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First-principle computation of zero-field splittings: Application to a high valent Fe(IV)-oxo model of nonheme iron proteins

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We report the computational implementation of a combined spin-density-functional theory and perturbation theory (SDFT-PT) methodology for the accurate calculation of zero-field splittings (ZFS) in complexes of the most diverse nature including metal centers in proteins. We have applied the SDFT-PT methodology to study the cation of the recently synthesized complex $[\text{Fe}^{\text{IV}}(\text{O})\text{-(TMC)}(\text{NCCH}_3)](\text{OTf})_2$, [J. Rohde *et al.*, *Science* **299**, 1037 (2003)] which is an important structural and functional analog of high-valent intermediates in catalytic cycles of nonheme iron enzymes. The calculated value ($D^{\text{Theory}} = 28.67 \text{ cm}^{-1}$) is in excellent agreement with the unusually large ZFS reported by experiment ($D^{\text{Exp}} = 29 \pm 3 \text{ cm}^{-1}$). The principal component D_{zz} of the ZFS tensor is oriented along the $\text{Fe}^{\text{IV}}=\text{oxo}$ bond indicating that the oxo ligand dominates the electronic structure of the complex. © 2005 American Institute of Physics.
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I. INTRODUCTION

Due to their physical origin, closely associated with spin-orbit coupling (SOC),¹ the accurate prediction and microscopic interpretation of zero-field splittings (ZFS) in metal complexes has remained a formidable challenge. Although nonrelativistic Kohn-Sham spin-density-functional theory²⁻⁴ (KS-SDFT) is an efficient method for incorporating electron correlation and studying ground-state electronic structures of metal complexes, it does not incorporate the effects of SOC and, by itself, cannot be used to compute zero-field splittings. For many cases of interest, SOC can be considered a perturbation to the electronic Hamiltonian of a multielectronic molecular system. Therefore, it has been of interest for several authors to develop and implement methodologies which take advantage of KS-SDFT in conjunction with perturbation theory (PT) to incorporate SOC, a relativistic effect.^{5,6} Most notably, the pioneering work of Pederson *et al.*^{6,7} has paved the way for the computation of spin-orbit effects on metal complexes.

At the same time, significant progress has been made in recent years towards the synthesis of complexes which are structural and functional analogs of oxygen-activating nonheme iron enzymes.^{8,9} In particular, a complex with formula $[\text{Fe}^{\text{IV}}(\text{O})\text{-(TMC)}(\text{NCCH}_3)](\text{OTf})_2$,⁸ hereafter referred to as Fe(IV)=O (Fig. 1), has been synthesized which, in addition to its high-valent oxidation state, displays an unusually large ZFS. Although the synthesis and spectroscopic characterization of high-valent complexes provides some understanding about the roles of nonheme iron centers,^{8,9} the detailed mechanisms of dioxygen activation are still poorly understood. Therefore, it is of interest to study the electronic struc-

ture and unusually large ZFS of Fe(IV)=O complexes as this may contribute to a deeper understanding of their roles in oxygen activation.

Zero-field splittings arise from the combined action of crystal fields and SOC.¹ Although the crystalline fields acting on valence electrons are accounted for in nonrelativistic spin density-functional theory, SOC is a relativistic effect which is not included in the usual Kohn-Sham formulation. Therefore, for studying large metal complexes, it is desirable to implement a methodology which incorporates the effects of SOC by means of perturbation theory (PT) after a nonrelativistic DFT calculation. Pederson *et al.*^{6,7} and other

FIG. 1. Crystallographic structure of Fe(IV)=O with formula $[\text{Fe}^{\text{IV}}(\text{O})\text{-(TMC)}(\text{NCCH}_3)]^{2+}$ (Ref. 8). The relative magnitudes and orientations of the principal components (D_{xx}, D_{yy}, D_{zz}) of zero-field splitting tensor $\tilde{D}$ are also shown. The largest component, D_{zz} , is oriented along the Fe=O bond.

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SCHEME 1.

authors¹⁰ have implemented related methods obtaining various degrees of accuracy relative to experiment. However, methodologies for computing ZFS have not been implemented in most standard *ab initio* packages used by bioinorganic scientists.

