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Broken Symmetry Approach to Density Functional Calculation of Magnetic Anisotropy or Zero Field Splittings for Multinuclear Complexes with Antiferromagnetic Coupling[†]

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Antiferromagnetic coupling in multinuclear transition metal complexes usually leads to electronic ground states that cannot be described by a single Slater determinant and that are therefore difficult to describe by Kohn−Sham density functional methods. Density functional calculations in such cases are usually converged to broken symmetry solutions which break spin and, in many cases, also spatial symmetry. While a procedure exists to extract isotropic Heisenberg (exchange) coupling constants from such calculations, no such approach is yet established for the calculation of magnetic anisotropy energies or zero field splitting parameters. This work proposes such a procedure. The broken symmetry solutions are not only used to extract the exchange couplings but also single-ion **D** tensors which are then used to construct a (phenomenological) spin Hamiltonian, from which the magnetic anisotropy and the zero-field energy levels can be computed. The procedure is demonstrated for a bi- and a trinuclear Mn(III) model compound.

Introduction

Polynuclear transition metal compounds have a tremendously complex electronic structure because of the large number of unpaired electrons. This complexity can be reduced substantially if one only considers eigenstates in an energy window well below electronic excitations of mononuclear complexes. This part of the spectrum can be rationalized by a simplified treatment in which the unpaired electrons of a given transition metal center i are first coupled to form an effective spin $\vec{\hat{S}}_i = (\hat{S}_{xi},\hat{S}_{yi},\hat{S}_{zi})$, and such effective spins are the only degrees of freedom in a (phenomenological) *spin Hamiltonian* which contains parameters that can be adjusted to reproduce the low-energy part of the spectrum of the full microscopic Hamiltonian. In the simplest case, there is an isotropic coupling of the spins $\vec{\hat{S}}_i$ in the form of a Heisenberg Hamiltonian

$$\hat{H}_{\mathrm{iso}} = \sum_{i<j} J_{ij}\vec{\hat{S}}_i \cdot \vec{\hat{S}}_j \qquad (1)$$

with the isotropic coupling parameters J_{ij}. Including the Zeeman term (interaction with an external magnetic field) and thermal averaging, the parameters J_{ij} determine the temperature dependence of the magnetic susceptibility and are determined by fitting to such experimental data.

The connection between the phenomenological parameters (coupling constants) J_{ij} and the microscopic electronic Hamiltonian is established through the low-energy part of its spectrum. Energy differences between low-lying states of the spin Hamiltonian are of course a function of the coupling constants, and in simple cases the knowledge of few such energy differences is sufficient to determine them. For a fully wave function based ab initio method, one calculates the ground and lowest excited states of the system and uses the computed energy levels to determine the coupling constants, thus identifying the energy levels of the microscopic Hamiltonian with the energy levels of the spin Hamiltonian. Consider, as a simple example, two weakly coupled octahedral Cr^{3+} centers, each of which has a local nondegenerate quartet ground state configuration. This gives a multiplet of 16 low-lying states split by the superexchange interaction between the two metal centers. A spin Hamiltonian for two $S_1 = S_2 = 3/2$ spins and an isotropic coupling $J_{12} > 0$ (antiferromagnetic coupling) gives a singlet ground state, above which there is a triplet, a quintet, and a septet with relative energies J_{12}, $3J_{12}$, and $6J_{12}$. With a full ab initio treatment, one not only can extract the parameter J_{12} as the energy difference between the lowest singlet and triplet state but also can test whether the other low-lying level agree with the “spin ladder” pattern of the spin Hamiltonian spectrum. Such calculations cannot be used for large systems, because a reliable quantum chemical description generally requires a CASSCF calculation on top of which dynamical electron correlation has to be added. Because the number of CASSCF wave function parameters grows exponentially with the size of the active space (or the number of open shell orbitals or the number of transition metal centers), this method can be used if there are at most four open shell metal centers. Beyond that, the method of choice is based on density functional theory. However, the Kohn−Sham density functional approach is built upon a single-determinant reference wave function that does not have the correct spin symmetry for most of the low-energy states. For the above example, only the high-spin septet state has a single-determinant description, so no energy differences can be obtained directly from density functional calculations. The standard approach to solve this problem goes back to Bagus[1] and Ziegler[2] and was adapted to magnetic coupling by Noodleman[3,4] (for a minireview, see ref 5). In this *broken symmetry* approach, one calculates Kohn−Sham energies for single-determinant reference functions, most of which break spin and (if present) spatial symmetry. In our example, one localizes the open shell orbitals on the two chromium centers and runs two calculations, one where all unpaired electrons are “spin up”, and another one

