# Noncollinear Spins Provide a Self-Consistent Treatment of the Low-Spin State of a Biomimetic Oxomanganese Synthetic Trimer Inspired by the Oxygen Evolving Complex of Photosystem II

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Ⓢ *Supporting Information*

ABSTRACT: We employ noncollinear density functional theory to show that the low-spin state of Mn_3 in a model of the oxygen-evolving complex of photosystem II avoids frustrated spin coupling by adopting a noncollinear arrangement of spins, thereby lowering the energy by 7 kcal/mol. The high-spin state also has noncollinear spins. The optimum self-consistent field solutions for this multinuclear oxomanganese complex correspond to states that cannot be described by the unrestricted Slater determinants used in Kohn−Sham collinear density functional methods. This kind of spin coupling can be important in many open-shell systems, and the conventional collinear spin interpretation of chemical bonding in such systems should be viewed with caution.

SECTION: Energy Conversion and Storage
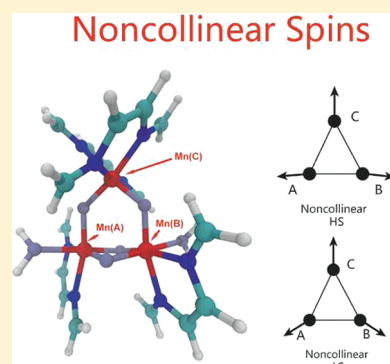
The photoenzymatic oxidation of water to dioxygen by the oxygen-evolving complex (OEC) of photosystem II (PS II) is a key step in the biological utilization of solar energy.[1−5] The necessity to understand fully the electronic structure of the high-valent polynuclear oxomanganese complex that constitutes the catalyst has stimulated considerable work on studies of oxomanganese complexes with structural features common to the OEC of PS II.[2−8] Density functional theory[9] (DFT) in the self-consistent-field (SCF) formalism of Kohn and Sham[10] (KS) has greatly advanced our ability to model transition-metal chemistry,[11] but it is limited by the need to approximate its central quantity, the exchange-correlation functional[9,10] (xcF), and the complexes under consideration have continued to pose challenges that are only partially solved.

In the KS formulation, DFT represents the density by a single Slater determinant with each electron in an up-spin or down-spin orbital. When the orbitals are not required to be doubly occupied, this is called an unrestricted determinant (UD); some states, such as open-shell singlets or doublets with three unpaired electrons, cannot be described by a UD. (We will call them non-UD-describable.) If all minority-spin electrons (β electrons) are in doubly occupied orbitals, then a UD always has $M_S = \pm S$, where M_S is the spin-component along the up−down axis and S is total spin; if, however, the UD has different orbitals for spin-up and spin-down electrons, then the UD is not a spin eigenfunction. The KS orbitals are found by an iterative SCF calculation. If the resulting orbitals occupied by the minority spins all have a high overlap with a corresponding majority-spin orbital (as in the variationally lowest-energy UD for Li atom, where the two 1s

orbitals are very similar), although the symmetry is broken, then in this Letter we will call this a spin-contaminated state to avoid confusion; it can still be a good approximation to a spin eigenfunction that is an eigenfunction of the real Hamiltonian. If, however, the corresponding orbitals are very different, for example, if they are located on different centers, then the solution is not a good approximation to any one real state, and it will be called a broken-symmetry (BS) state. A procedure,[11−13] which we will call the weighted-average BS method (because it treats the BS state as a weighted average of pure spin states), has shown the ability to reproduce some spectroscopic results on non-UD-describable low-spin (LS) systems with good accuracy,[13−21] and has gained increasing popularity.[22]

In the treatment of LS states in polynuclear transition-metal complexes by the weighted-average BS method, the LS state is not calculated self-consistently, but rather its energy is obtained by diagonalization of an effective Hamiltonian using coupling parameters that are calculated from other spin states (usually one state with the highest spin, together with one or more BS states formed by flipping the spins at some center, see Figure 2b for a simple illustration). (The BS states represent a mixture of the HS state and one or more non-UD-describable lower-spin states.) In this Letter, we differentiate the use of BS determinants in DFT, which can be called BS-DFT, from the more specific weighted-average BS method, which is a specific procedure for the
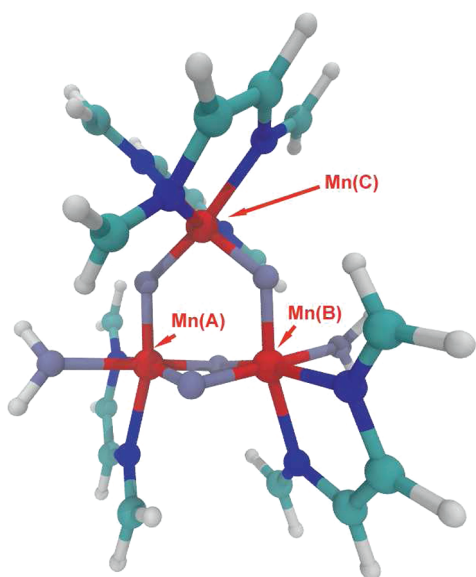
Figure 1. Structure of the Mn model trimer $[(Mn^{IV})_3O_4L_4(H_2O)]$, with L = N,N'-bis(methylene)-Z-1,2-ethenediamine, referred to as complex **1s** in the text.