In this work we report the implementation of a combined (SDFT-PT) methodology for the accurate computation of ZFS parameters by incorporating the effects of spin-orbit coupling via perturbation theory on top of a nonrelativistic KS-SDFT calculation. In addition, we have used this methodology to compute and interpret the unusually large ZFS parameters of Fe(IV)=O and show that the method is capable of unprecedented accuracy.

II. THEORETICAL METHODS

The ZFS Hamiltonian for bioinorganic complexes is written in terms of the operator $\mathbf{S}$ corresponding to the spin ground state of the complex and the ZFS tensor $\tilde{D}$,^{1,11}

$$\mathcal{H} = \mathbf{S} \cdot \tilde{D} \cdot \mathbf{S}. \quad (1)$$

When the tensor $\tilde{D}$ is chosen to be traceless, the ZFS interaction can be expressed in terms of axial (D) and rhombic (E) parameters. In particular, for complexes with biaxial symmetry the ZFS is represented as¹¹

$$\mathcal{H}_{\text{ZFS}} = D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2), \quad (2)$$

$$D = \frac{3}{2} D_{zz}, \quad (3)$$

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

where D_{xx} , D_{yy} , and D_{zz} are the diagonal components of the ZFS tensor $\tilde{D}$ in its principal axes xx , yy , and zz , respectively. However, for complexes with uniaxial symmetry, the rhombic term vanishes ($|D|>0$, $E=0$). For the latter case, Scheme 1 illustrates the effect of the ZFS on the spin states of a complex with uniaxial symmetry and triplet ($S=1$) ground state such as Fe(IV)=O.

The phenomenological Hamiltonian (2) has been extensively used in the interpretation of experimental data (e.g.,

Mössbauer, electron paramagnetic resonance (EPR), susceptibility) of bioinorganic complexes and metalloenzymes.^{1,8,11} However, fitting such data with Eq. (2), in general, does not allow correlating the empirical ZFS parameters with the actual crystallographic structure of the complex under study. Thus, often, experimental ZFS parameters have been obtained but their formal relationship to the three-dimensional structure has remained unclear.^{8,12,13} It is, therefore, highly desirable to implement accurate first-principle methods which allow a direct mapping of the ZFS parameters to their corresponding crystallographic structures. This in turn will provide a much needed link between spectroscopy and molecular structure.

Due to its technical difficulty and computational cost, little attention has been given to the first-principle prediction of ZFS parameters of bioinorganic complexes but previous work has been done on molecular magnets.^{6,7} The ability to accurately predict the sign and magnitude of ZFS parameters is a challenging theoretical and computational problem. However, this is important not only due to its fundamental scientific value but also to elucidate the physical origin of experimental ZFS parameters and their role in the complex's electronic structure. Kohn-Sham spin density-functional theory²⁻⁴ is a powerful method for studies of the ground-state electronic structure of large transition-metal-containing complexes (e.g., 60–200 atoms).^{11,14,15} The theory yields the ground-state electronic density $\rho(\mathbf{r})$ and energy of a many-electron system from self-consistent solutions of one-electron eigenvalue equations $\mathcal{H}^{\text{KS}} \phi_i^{\text{KS}}(\mathbf{r}) = \epsilon_i \phi_i^{\text{KS}}(\mathbf{r})$ subject to the condition $\rho(\mathbf{r}) = \sum_{i=1}^{\text{occ}} |\phi_i^{\text{KS}}(\mathbf{r})|^2$. To allow for spin polarization one can apply a spin unrestricted (U) formalism which allows α and β electrons to occupy orbitals with different energy and spatial localization.^{3,16}

By doing sum-over-states perturbation theory over the space of the Kohn-Sham orbitals,⁵ we have derived theoretical expressions and implemented a computational algorithm to accurately predict the zero-field splittings of any inorganic or bioinorganic complex. As outlined by Pederson *et al.*^{6,7} and Malkin *et al.*⁵ the methodology is based on calculation of corrections to the nonrelativistic SDFT energies by incorporating the effects of spin-orbit coupling via sum-over-states second-order PT. The SOC operator can be written (in a.u.) as

$$h_{\text{SOC}}(1) = \frac{1}{2c^2} \mathbf{S} \cdot \mathbf{p} \times \nabla \Phi(\mathbf{r}), \quad (5)$$