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where "spin up" open shell orbitals are occupied on one chromium center while "spin down" orbitals are occupied on the other. The Kohn−Sham energies thus obtained from two self-consistent calculations are then identified with the expectation value of the Spin Hamiltonian $\hat{H}_{\mathrm{iso}}$ for Ising configurations (where each spin has either maximum or minimum value of the spin projection). In our example, these are the configurations $|(3/2)(3/2)\rangle$ and $|(3/2)(-3/2)\rangle$ whose energy expectation value is $(9/4)J_{12}$ and $(-9/4)J_{12}$. The coupling parameter J_{12} is thus calculated by multiplying the difference of the two *broken symmetry* Kohn−Sham energies with 2/9. Note that, unlike the Ising configurations of the spin Hamiltonian, the *broken symmetry* Kohn−Sham wave functions are not orthogonal to each other (due to overlapping spin densities from different metal centers), which may require additional corrections.[6]

Multiplets with total spin $S > 1/2$ may further be split by relativistic corrections to the Hamiltonian, because spin then no longer is a good quantum number. This phenomenon is called *zero field splitting* (ZFS) which alludes to the fact that the degeneracy is lifted even in the absence of an external magnetic field (no Zeeman splitting). ZFS is related to *magnetic anisotropy*, that is, the variation of the ground state energy of a (laboratory fixed) system in an external homogeneous magnetic field $\vec{B}$ of given strength $B = |\vec{B}|$ and varying direction $\vec{n} = \vec{B}/B$. For a given value of B, the magnetic anisotropy energy (MAE) $W(\vec{n})$ is the total energy as a function of the direction $\vec{n} = \vec{B}/B$ of the magnetic field. This is formally a ground state property which is more amenable to a density functional treatment than multiplet splittings. In the strong exchange limit, which means that zero field splitting is small compared to isotropic (Heisenberg) couplings, the whole system behaves to a good approximation as a single effective (collective) spin $\vec{\hat{S}}$ described by a spin Hamiltonian

$$\hat{H} = \sum_{\alpha,\beta} D_{\alpha\beta}\hat{S}_{\alpha}\hat{S}_{\beta} - g\mu_{\mathrm{B}}\sum_{\alpha} B_{\alpha}\hat{S}_{\alpha} = \vec{\hat{S}}\cdot\mathbf{D}\cdot\vec{\hat{S}} - g\mu_{\mathrm{B}}\vec{B}\cdot\vec{\hat{S}} = \hat{H}_{\mathrm{ZFS}} + \hat{H}_{B} \qquad (2)$$

(we use a Cartesian representation where α,β run over the Cartesian coordinates x,y,z). For different orientations of the system the numbers $D_{\alpha\beta}$ transform like a tensor. For the sake of simplicity, we have assumed a Zeeman interaction $\hat{H}_{\vec{B}} = -g\mu_{\mathrm{B}}\vec{B}\cdot\vec{\hat{S}}$ with an isotropic g value (μ_{B} is the Bohr magneton). In the general case, there is an anisotropic **g** tensor which gives no contribution to zero field splitting but adds an "orbital" contribution to the magnetic anisotropy. If there is no zero field splitting ($\mathbf{D} = 0$), the ground state energy of this Hamiltonian is $-g\mu_{\mathrm{B}}SB$. This value does not depend on the direction of $\vec{B}$ such that there is no magnetic anisotropy. This is so because the unperturbed ($\mathbf{D} = 0$) ground state wave function is an eigenfunction of $\vec{B}\cdot\vec{\hat{S}}$, that is, the spin aligns to the magnetic field. In a strong magnetic field, $\hat{H}_{\vec{B}}$ is much larger than $\hat{H}_{\mathrm{ZFS}}$ such that the latter can be treated by first-order perturbation theory. Through first order, the only energy contribution that depends on $\vec{n}$ is the expectation value of $\hat{H}_{\mathrm{ZFS}} = \vec{\hat{S}}\cdot\mathbf{D}\cdot\vec{\hat{S}}$ with the ground state wave function for $\mathbf{D} = 0$. A little algebra shows that the ground state energy $W(\vec{n})$ is given by[7]

$$\begin{aligned} W(\vec{n}) &= S\left(S - \frac{1}{2}\right)\vec{n}\cdot\mathbf{D}\cdot\vec{n} + \text{constant terms} \\ &= \vec{n}\cdot\mathbf{M}\cdot\vec{n} + \text{constant terms} \end{aligned} \qquad (3)$$

The "constant terms" are the angular avarage of the function $W(\vec{n})$ and include everything that does not depend on the direction $\vec{n}$ of the magnetic field, including the energy contribution from the Zeeman interaction. The elements of the tensor **M** (or **D**) can easily be extracted from the value of $W(\vec{n})$ for just a few directions $\vec{n}$. For sufficiently strong magnetic fields where the first-order treatment is valid, the MAE tensor **M** does not depend on the magnetic field strength B. One might ask why we differentiate between the ZFS tensor **D** and the MAE tensor **M** if they only differ by a constant. The reason is, that the MAE function is also defined for systems that cannot be described by the single-spin Hamiltonian eq 2. Here, the ZFS tensor **D** is not defined but the magnetic anisotropy function can still be of the second form of eq 3. This case is realized, for example, for an ensemble of two isolated effective spins. We follow the widely used convention to make the MAE tensor traceless by defining the "constant terms" as the angular average of the MAE function.