construction of an energetic ladder; it involves the use of both BS-DFT and spin-symmetry-adapted DFT. Furthermore, even if it yields approximately correct energies in some cases, the weighted-average BS method or any other method based on single determinants formed from only spin-up and spin-down orbitals, does not provide a self-consistent approximation to wave functions for which the spins at the various atomic centers are not collinear (i.e., parallel or antiparallel).

An example of a complex where these considerations are very relevant is

$$[(Mn^{IV})_3O_4(bpy)_4(OH_2)_2]^{4+} \qquad (1)$$

which has Mn centers linked by μ-oxo bridges as in the "3 + 1 Mn tetramer"[4,5] of the OEC; this complex has been experimentally determined to have an LS ($S = 1/2$) ground state with more than one unpaired orbital and an HS ($S = 3/2$) first excited state with an energy difference ΔE (= $E_{LS} - E_{HS}$) of -0.2 kcal/mol.[7] (Another system, $[(Mn^{IV})_3O_4]^{4+}$, that also has a triangular Mn$_3$ core and a non-UD-describable LS ground state has $\Delta E = -0.3$ kcal/mol.[6]) In the present Letter, we consider the structure[23]

$$[(Mn^{IV})_3O_4L_4(H_2O)] \qquad (1s)$$

which is shown in Figure 1, where L is N,N'-bis(methylene)-Z-1,2-ethenediamine). This is a simplified version of **1**.

Label the three Mn atoms as A, B, and C, and let S_{AB} be the total spin of the two closest Mn atoms A and B, which are the ones in the $(\mu$-O)$_2$Mn$_2$ unit. Because A and B are closer to each other than to C, which is coupled to them by a O—Mn—O linkage, the EPR measurements[7] were interpreted by first coupling the spins of centers A and B and then coupling the total spin of AB with the spin of C. This analysis led to the AB subsystem of the LS state being in an $S_{AB} = 1$ state, with equivalent Mn^{IV} ions (that are likely to be both in a local HS state with $S_A = S_B = 3/2$ because this arrangement avoids pairing of d electrons on any Mn center). In addition, the total spin of the complex in the ground state was determined to be $S = 1/2$ and $S_C = 3/2$. The HS spin state with $S = 3/2$ is an excited state, again with all
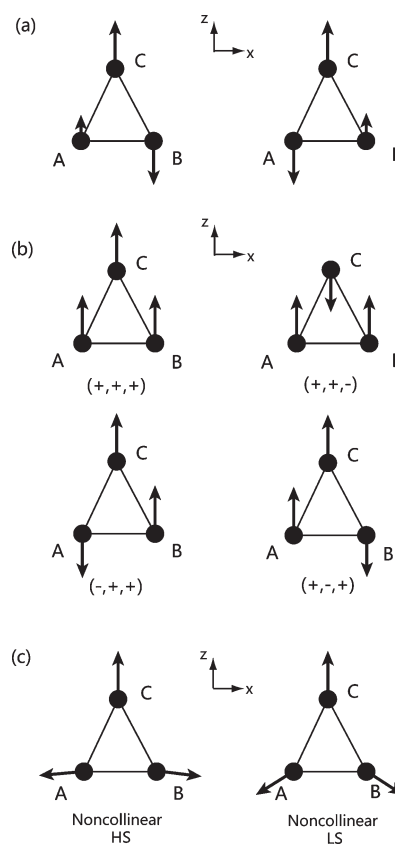
Figure 2. (a) Best LS that could be directly calculated by collinear DFT. A pair of d electrons on either A or B is forced to be paired. (b) Four spin states used for the collinear BS method, represented by their spin directions (+ is α spin, − is β spin) on three Mn atoms A, B, and C. Note that the (+,+,−) state is used for geometry optimization. (c) Directions of the Mn magnetic moments in **1s** as projected onto the plane of the Mn$_3$. The Mn$_3$ is in the xz plane, with the x axis parallel to the A—B axis. Note that the spin directions in the LS state (ground state) are close to the (+,+,−) state if the spins on the latter are all flipped.

three Mn^{IV} ions also in the local HS state ($S_A = S_B = S_C = 3/2$), but the AB subsystem is an $S_{AB} = 0$ state. On the basis of this analysis, neither the HS nor the LS state of the system is UD-describable.