where the Coulomb potential is given by $\Phi(\mathbf{r}) = -\sum_n Z_n / |\mathbf{r} - \mathbf{R}_n| + \int d^3 r' \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|$ and the electron density, $\rho(\mathbf{r})$, is related to the Kohn-Sham orbitals $\phi_i(\mathbf{r})$ as mentioned above. Using sum-over-states second-order perturbation theory we can derive the contribution from h_{SOC} to the total electronic molecular energy as follows:

$$\begin{aligned}
\Delta_{\text{SOC}} &= \sum_{i\sigma} \sum_{j\sigma'} \frac{|\langle \psi_{i\sigma} | h_{\text{SOC}}(1) | \psi_{j\sigma'} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \\
&= \sum_{i\sigma} \sum_{j\sigma'} \frac{|\langle \psi_{i\sigma} | \mathbf{V} \cdot \mathbf{S} | \psi_{j\sigma'} \rangle|^2}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \\
&= \sum_{i\sigma} \sum_{j\sigma'} \frac{\langle \psi_{i\sigma} | \mathbf{V} \cdot \mathbf{S} | \psi_{j\sigma'} \rangle \langle \psi_{j\sigma'} | \mathbf{V} \cdot \mathbf{S} | \psi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \\
&= \sum_{i\sigma} \sum_{j\sigma'} \frac{\langle \psi_{i\sigma} | \sum_p V_p \cdot S_p | \psi_{j\sigma'} \rangle \langle \psi_{j\sigma'} | \sum_q V_q \cdot S_q | \psi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \quad |\psi_{i\sigma}\rangle = |\phi_{i\sigma}\rangle |\chi_{\sigma}\rangle, \\
&= \sum_{i\sigma} \sum_{j\sigma'} \sum_{p,q=x,y,z} \frac{\langle \phi_{i\sigma} | V_p | \psi_{j\sigma'} \rangle \langle \chi_{\sigma} | S_p | \chi_{\sigma'} \rangle \langle \phi_{j\sigma'} | V_q | \phi_{i\sigma} \rangle \langle \chi_{\sigma'} | S_q | \chi_{\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \\
&= \sum_{i\sigma} \sum_{j\sigma'} \sum_{p,q=x,y,z} \frac{V_{ipj}^{\sigma\sigma'} S_p^{\sigma\sigma'} V_{jq i}^{\sigma'\sigma} S_q^{\sigma'\sigma}}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \\
&= \sum_{\sigma\sigma'=\alpha,\beta} \sum_{p,q=x,y,z} \left(\sum_{ij} \frac{V_{ipj}^{\sigma\sigma'} V_{jq i}^{\sigma'\sigma}}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}} \right) S_p^{\sigma\sigma'} S_q^{\sigma'\sigma}, \tag{6}
\end{aligned}$$

$$\Delta_{\text{SOC}} = \sum_{\sigma\sigma'=\alpha,\beta} \sum_{p,q=x,y,z} M_{pq}^{\sigma\sigma'} S_p^{\sigma\sigma'} S_q^{\sigma'\sigma} \quad (\text{in a.u.}), \tag{7}$$

where the matrices M_{pq} and the matrix elements $S_{p,q}$ are more explicitly written as

$$M_{pq}^{\sigma\sigma'} = M_{qp}^{\sigma\sigma'*} \equiv \sum_{ij} \frac{\langle \phi_{i\sigma} | V_p | \phi_{j\sigma'} \rangle \langle \phi_{j\sigma'} | V_q | \phi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{j\sigma'}}, \tag{8}$$

$$S_p^{\sigma\sigma'} \equiv \langle \chi_{\sigma} | S_p | \chi_{\sigma'} \rangle, \tag{9}$$

where $V_p \equiv (-i/2c^2)[\nabla \times \nabla \Phi(\mathbf{r})]_p$, $p, q = x, y, z$, and $\phi_{i\sigma}$ and $\phi_{j\sigma'}$ represent occupied and unoccupied Kohn-Sham orbitals in the space-only representation, respectively. In (9) χ are spinor functions⁶ and σ and σ' represent up or down spin. The matrix elements $\langle \phi_{i\sigma} | V_p | \phi_{j\sigma'} \rangle$ are given by