The theory of the calculation of magnetic anisotropy energies or zero-field splittings based on density functional theory has been developed for high-spin states which can directly be represented in single-determinant Kohn−Sham calculations.[8−11] For the microscopic Dirac−Coulomb operator, the magnetic anisotropy stems from the spin−orbit interaction (including the two-electron *spin same orbit* terms). Relativistic corrections to the electron interaction (loosely speaking, the Breit interaction) lead to corrections of the spin orbit interaction (the so-called *spin other orbit* terms) as well as to the magnetic interaction between electron spins (spin-dipolar interaction). We refer to recent discussions of the relative importance of these terms[12,13] as this is not in the focus of the present paper.

The density functional methods for the evaluation of zero field splittings or magnetic anisotropies developed so far are valid for the high-spin case only. While this is explicitly stated by Neese[13] for his method, Pederson and Khanna,[9] applied their method from the very beginning to antiferromagnetically coupled systems where the Kohn−Sham wave function is not spin adapted, without analyzing the implication thereof. The purpose of the present work is to discuss how the *broken symmetry* approach, which has proven very useful for the calculation of Heisenberg (exchange) couplings in such systems, could be extended to the calculation of magnetic anisotropy energies.

The Many-Spin Hamiltonian and Magnetic Anisotropy of Ising Configurations

The simplest possible extension to include magnetic anisotropy in the isotropic Heisenberg Hamiltonian (eq 1) for a collection of effective spins is

$$\hat{H}_{\mathrm{sp}} = \sum_{i<j} J_{ij}\vec{\hat{S}}_i\cdot\vec{\hat{S}}_j + \sum_i \vec{\hat{S}}_i\cdot\mathbf{D}_i\cdot\vec{\hat{S}}_i - \mu_{\mathrm{B}}\sum_i g_i\vec{B}\cdot\vec{\hat{S}}_i \qquad (4)$$

Here we have only included so-called *single ion* contributions to the magnetic anisotropy through the tensors $\mathbf{D}_i$. For systems with localized spin densities that we have in mind, such a form of the Spin Hamiltonian covers all microscopic effects reasonably well except the spin−dipolar interaction. The latter can be separated into one-center and two-center terms. While the one-center terms of the spin-dipolar interaction are encompassed by the above form of the Spin Hamiltonian, the two-center terms have to be separated off. These can be evaluated to a good approximation through pointlike effective spins (magnetic dipoles) on the open shell metal centers. In the strong exchange limit, where superexchange couplings are considered much stronger than zero field splitting such that the latter can be treated by first-order perturbation theory, the magnetic anisotropy $W(\vec{n})$ for an eigenstate of the spin Hamiltonian is calculated by *first* finding the ground state of the isotropic Heisenberg Hamiltonian (first term of $\hat{H}_{\mathrm{sp}}$), *second*, aligning the spin of that state in the direction of $\vec{n}$ (this is what a strong external magnetic field would do) and then, *third*, evaluating the expectation value with the ZFS part (the second term of $\hat{H}_{\mathrm{sp}}$). When there are antiferromagnetic couplings, the state of interest can usually not be described microscopically by a single Slater determinant, and therefore a DFT calculation does not correspond to what we just described in terms of the Spin Hamiltonian. This is exactly the analogue of the situation encountered in the calculation of magnetic exchange coupling constants. It is now suggested to identify the magnetic anisotropy function obtained by a *broken symmetry* Kohn−Sham calculation with the $\vec{n}$-dependent energy expectation value (with the Hamiltonian equation (4)) of an Ising configuration that is rotated in spin space as to align the spins in the direction of $\vec{n}$. Note that the isotropic Heisenberg part of $\hat{H}_{\mathrm{sp}}$ gives a contribution that does not depend on $\vec{n}$ and is thus part of the "constant terms". The central question is, of course, whether this mapping between the spin Hamiltonian and the Kohn−Sham calculations makes sense and whether enough information can be extracted this way to determine the magnetic anisotropy of the state under consideration.

