiguous, even for the CP-SOC method. This conclusion needs to be confirmed by studies on other transition metal compounds to determine its range of validity.

Comparison with CASSCF Results. In ligand field theory of high-spin d^5 systems, the entire ZFS arises from the SOC between the only possible sextet configuration and the low-lying spin quartet states that arise from excitations and de-excitations within the metal d -shell.⁴² Furthermore, Solomon and co-workers pointed out that in the special case of the high-spin d^5 configuration, the contributions from anisotropic covalency may become significant.^{22,43} These contributions frequently oppose the contributions from low-symmetry distortions that lead to deviations from cubic symmetry.

An ab initio way of implementing a ligand-field type treatment is a CASSCF approach with only the metal d -orbitals in the active space. The SOC (and SS) effects are treated upon diagonalizing the SOC (and SS) operators in the basis of the sextet and quartet roots (this amounts to QDTP^{7,44}). In this approach, one obtains the anisotropic covalency through optimization of the orbitals and the low-symmetry split d - d multiplets from the full CI calculation within the active space. The anticipated shortcomings are also

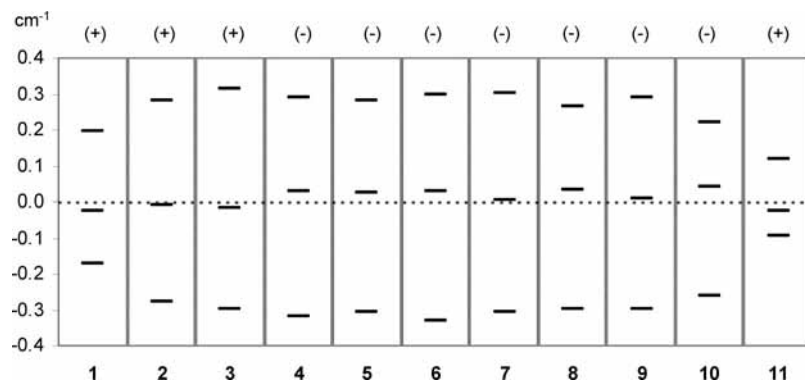


Figure 8. Top: Predicted sign of D . Middle: The three horizontal bars represent the Kramers doublets energies, putting their center of gravity at the origin (i.e., = 0.0). In this case, when two of the three energies are positive, D is negative and vice versa. Bottom: Complex no.

obvious: (i) the CASSCF orbitals will underestimate metal–ligand mixing (covalency) because of the generally exaggerated ionicity of metal–ligand bonds in the HF method, (ii) the excitation energies lack contributions from dynamic correlation, and (iii) one does not include contributions to the \mathbf{D} -tensor from charge-transfer states (doubly occupied \rightarrow singly occupied and singly occupied \rightarrow empty) and shell-opening excitations. The importance of these shortcomings must be investigated for the specific case under investigation. We have therefore investigated the case of Mn^{II} complexes. The results are shown in Figure 6.

Obviously, the CASSCF(5,5) treatment leads to a pronounced underestimation of the experimental values. It is interesting to compare these results to the CP(B3LYP) ones that led to an essentially correct estimation of D . The plot in Figure 7 demonstrates that a large part of the underestimation originates from the underestimation of the spin-flip contributions by the CASSCF method.

The reason for the underestimation is readily traced back to grossly overestimated sextet–quartet excitation energies by the CASSCF method. This problem is well-known.^{45,46} As discussed at length elsewhere,⁴⁷ the sextet–quartet excitation energies in high-spin d^5 systems are associated with tremendous dynamic correlation contributions that are very difficult to calculate with ab initio methods—even CASPT2, CCSD(T), or SORCI calculations with large basis sets appear to yield transition energies that are too high by about 0.5 eV for prototypical complexes such as $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (for a detailed discussion about this point, see ref 46). For the complexes in this study, realistic energies for the lowest sextet–quartet transitions [$^4\text{T}_{1g}(\text{e}_g \rightarrow \text{t}_{2g})$ parentage in octahedral symmetry) fall in the region 17000–20000 cm^{-1} .⁴⁷ However, the CASSCF results are in the range of 27000–30000 cm^{-1} . We note in passing that the calculated E/D values from the CASSCF method are as poor as those from the DFT treatments.

Exact vs Perturbation Approaches. Because the CASSCF method treats the spin-flip excitations to infinite order, we can assess the validity of second-order perturbation theory for the ZFSs of Mn^{II} complexes by comparing the infinite order results with second-order results that were obtained by evaluating the perturbation equations of ref 22 using the CASSCF wave functions.

In this case, it is possible to derive an analytic solution to the SH eigenvalue problem. The characteristic polynomial of the 6×6 ZFS matrix as written in the $|5/2, M_S\rangle$ basis takes the form: $(\lambda^3 + p\lambda + q)^2$, where $p = -28(E^2 + 1/3D^2)$, and $q = 160/3(E^2D - 1/9D^3)$. Following the determination of the three

λ 's, the D and E/D values can be estimated from the roots of the following polynomial: $D^3 + 9/112(\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)D + 27/640\lambda_1\lambda_2\lambda_3$. According to the Viète⁴⁸ formula, the axial D parameter takes the value:

$$|D| = \max\left(2\sqrt{-x/3}\cos(\phi/3), \left|2\sqrt{-x/3}\cos\left(\frac{\phi + 2\pi}{3}\right)\right|\right) \quad (15)$$

with $x = 9/112(\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3)$, $\cos \phi = 3y/2x(-x/3)^{1/2}$, and $y = 27/640\lambda_1\lambda_2\lambda_3$. The E value can then be evaluated from the relationship:

$$E^2 = -\frac{1}{3}D^2 - \frac{\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_1\lambda_3}{28} \quad (16)$$

The signs of D and E may be determined according to the condition that $0 \leq E/D \leq 1/3$. If two of the three Kramers doublets are higher in energy than the center of gravity, D is negative (Figure 8).