If one tries to force KS DFT to describe a $S_{AB} = 1$ subsystem, then d electrons must be paired in either A or B, leading to $S_A = 1/2$, $S_B = 3/2$ or $S_A = 3/2$, $S_B = 1/2$, with opposite signs for M_S. (See Figure 2a.) This is the best result for the observed LS state that can be directly obtained by KS DFT without using the weighted-average BS method. (Note that this calculation uses BS-DFT and results in a BS state, but it does not include calculations of a series of spin states to obtain the effective Hamiltonian and then indirectly obtain the energy of the LS state so it is not an example of the weighted-average BS method.) As expected, this state with paired d orbitals is high in energy; it was found previously,[23] using the B3LYP[24] density functional, to give an LS state that is 22 kcal/mol higher than the HS state. This occurs because pairing two of the d electrons on one of the centers raises the energy much higher than the real LS state.

To understand the self-consistent treatment of the LS state that we will present here, we must consider the description of open-shell systems in wave function theory (WFT) and in a more complete version[25,26] of open-shell DFT. In WFT, one builds wave functions as a superposition of configuration state functions

(CSFs) that are themselves usually either single determinants or symmetry-adapted linear combinations of determinants. Each determinant is an antisymmetrized product of spin orbitals, each of which is a product of a spatial orbital (depending on electron position $\mathbf{r}$) and an eigenfunction of spin angular momentum corresponding to spin up (α) or down (β) along a chosen axis. One such determinant is not general enough to describe an arbitrary open-shell system, but a linear combination of α and β can represent spin angular momentum in an arbitrary direction; therefore, a linear combination of CSFs can represent a state with arbitrary magnetic properties. But reliable WFT calculations are impractical for large, complex systems, so we turn to DFT, which is usually carried out by the KS formalism based on a single reference determinant with the same electron density as the molecule under consideration. This would be exact if the exact xcF was known, but it is not.

However the main practical limitation of DFT is not always the approximate nature of the xcF. Because the electron density is represented by a single determinant, the generalization of the magnetic state must occur at the spin orbital level rather than by a superposition of CSFs, and a better treatment of open-shell systems involves generalizing the spin orbitals $\phi(\mathbf{r})\alpha$ or $\phi(\mathbf{r})\beta$ to more general spinors[25−27]

$$\theta = \phi_\alpha(\mathbf{r})\alpha + \phi_\beta(\mathbf{r})\beta$$

Such a determinant is even more unrestricted than a UD, and it is called a general determinant (GD); GDs can also be used in WFT.[28−31] Because θ (usually a complex function) can represent a spin in an arbitrary direction, the spins need not be aligned along a single axis, and the generalization is therefore called noncollinear DFT.[32,33] Noncollinear DFT has been applied to metals,[27,34,35] metal alloys,[36] and bare metallic clusters,[37−41] but its utility to overcome the limitations of the weighted-average BS method[16] has not been sufficiently appreciated for transition-metal chemistry.

The complex **1s** provides a prime example of an organometallic system where a noncollinear treatment can be useful. We show this by calculations with the Quantum Espresso program[42] with the local spin density approximation[43,44] for the xcF, a norm-conserving pseudopotential[45] with a nonlinear core correction,[46] a supercell of (70 bohr^3), a cutoff energy of 190 Ry, and the Makov−Payne correction[47] to account for the net charge of +4.

Spin−orbit coupling is neglected. Spin symmetry is not enforced; if it was, then the magnitude S of total spin would be 1/2 (LS) or 3/2 (HS). (The calculated value of $\langle S^2 \rangle$ is not reported here because the calculation of this quantity is not currently supported in the software we used.)

Geometries were optimized by ADF[48] using collinear calculations with the TZP basis for the spin state with $S_{AB} = 3$ and $S = 3/2$ (the $(+,+,-)$ state in Figure 2b). This choice is justified below; it yields A−B, B−C, and A−C distances of, respectively, 2.63, 3.20, and 3.20 Å, in good agreement with X-ray[7] results. This optimized geometry, which is used for all calculations reported in this Article, is given in the Supporting Information.

Our noncollinear solutions have all three Mn^{IV} ions in the local HS state ($S_A = 3/2$, $S_B = 3/2$, and $S_C = 3/2$). In LS ground state, the component of spin of the AB subsystem along the AB-to-C direction is approximately −1, whereas in the HS excited state, the component of spin of the AB subsystem along the AB-to-C axis is ∼0. The energetic results are in Table 1, and the local spins are in Table 2 and Figure 2.