For the above spin Hamiltonian, one can analytically execute the above recipe. Unfortunately, the magnetic anisotropy calculated for all the Isinig configurations is the same, since their $\vec{n}$-dependent energy expectation value is in either case

$$W(\vec{n}) = \sum_i \left\{ S_i\left(S_i - \frac{1}{2}\right)\vec{n}\cdot\mathbf{D}_i\cdot\vec{n}\right\} + \text{constant terms} \tag{5}$$

This behavior is also observed in Kohn−Sham calculations which include the spin−orbit contribution only. For this case, the perturbative method of Pederson and Khanna[9] starts with a scalar-relativistic spin-unrestricted Kohn−Sham calculation and computes a second-order energy lowering through the spin−orbit interaction as

$$W(\vec{n}) = -\sum_i^{\mathrm{occ}}\sum_a^{\mathrm{virt}} \frac{\langle\phi_i(\vec{n})|\hat{H}^{\mathrm{SO}}|\phi_a(\vec{n})\rangle\langle\phi_a(\vec{n})\hat{H}^{\mathrm{SO}}\phi_i(\vec{n})\rangle}{\varepsilon_a - \varepsilon_i} \tag{6}$$

where the indices i (a) run over all occupied (virtural) orbitals, both spin-up and spin-down, and $\hat{H}^{\mathrm{SO}}$ is the spin−orbit part of the effective (one-particle) Kohn−Sham operator. The orbitals $\phi_i(\vec{n})$ and $\phi_a(\vec{n})$ are two-component orbitals that are obtained by rotating the spin of the scalar relativistic orbitals away from the z axis into the direction $\vec{n}$ before plugging them into the second-order energy expression. If the electronic structure can be described with doubly occupied, singly occupied, and virtual orbitals which are well localized on fragments containing the metal centers, then not only the total magnetic anisotropy can be decomposed into "single ion" contributions but also the magnetic anisotropy is invariant with respect to a spin flip of all open shell scalar relativistic orbitals at a single site. Different Kohn−Sham *broken symmetry* wave functions should therefore give similar magnetic anisotropies, and the behavior of Ising configuration of $\hat{H}_{\mathrm{sp}}$ is simulated to some extent. For first-row transition metal atoms, the above equation is a crude approximation as Neese has shown[13] that both the *spin other orbit* terms as well as the spin−dipolar interaction have a substantial contribution to the magnetic anisotropy for a prototype mononuclear manganese(III) complex, and even if they are taken into account, only about 70% of the experimental value is obtained in the DFT calculation. Note that the "PKK" results in Table 1 of ref,[13] which come from a procedure involving eq 6, have to be multiplied by 4/3 because Pederson and Khanna treated spin classically to relate the **M** and **D** tensors, the latter is therefore too small by a factor $(2S - 1)/2S$.[7] The point we want to make here is that taking into account the *spin other orbit* and spin−dipolar terms will not change the observation that all *broken symmetry* DFT calculations give very similar magnetic anisotropies, provided one first subtracts the two-center contributions from the spin−dipolar interaction, for example through a point−dipole approximation.

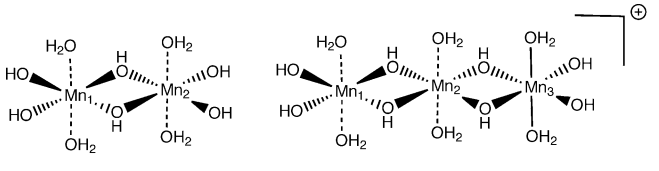
TABLE 1: Kohn−Sham (KS) and Magnetic Anisotropy Energies (MAE) for Different Ising-Type Configurations of the Model Compounds (PBE Exchange Correlation Functional, Results for the BP Functional in Parentheses)

				MAE (K)	
model	Ising configuration	Ising energy	KS energy (E_{h})	axial	in-plane
1	UU[a]	$4J$[b]	−3086.442642 (−3088.153400)	−21.51 (−21.39)	0.88 (0.87)
	UD	$4J$	−3086.450734 (−3088.161333)	−19.91 (−19.85)	0.15 (0.15)
2	UUU	$8J + 4J'$	−4553.612953 (−4556.088895)	−34.15 (−33.77)	2.52 (2.36)
	UUD	$-4J'$	−4553.622156 (−4556.097906)	−30.85 (−30.86)	0.11 (0.12)
	UDU	$-8J + 4J'$	−4553.629853 (−4556.105467)	−29.24 (−29.13)	1.22 (1.21)

[a] "U/D" denotes "spin up" or "spin down" at the manganese centers. [b] J is the coupling constant between adjacent manganese centers, and J' is the coupling constant between the terminal manganese centers in **2**.