$$\begin{aligned}
\langle \phi_{i\sigma} | V_p | \phi_{j\sigma'} \rangle &= \frac{-i}{2c^2} \left\langle \left\langle \frac{d\phi_{i\sigma}}{dq} \right| \Phi \left| \frac{d\phi_{j\sigma'}}{ds} \right\rangle \right. \\
&\quad \left. - \left\langle \frac{d\phi_{i\sigma}}{ds} \right| \Phi \left| \frac{d\phi_{j\sigma'}}{dq} \right\rangle \right\rangle, \tag{10}
\end{aligned}$$

where $p, q, s = (x, y, z)$, (y, z, x) , or (z, x, y) . We compute $\langle d\phi_{i\sigma}/dq | \Phi | d\phi_{j\sigma'}/ds \rangle$ by expanding the Kohn-Sham orbitals $\phi_{i\sigma}$ in terms of Cartesian Gaussian-type orbitals (CGTO). Finally, we have derived the following expression for the spin-orbit coupling contribution to the ZFS parameter D :

$$\begin{aligned}
D &= \left(\frac{1}{\Delta N} \right)^2 \left[M_{zz}^{11} + M_{zz}^{22} - M_{zz}^{12} - M_{zz}^{21} + \frac{1}{2}(M_{xx}^{12} + M_{xx}^{21} \right. \\
&\quad \left. + M_{yy}^{12} + M_{yy}^{21}) - \frac{1}{2}(M_{xx}^{11} + M_{xx}^{22} + M_{yy}^{11} + M_{yy}^{22}) \right], \tag{11}
\end{aligned}$$

where ΔN is the difference between the number of electrons with up and down spin.

We have also extended the model of previous authors⁶ by including an extra term in (8),

$$M_{pq}^{\sigma\sigma'} = M_{qp}^{\sigma\sigma'*} \equiv \sum_{ij} \frac{\langle \phi_{i\sigma} | V_p | \phi_{j\sigma'} \rangle \langle \phi_{j\sigma'} | V_q | \phi_{i\sigma} \rangle}{\epsilon_{i\sigma} - \epsilon_{j\sigma'} + \int \frac{\partial v_{xc}[\rho]}{\partial \rho} \rho_i \rho_j d\mathbf{r}}, \tag{12}$$

where the last term in the denominator is a correction dependent on the particular exchange correlation functional and $\rho_i \equiv \phi_i^* \phi_i$. This correction can be approximately written as follows:⁵

$$\int \frac{\partial v_{xc}[\rho]}{\partial \rho} \rho_i \rho_j d\mathbf{r} \approx \mathcal{D} \frac{C_x}{3} \int \rho^\alpha(\mathbf{r})^{-2/3} \rho_i(\mathbf{r}) \rho_j(\mathbf{r}) d\mathbf{r}, \tag{13}$$

where $C_x = (3/2)(3/4\pi)^{1/3}$, $\mathcal{D} = 4/3$, and $\rho^\alpha(\mathbf{r}) = \sum_i^{\text{occ}} \psi_i^* \psi_i^\alpha(\mathbf{r})$. Our initial estimates indicate that this term affects the computed ZFS by only a small fraction ($\approx 1.5\%$ for the diatomic molecule S_2)¹⁷ and was not included in the present calculations. We have also implemented more general expressions for arbitrary symmetry (i.e., not

TABLE I. Predicted and experimental values of ZFS parameters for Fe(IV)=O.

	SDFT-PT		Experiment ^a
	U-BLYP/6-311G*	U-BPW91/6-311G*	
D (cm ⁻¹)	28.17	28.67	29±3
(D_{xx}, D_{yy}, D_{zz})	(-9.1397, -9.6434, +18.7831)	(-9.2894, -9.8266, +19.1160)	NA ^b

^aReference 8.^bExperimental tensor components not explicitly reported.

necessarily uniaxial),¹⁷ however, these do not apply for the essentially uniaxial complex under study. In what follows, we discuss the application of the SDFT-PT methodology to Fe(IV)=O.