The results of this analysis demonstrate that second-order perturbation theory is completely adequate for all cases considered in this study. Deviations between the second- and infinite-order results amount on average to only $\sim 0.002 \text{ cm}^{-1}$. The latter number is an estimate for the cumulative higher order ZFS effects in these systems. These effects are known to be limited.^{49–51} For example, it has been shown by EPR studies on the ZFS of Mn^{II} doped in $\text{Mg}[\text{C}_4\text{H}_3\text{O}_4]_2 \cdot 6\text{H}_2\text{O}$ that the higher order terms represent about 0.3% of the total D or about 3.5% in another study on doped crystals.⁵⁰

Finally, the CASSCF approach also allows us to check for the influence of the spin-doublet ligand field excited states. In an approach that approximates the SOC as an effective one-electron operator, they do not couple directly to the sextet ground state but may couple through third and higher orders and thereby influence the higher order terms in the SH. We have acquired numerical results for $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ together with the TZVPP basis set (numerical data are given in the Supporting Information). At least in this case, inclusion of the spin-doublet states changes the D value by less than 0.0001 cm^{-1} . Hence, the neglect of these states for the treatment of ZFSs in high-spin d^5 systems appears to be justified.

Discussion and Conclusions

The present paper presents a detailed analysis of several modern computational approaches for the calculation of the ZFS parameters in transition metal complexes of the Mn^{II} ion. Our recent studies of the ZFS in Mn^{II} complexes^{10–13,52} showed the importance of including the direct SS coupling contribution to

obtain a better correlation between HF-EPR and calculated *D* parameters. The inclusion of the SS terms led to an improved correlation coefficient and lower standard error, but the slope of the correlation line was increased.¹⁰ We argued that it is necessary to account for the SS terms and that it is the systematic overestimation of the SOC contributions to the ZFS that should be corrected. The main conclusion of this paper is that the linear response, CP treatment of SOC, corrects this artifact. Thus, within a DFT framework, this is presently the only approach that leads to a physically complete prediction of the *D*-matrix. This statement is supported by a slope of the correlation between experiment and theory that is essentially unity as obtained from the CP(B3LYP) calculations. Our present conclusions are consistent with those previously found for the ZFSs of diatomics.²¹ However, in the latter case, the revised method cured the underestimation of the ZFS by DFT method, while in the present case, it cures the previously observed overestimation. Hence, we believe that important and correct new physics has been incorporated into the theory.

The present approach that treats all contributions to the SOC part of the ZFS through linear response theory is valid for hybrid functionals and takes the entire SS part into account. However, the fact that we treat the spin-flips with the correct prefactors does not mean that they are highly accurate from DFT, and we believe that they still represent a substantial if not the dominant part of the remaining error. Of the alternative methods, the PK method treats the spin-flip contributions to the SOC part of the ZFS incorrectly, is only applicable to nonhybrid functionals, and neglects the important SS contribution. The two-component approaches do also treat the spin-flips incorrectly and presently take no account of the SS interaction. They are, however, applicable to hybrid functionals.

Unfortunately, we have to refrain from generalizing our conclusions to all kinds of molecules since the physics that governs the ZFSs varies greatly from one system to the next, for example, from one transition metal *d^N* configuration to another. For example, in the high-spin *d⁵* systems studied here, the ZFS is dominated by spin-flips and the SS interaction. In high-spin *d⁴*, it is a balance between spin-flips and spin-conserving excitations. In organic triplets, it is the SS interaction that dominates. Thus, there appears to be no substitute for a careful investigation of different bonding situations to determine the range of validity of the employed methodology.

It is pointed out that the reduction of the SOC contribution observed for hybrid functional cannot be simply attributed to the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap or, more generally, occupied-virtual orbital energy differences (as has often been done in the literature). Arguments about the HOMO–LUMO gap in connection with hybrid DFT methods are generally invalid since the interpretation of the virtual orbital energies is entirely different as soon as nonlocal HF exchange is mixed into a density functional. Rather, our analysis once more shows that SOC contributions result from a subtle balance between *d*–*d*, LMCT, MLCT, etc. excited states contributions that strongly change from one coordination environment to the other.

Unfortunately, rigorous full-CI studies of magnetic parameters of transition metal complexes are not feasible and will remain elusive for the foreseeable future. Thus, one is always constrained to limited sized one- and many-electron bases in the *ab initio* treatment of systems of “realistic” size. In the special case of transition metal complexes, the *d*-orbital configuration is usually considered to contain the essential physics of a given coordination complex. Our *ab initio* CASSCF results, in

comparison with DFT and experiment, show that some care must be exercised in this respect. In particular, for the case of the high-spin *d⁵* configuration, the sextet–quartet excitation energies are strongly overestimated by moderately correlated wave function approaches, which together with the neglect of effects that are outside the active space, accounts for the underestimation of the ZFS from CAS(5,5) calculations by about a factor of 2. Nevertheless, the present study shows that the second-order perturbation theory used to calculate ZFS parameters is generally valid for the high-spin *d⁵* configuration.

The present results represent the state of affairs for the application of DFT methods to magnetic properties of mononuclear transition metal complexes. In the future, many additional challenges have to be met. In particular, treatments of the local ZFS in exchange coupled systems as well as anisotropic and antisymmetric exchange³ resulting from SOC must be dealt with in a satisfactory way.

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Supporting Information Available: Tables with the values presented in the figures above (with relative errors), as well as results of ZFS calculations on the Mn^{II} hexaquo complex. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

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