In their calculation on the $Mn_{12}O_{12}$ acetate, an extensively studied system and a sort of guinea pig for investigators interested in magnetic anisotropy energies, Park et al.[14] have also observed that different *broken symmetry* calculations gave very similar magnetic anisotropy energies. They found very similar values, between 54.1 and 55.4 K, for 12 different cases. While they were fully aware the DFT calculations are not spin eigenfunctions (which can only be described by a linear combination of many Slater determinants), they developed an argument that led to the conclusion that all low-energy spin eigenfunctions have the same magnetic anisotropy, which should match the result obtained from the various calculations. Central to their argument is the conjecture that no Slater determinants generated by single-orbital spin flips are present in the true many-particle wave function because of their high energy expectation value. This is not true and it does not even hold for the single-ion spin multiplets. Furthermore, if their argument is applied to singlet states (if they are present in the spectrum of the Heisenberg Hamiltonian) it would assign a sizable magnetic anisotropy which is absurd because singlets cannot have a magnetic anisotropy. As an aside, if they had properly

SCHEME 1: Model Systems “Mn_2O_2” (1) and “Mn_3O_4” (2)



1 **2**

taken into account the multideterminantal nature of the ground state, their computed magnetic anisotropy would have been smaller—the agreement with experimental data would be worse but the result would also be more consistent with what has been observed for mononuclear complexes.

Extracting Single-Ion Tensors from DFT Calculations, Results for Model Systems

While the exchange coupling constants J_{ij} can be obtained from the energy differences obtained by running DFT calculations for several *broken symmetry* configurations, we have just seen that the magnetic anisotropy parameters obtained in these calculations are very similar and do not provide enough information to extract the single-ion $\mathbf{D}_i$ tensors of the spin Hamiltonian. The key idea is now to perform a series of computer experiments, namely, DFT calculations, which do not model an actual physical system but one which correspond to a spin Hamiltonian in which all $\mathbf{D}_i$ are zero except a single one. The molecular magnetic anisotropy obtained in that calculation then allows us to extract the tensor components of that particular nonzero $\mathbf{D}_i$. The whole set of single-ion tensors can be obtained if such an experiment is repeated for all open shell metal centers. Together with the exchange coupling constants J_{ij} obtained from the energy differences of the *broken symmetry* configurations, all parameters of the spin Hamiltonian are known and one can compute its spectrum, or the magnetic anisotropy of the state of interest (usually the ground state). It is interesting to note that this approach is related to “real” experiments[15] where in a multinuclear iron complex, all iron(III) ions except one have been replaced by a magnetically inactive gallium ion, and the measured magnetic anisotropy was then used to extract the iron single-ion tensor.

Currently, we do not include the spin−dipolar interaction in our magnetic anisotropy calculations; therefore it is sufficient to “switch off” the spin−orbit coupling at all metal centers except one to extract the single-ion tensor of that center. With what remains from the spin−orbit operator one can then compute magnetic anisotropies, either by a second-order perturbation theory approach or by self-consistent two-component density functional calculations using the collinear approach for the exchange-correlation potential.[7,8,16] The computed molecular magnetic anisotropy tensor is then divided by $S_i(S_i - 1/2)$ and thus converted to a single-ion $\mathbf{D}_i$ tensor.

To illustrate how the suggested procedure works, we have performed calculations on two model systems $Mn_2(OH)_6(OH_2)_4$ (compound **1**, Scheme 1) and $[Mn_3(OH)_8(OH_2)_6]^+$ (compound **2**) which we will name “Mn_2O_2” and “Mn_3O_4” for short. All manganese atoms are in the oxidation state +III (d^4 configuration). Because we are interested in a proof of the concept here, we used an idealized molecular geometry in which the Mn−OH_2 bonds are set to 220 pm, while all other Mn−O bonds are set to 190 pm. All O−Mn−O angles are 90° or 180°. Although idealized, this geometry shows the main features observed in Mn(III) complexes, where an elongation of the Mn−O bonds along one axis is often observed because of a Jahn−Teller instability of an octahedral d^4 configuration. The molecule-fixed Cartesian coordinate system is oriented such that the (elongated) Mn−OH_2 bonds are parallel to the z axis, while the x axis connects the manganese atoms. We performed quasi-relativistic calculations using the ZORA(MP) operator[17,18] with basis sets of triple-ζ quality (see Supporting Information). The contribution of a certain atom to spin−orbit coupling is “switched off” by removing the contributions of that atom to the effective (model) potential in the spin−orbit operator (for technical details, see Supporting Information). However, our approach does not critically depend on how the spin−orbit interaction is switched off for a certain atom. For example, a one-center approximation is a key ingredient in the atomic mean field approximation[19] much used for the two-electron contributions to spin−orbit coupling, in order to get rid of the multicenter two-electron spin−orbit integrals. This operator also found use in the calculation of magnetic anisotropies[12,13] and has already “built in” the recipe to be switched off for certain atoms, and the extension to the one-electron terms is straightforward. The PBE[20] and BP[21,22] exchange-correlation functionals were used (these acronyms are built from the names of the authors involved).