III. RESULTS AND DISCUSSION

By implementing and applying the methodology described above we have made an extremely accurate prediction of the ZFS parameters of Fe(IV)=O. The initial set of nonrelativistic Kohn-Sham orbitals were computed by means of spin unrestricted (*U*) calculations with BLYP (Refs. 18 and 19) and BPW91 (Refs. 18 and 20) functionals and the all-electron basis 6-311G* (Ref. 16) as implemented in

GAUSSIAN 98.²¹ The sum-over-states perturbation theory calculations described above were done with a locally developed algorithm yielding ZFS parameters which were nearly identical for both functionals. As shown in Table I, the calculated values for the two exchange-correlation functionals ($D^{\text{SDFT-PT}} = 28.17$ cm⁻¹ and 28.67 cm⁻¹) were in excellent agreement with experiment ($D^{\text{Exp}} = 29 \pm 3$ cm⁻¹),⁸ both theoretical values being within the reported experimental uncertainty. This illustrates the accuracy of the present SDFT-PT methodology and its potential for predicting, quite generally, ZFS parameters of metal and nonmetal complexes. As implied by Eq. (8), the computed ZFS depends on the energy denominators $\epsilon_{i\sigma} - \epsilon_{j\sigma'}$ which were computed with the previous functionals to yield accurate D values. We point out, however, that SDFT-PT calculations based on other (i.e., hybrid) functionals which incorporate an admixture of Hartree-Fock exchange²² tend to give ZFS values which are low relative to experiment due to their tendency to overestimate $\epsilon_{i\sigma} - \epsilon_{j\sigma'}$ gaps.

The ground-state electronic structure of Fe(IV)=O can

FIG. 2. Total and partial density-of-states (DOS) plots corresponding to (a) spin up (α) and (b) spin down (β) orbitals of Fe(IV)=O. The left and right vertical dashed lines indicate the energies of the (α, β)-HOMO and (α, β)-LUMO, respectively.

FIG. 3. Relative energies of frontier orbitals of $[\text{Fe}^{\text{IV}}(\text{O})-(\text{TMC}) \times (\text{NCCH}_3)_2]^{2+}$ obtained from spin unrestricted calculations at the BPW91/6-311G* level.

FIG. 4. Lowest unoccupied and highest occupied α orbitals of $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$. (a) Contour of the α -LUMO in the plane of the four equatorial nitrogens which are bound to iron. The main contribution from an $\text{Fe}(3d)$ orbital is antibonding with nitrogen orbitals. (b) Contour of the α -HOMO in a plane perpendicular to the equatorial nitrogens. The main contribution from an $\text{O}(2p)$ orbital is antibonding with an $\text{Fe}(3d)$ orbital.

be conveniently interpreted in terms of total and partial density-of-states (DOS) plots as shown in Fig. 2. Spin-unrestricted calculations give rise to two sets of molecular orbitals corresponding to majority spin (α) and minority spin (β) electron occupation. Figure 3 shows that, in terms of absolute energy, the α -HOMO (MO 100 α) and β -LUMO (MO 99 β) are the highest occupied and lowest unoccupied molecular orbitals of the complex, respectively. The dominant importance of the $\text{Fe}(\text{IV})=\text{O}$ fragment on the electronic structure of the complex is manifested in the composition of these two orbitals which, as shown in Figs. 4 and 5, have main oxygen character and are antibonding combinations of $\text{O}(2p)$ and $\text{Fe}(3d)$ orbitals. The partial DOS for the α set reveals that some of α -HOMOs have substantial contributions from $\text{Fe}(3d)$ and $\text{O}(2p)$ shells and are fairly delocalized throughout the $\text{Fe}=\text{O}$ bond [Fig. 2(a)]. This is particularly true for the α -HOMO. Figure 4(b) shows a contour of the α -HOMO, which, being an antibonding combination of $\text{O}(2p)$ and $\text{Fe}(3d)$ orbitals, is delocalized throughout the $\text{Fe}(\text{IV})=\text{O}$ fragment. By contrast, the α -LUMO is of main $\text{Fe}(3d)$ character with essentially no contribution from the

FIG. 5. Lowest unoccupied and highest occupied β orbitals of $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{NCCH}_3)]^{2+}$. (a) Contour of the β -LUMO in a plane perpendicular to the four equatorial nitrogens which are bound to iron. The main contribution from an $\text{O}(2p)$ orbital is antibonding with an $\text{Fe}(3d)$ orbital. (b) Contour of the β -HOMO in the plane of the equatorial nitrogens. The main contribution is from an $\text{Fe}(3d)$ orbital.