The manganese atoms are connected by two hydroxy bridges from which we expect strong antiferromagnetic coupling. First, a scalar-relativistic spin-unrestricted Kohn−Sham calculation was converged for a given Ising configuration where all unpaired electrons at a given center are either “spin up” or “spin down”, and then Pederson’s formula (eq 6) was used to compute the spin−orbit correction $W(\vec{n})$ which depends on the spin alignment direction $\vec{n}$ and is of the form given by eq 3. For both model compounds studied, the MAE tensor is diagonal in the Cartesian frame described above. Since we have made it traceless, it is characterized by two numbers, namely, the *axial* anisotropy, $M_{zz} - (1/2)(M_{xx} + M_{yy})$, and the *in-plane* anisotropy $(1/2)|M_{xx} - M_{yy}|$.

Table 1 shows the Kohn−Sham energies and magnetic anisotropies for the Ising-type configuration of model compounds **1** and **2** (the others are symmetry equivalent). The UD and UDU configurations are lowest in energy for these two compounds, which shows the antiferromagnetic coupling. For Mn_2O_2 (**1**), we compute an exchange coupling constant of $J = 319$ K (27.5 meV) from the PBE functional, which is in the right ballpark for manganese couplings of this type. The BP functional gives a quite similar result ($J = 313$ K). The computed Kohn−Sham energies for Mn_3O_4 (**2**) do not form an equidistant series. These energies can be fitted assuming an exchange coupling J' between the terminal manganese centers in addition to the coupling between adjacent ones. From the PBE energies one gets $J = 334$ K (28.7 meV) (similar to Mn_2O_2) and a weak antiferromagnetic coupling $J' = 30$ K (2.5 meV) between the terminal ions. The BP results are quite close ($J = 327$ K, $J' = 29$ K). The axial MAE is similar for the different configurations of a model (∼10% larger in absolute value for the high-spin configurations). The difference probably comes from the “leaking” of the spin density from different metal centers to same ligand atoms, especially the bridging oxygens.

The *broken symmetry* Kohn−Sham energies provide enough information to set up the isotropic Heisenberg Hamiltonian, and the energies of the true many-electron states can be computed. For Mn_2O_2 (**1**), one gets a singlet ground state ($S = 0, E = -6J$) and the lowest excited state is a triplet ($S = 0, E = -5J$). For Mn_3O_4 (**2**), the ground state is a quintet ($S = 2, E = -10J + 4J'$) followed by a triplet ($S = 1, E = -8J$). The MAEs from the *broken symmetry* calculations on the other hand are not directly

TABLE 2: Single-Ion ZFS Tensors $\mathbf{D}_i$ for Models 1 and 2 for Various Broken Symmetry Configurations (PBE Functional, Results from the BP Functional in Parentheses)

			D_i tensor components		
model	Ising configuration	center[a]	D_{zz}	D_{xx}	D_{yy}
1	UU[b]	Mn_1	−2.36 (−2.35)	+ 1.29 (+1.28)	+ 1.07 (+1.06)
	UD	Mn_1	−2.21 (−2.20)	+1.08 (+1.08)	+1.13 (+1.13)
2	UUU	Mn_1	−2.42 (−2.40)	+1.47 (+1.44)	+0.95 (+0.95)
		Mn_2	−2.49 (−2.46)	+1.31 (+1.29)	+1.18 (+1.17)
	UUD	Mn_1	−2.36 (−2.34)	+1.35 (+1.34)	+1.01 (+1.01)
		Mn_2	−2.31 (−2.29)	+1.07 (+1.06)	+1.24 (+1.23)
		Mn_3	−2.11 (−2.10)	+0.90 (+0.90)	+1.21 (+1.20)
	UDU	Mn_1	−2.16 (−2.15)	+1.01 (+1.01)	+1.15 (+1.14)
		Mn_2	−2.19 (−2.18)	+0.90 (+0.90)	+1.29 (+1.29)

[a] Only symmetry unique atoms shown. [b] “U/D” denotes “spin up” or “spin down” at the manganese centers.

TABLE 3: Relative Energies, ZFS Parameters *D* and *E* and Magnetic Anistropy (all values in K) for Low-Lying Spin States of Mn_2O_2 (1) and Mn_3O_4 (2), from a Spin Hamiltonian with Parameters Extracted from Kohn−Sham Calculations (PBE functional)[a]

	state		ZFS parameter		magnetic anisotropy	
model	S	E_{rel}	*D*	*E*	axial	in-plane
1	0	0	0.00	0.00	0.00	0.00
	1	319	+13.92	0.10	+6.96	0.05
	2	954	+1.42	0.01	+4.26	0.03
	3	1914	−0.66	0.00	−4.97	0.04
	4	3190	−0.71	0.02	−21.24	0.66
2	2	0	−4.58	0.13	−13.73	0.40
	1	548	−4.30	0.17	−2.15	0.08
	3	1002	−0.45	0.02	−3.39	0.16
	0	1126	0.00	0.00	0.00	0.00
	2	1216	+1.60	0.11	+4.80	0.32
	...					
	4	4466	−0.43	0.02	−6.09	0.27
	5	5224	−0.74	0.03	−16.65	0.59
	6	6012	−1.00	0.05	−32.99	1.76

[a] The strong exchange limit has been imposed.

related to true the ground state MAE, which for example vanishes for Mn_2O_2 (**1**) because it is a singlet. It becomes clear that the assumption[14] that all low-energy states have the same MAE makes absolutely no sense in this case. What one gets from *all* broken symmetry configurations is more or less the magnetic anisotropy of the high-spin state. In order to make progress within a density functional computational scheme, one must extract single-ion tensors $\mathbf{D}_i$ from the calculation such that one can set up the spin Hamiltonian (eq 4) and compute the MAE of the ground state of that Hamiltonian. One suggestion to extract such information comes from Baruah and Pederson.[23] Here, to extract a single-ion MAE tensor, the orbitals in the numerator of eq 6 are expanded in compact atom-centered basis functions and only those contributions are retained where all four basis functions are associated with that ionic center. Since our ZORA(MP) method,[17,18] unlike other implementations of ZORA, does not need a mapping of basis functions to atomic centers, we keep this property and use a technically different procedure to extract single-ion tensors by “switching off” the contributions to spin−orbit coupling from certain atoms (see above), that we have already used in ref 7. If we switch off the spin−orbit interaction at the manganese atoms, we get a vanishing MAE (<0.02 K) for both compounds. Doing the reverse experiment, and switching off spin−orbit coupling at all non-manganese atoms, one does not retrieve the magnetic anisotropy of the “full” calculation (for a detailed experiment, see ref 7). To extract a single-ion tensor associated with a specific metal ion, it is therefore suggested to “switch off” spin−orbit coupling at all *other* metal centers.

For the various *broken symmetry* configurations we have extracted the single-ion anisotropy of the manganese centers using this recipe. This gives single-ion MAE tensors which are divided by $S_i(S_i - (1/2))$ ($S_i = 2$ for Mn^{3+} centers) to produce the local $\mathbf{D}_i$ tensors. These tensors are diagnoal in our molecular frame, and the diagonal elements are presented in Table 2 for symmetry unique atoms. Note that the two terminal manganes atoms Mn_1 and Mn_3 become nonequivalent for the *broken symmetry* (hence the name!) configuration UDU and produce two different single-ion tensors.

Having evaluated the parameters of the spin Hamiltonian, we can now proceed and calculate the magnetic anisotropy energy and/or the ZFS energy levels. For the examples worked out here, the spacing of the energy levels of the Heisenberg Hamiltonian is much larger than the width of the ZFS multiplets, so we can assume the strong exchange limit and proceed as described above. Within the strong exchange limit, the final result is invariant with respect to a uniform scaling of the exchange coupling constants as long as their sign is not reversed. The famous $Mn_{12}O_{12}$ acetate molecule with its high degree of spin frustration is an example where the strong exchange limit is not valid. This case can be handled with the proposed method simply by a one-shot full diagonalization of the spin Hamiltonian. This is not difficult but the disadvantage is that then the energy levels can no longer be rationalized in terms of a **D** tensor of a single effective spin.

Because the single-ion tensors differ somewhat for different *broken symmetry* configurations, it is suggested to use the tensors extracted from the configuration closest in energy to the state under consideration (for ground states, the lowest-energy *broken symmetry* calculation). If we apply our procedure to model system **1**, we get zero magnetic anisotropy for the ground state (no matter how we choose the $\mathbf{D}_i$) because the ground state is a singlet. While it is of course pointless to *compute* the MAE of a singlet, it is assuring that our computational procedure correctly assigns zero anisotropy in this case. Since it might be interesting to see how different the magnetic anisotropy can be for the different spin states, we document in Table 3 the results for the low-energy spin states, as extracted from the spin Hamiltonian equation (4) and the single-ion tensors (PBE results) from Table 2. In the strong exchange limit, the results for Mn_2O_2 do not depend on the exchange coupling constant J, while those for Mn_3O_4 depend on the ratio J/J', which has been taken from the PBE results. The **D** tensors of all the states are diagonal in our Cartesian frame, and we give the axial and rhombic ZFS parameters D and E for the various states together with the axial and in-plane magnetic anisotropy. For Mn_2O_2 (**1**), we get zero anisotropy for the ground state singlet and the anisotropy of the high-spin ($S = 4$) state is close to the value computed for the UU configuration, which is a single Slater determinant spin eigenfunction. The small differences reflect the errors introduced by a reduction of the molecular properties to three effective spins. We see very significant variations of the magnetic anisotropy for the different spin states: for example, the two lowest excited states ($S = 1$ and $S = 2$) have a magnetic anisotropy with an easy plane instead of an easy axis, in other words, the lowest-energy component of the ZFS multiplet is the $M_S = 0$ state. Note that for the $S = 3$ state, we have extracted the $\mathbf{D}_i$ single-ion parameters from the UD configuration. Since energy expectation valus of both the UD and UU configuration have the same distance (1276 K) to the $S = 3$ state, we may extract $\mathbf{D}_i$ from either configuration. If we use the parameters from the UU configuration for this state, we get an axial anisotropy of −5.31 K and an in-plane anisotropy of 0.17 K.