$\text{O}(2p)$ shell [Figs. 2(a) and 4(a)]. Slightly above the α -LUMO energy, however, some orbitals have mixed $\text{Fe}(3d)$ and $\text{O}(2p)$ character [Fig. 2(a)]. By contrast to the α set, the β -HOMO is almost completely localized on the metal ion with dominant $\text{Fe}(3d)$ character as shown in Fig. 5(b). The β -LUMO, however, has significant contributions from $\text{O}(2p)$ and $\text{Fe}(3d)$ shells [Fig. 2(b)] and represents an antibonding combination of $\text{O}(2p)$ and $\text{Fe}(3d)$ orbitals [Fig. 5(a)].

To obtain a microscopic understanding of the unusually large ZFS of $\text{Fe}(\text{IV})=\text{O}$, we analyzed the contributions to the $M_{pq}^{\sigma\sigma'}$ matrices defined in Eq. (8). In our calculations we used a full active space whereby pairs of all occupied and all unoccupied orbitals of either spin (α or β) were allowed to interact via the V_p operators (*vide supra*). The net value of the ZFS depends on a very complex admixture of interactions between occupied and unoccupied orbitals and also on their energy differences $\epsilon_{i\sigma} - \epsilon_{j\sigma'}$. We found that some of the largest contributions to D , as defined by Eq. (12), arise from coupling of minority (β) HOMOs with majority (α) LUMOs. Thus, some large contributions to D involved coupling of $\text{Fe}(3d)$ -centered β -occupied orbitals (e.g., MO 98 β) with

Fe(3d)-centered α -unoccupied orbitals (e.g., MO 101 α). In addition, the coupling of α -HOMOs [e.g., MO 100 α , Fig. 4(b)] with β -LUMOS [e.g., MO 99 β , Fig. 5(a)] gives rise to cumulative and substantial contributions to D . This indicates that the Fe=O bond of Fe(IV)=O not only dominates the electronic structure of the metal complex, since the oxo bond acts as a strong-field ligand, but it also substantially contributes to the large ZFS of the complex. This is consistent with the orientation of the largest component of the ZFS tensor (D_{zz}) which is along the Fe=O axis (Fig. 1).

The ZFS parameters of Fe(IV)=O were originally determined from fits of Mössbauer data with a spin Hamiltonian.⁸ However, the physical origin and detailed microscopic electronic structure that gives rise to the unusually large ZFS (Table I) remained poorly understood. The previous analysis provides insight about the origin of the large ZFS. In addition, spin Hamiltonian fits to Mössbauer data by themselves do not allow for a rigorous mapping of the ZFS parameters to the molecular structure. By contrast, as shown in Fig. 1, the magnitudes and relative orientations of the ZFS tensor ($\tilde{D}$) obtained from the present SDFT-PT calculations have been plotted with respect to the molecular structure of Fe(IV)=O. Thus, the current SDFT-PT methodology provides important magnetostructural correlations which are in addition and complementary to the experimental results.

IV. CONCLUSION

In summary, by incorporating via second-order perturbation theory the effects of spin-orbit coupling on top of a nonrelativistic SDFT calculation, we have implemented a very general method for calculating ZFS of arbitrary complexes. In particular, we have computed the ZFS of Fe(IV)=O with great accuracy. Our work based on the SDFT-PT methodology constitutes the first *extremely accurate* prediction of D for this intriguing complex. We have also extended ZFS models of previous authors and computed the contribution of the extra term in expression (12) for a diatomic molecule. The present results are particularly important not only due to their unprecedented accuracy but also in view of the current interest in understanding electronic structures of Fe(IV)=oxo intermediates in catalytic cycles of nonheme iron proteins. In particular, we showed that the largest component (D_{zz}) is perfectly oriented along the Fe^{IV}=oxo bond. Fits to Mössbauer data, by themselves, did not allow for a rigorous mapping of the ZFS parameters to the molecular structure. By contrast, the present SDFT-PT calculations

have allowed us to interpret the spin Hamiltonian parameters in terms of the microscopic electronic structure of the complex and, in addition, these naturally map the magnitudes and orientations of the ZFS tensor to the molecular structure. Thus, our results provide an important link between molecular structure, ZFS parameters, and spectroscopic data. The present SDFT-PT methodology can be quite generally applied to the most diverse class of molecular systems including metal centers in proteins and transition-metal-containing molecular magnets.

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