For Mn_3O_4, we get 19 low-energy states, and some of them are rather close in energy (they become degenerate for $J' = 0$). In order not to overload the table, we document the magnetic anisotropy for the five lowest and the three highest states. Again we see interesting features, such as the reversal of the sign of the axial anisotropy for the lowest spin states. The lowest septet ($S = 3$) state has a lower magnetic anisotropy than the lowest quintet ($S = 2$) state, so the anisotropy is not a simple function of S. The calculated axial anisotropy of the high-spin ($S = 6$) state matches the Kohn−Sham result for the UUU configuration with a deviation <5%, which again can be used to assess the validity of the many-spin Hamiltonian (eq 4). For the highest $S = 4$ state, which is energetically closest to the UUD configuration, the question may arise which single-ion tensors $\mathbf{D}_i$ one should choose, because the UUD configuration breaks spatial symmetry and the tensors $\mathbf{D}_1$ and $\mathbf{D}_3$ are not properly related by symmetry. This is not a severe problem since the eigenfunctions of the spin Hamiltonian are spatially nondegenerate in our case, and therefore a correct symmetrization automatically takes place. If one does not impose the strong exchange limit, one may however want to do a symmetrization (of the nonequivalent tensors for symmetry equivalent atoms) beforehand.

Finally we investigated how the results for Mn_3O_4 obtained here depend on the values of the exchange coupling constants (more specifically, the ratio J/J'). We do so because the coupling constant between the terminal ions in Mn_3O_4 (**2**) looks somewhat dubious and has been extracted from the nonequidistance of the *broken symmetry* energies (see Table 1). Fortunately, the calculated magnetic anisotropy for the ground state of Mn_3O_4 (**2**) is rather insensitive to the value of the coupling constant J'. Keeping J fixed at 334 K and increasing J', the calculated magnetic anisotropy of the ground state does not change until $J' = (1/2)J = 168$ K, when the triplet becomes the ground state. If J' is smaller than 30 K or even negative, the multiplicity of the ground state as well as the calculated magnetic anisotropy does not change. What happens at $J' = 0$ is that the third ($S = 0$) and fourth ($S = 2$) excited states become degenerate, but this is of no concern for the ground state properties. On the whole, the ratio J/J' is not critical for the magnetic anisotropy.

Conclusions

A procedure for the calculation of magnetic anisotropy energies and zero field splitting parameters for multinuclear transition metal complexes with antiferromagnetic coupling has been proposed. The final results come from a spin Hamiltonian calculation and the parameters used to setup the Spin Hamiltonian are extracted from Kohn−Sham broken symmetry density functional calculations. This is formally an extension of the well-established procedure to extract exchange coupling constants from such calculations. Since the calculated magnetic anisotropy energies for the various broken symmetry solutions do not provide enough information, one has to extract single-ion information from the Kohn−Sham calculations. The procedure has been demonstrated using two simple bi- and trinuclear model systems, thus also providing a challenge to wave function based ab initio quantum chemistry to check whether the presented data is qualitatively correct.

If the spin-dipolar interaction is to be included in the calculation, the two-center terms have to be subtracted from the results for the broken-symmetry solutions before extracting single-ion tensors. This is necessary because we suggest to use a spin Hamiltonian with single-ion terms only. Subtracting the two-center spin-dipolar contribution from the *broken symmetry* results can be done using a point−dipolar approximation. At the very end, the contribution of this two-center term can be evaluated and added to form the final result, for any state under consideration, using a spin-dipolar approximation with effective atomic spin moments that can be obtained from the eigenfunctions of the Heisenberg spin Hamiltonian.

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Supporting Information Available: Details on how atomic spin−orbit contributions are "switched off" within the ZORA(MP) approach, on the basis set used, and the molecular structure of the two model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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