Table 1. Calculated ΔE (kilocalories per mole) of 1s by Collinear BS DFT and Noncollinear DFT

software	method	ΔE
ADF	collinear weighted-average BS	−1.5
Quantum Espresso	collinear weighted-average BS	−1.6
Quantum Espresso	noncollinear	−0.2
experiment		−0.2

Table 2. Magnitudes and Directions of Local Spins on Mn Atoms

state	spin[a]			
	total	Mn(A)	Mn(B)	Mn(C)
noncollinear LS	0.45, −2	1.24, −114	1.25,111	1.22, −2
noncollinear HS	1.45,0	1.25, −96	1.26,98	1.23,0

[a] S, θ, where S is the magnitude of the expectation value of the spin, and θ is the angle in degrees between $\mathbf{S}$ and the z axis; all spins are in the xz plane. (See Figure 2.)

Consider first the collinear BS calculations, which are carried out using the weighted-average BS method that is described in detail elsewhere.[11−21] This method involves calculations on four UDs (Figure 2b) and phenomenological magnetic coupling constants J_{AB}, J_{BC}, and J_{AC} are calculated from the energy differences of these four calculations; then, the ground and excited state energies are obtained by direct diagonalization of an effective spin Hamiltonian. We used both ADF and Quantum Espresso to perform independently these weighted-average BS calculations, giving consistent results of $\Delta E = -1.5$ and -1.6 kcal/mol, respectively. Whereas the energetic results are reasonably close to experiment, as also reported by others,[20] the LS state is not calculated directly in this method but rather is obtained from a set of calculations on nonphysical states, in all of which the spins are collinear (up or down with respect to single axis). For the HS state of the weighted-average BS method, which is represented as either $(+,-,+)$ or $(-,+,+)$ in Figure 2, the spins on A and B cannot be simultaneously antiferromagnetically coupled to C, resulting in a kind of spin frustration. If a variational calculation that allows the spins to be noncollinear shows that indeed they are noncollinear in the LS or HS state or both, then the UD calculations upon which the weighted-average BS method rests do not contain the correct physics.

Consider next the calculations in which we allowed noncollinear spins. The magnetic moments used to initiate the SCF calculation are specified as 120° between A−B, A−C, and B−C, all in the xz plane. The HS and LS states are obtained by adding a penalty function to the total Hamiltonian to restrain the value of M_S to be approximately 3/2 and 1/2. Other initial magnetic moments configuration (for example, 140° between A−B and 110° between A−C and B−C) have also been tested and lead to the same HS and LS. (This shows that the final SCF state is not an arbitrary artifact of the initialization of the iterations.) Both the HS and LS states can be directly calculated self-consistently, and we find noncollinear spins in both states and ΔE equal to -0.2 kcal/mol, in good agreement with the experiment. Furthermore, centers A and B are treated nearly symmetrically; all three atomic spins are greater than one (avoiding the pairing of d orbitals), and spin frustration is eliminated.

When the spins are allowed to be noncollinear, the energy of the LS state is lowered by 7 kcal/mol relative to the best result that could be directly calculated by collinear DFT without BS (Figure 2a). For the HS state, noncollinear DFT also gives a state that is lower than the lowest HS obtained by BS-DFT, the $(+,-,+)$ state in Figure 2b; in particular, the lowering in this case is 2 kcal/mol.

Take the LS state as an example for more detailed discussion; when projected onto the xz plane (the y components are negligible in our self-consistent solution), the angle between the spin of A and that of B is $135°$, the angle between the spin of B and that of C is $113°$, and the angle between the spin of C and that of A is $112°$. Because they are all $>90°$, all three spin couplings can be described as more antiferromagnetic than ferromagnetic. Furthermore, because the local spins at the three atomic centers are not even approximately collinear, no version of KS DFT can approximate the wave function of such an LS state, and any KS calculation, including the previous and present BS calculations, because they are based entirely on collinear spins, contains a physically incorrect description.

Finally, we return to the choice of state used to optimize the geometry. Comparing Figure 2b to Figure 2c and noting that flipping all signs in any of the Figure 2b models does not change the state, we see that of the four states in Figure 2b the $(+,+,-)$ one is the one that most resembles the actual LS ground state. Therefore, we chose the $(+,+,-)$ state for geometry optimization.

The use of better density functionals for noncollinear calculations and the optimization of geometries with noncollinear calculations may further improve the quality of the calculations, and we look forward to being able to do those kinds of calculations, but the present calculations already demonstrate that noncollinear DFT provides a practical way to perform self-consistent calculations on organometallic complexes with noncollinear magnetic states. We conclude that both the HS and LS states of the Mn_3 core have noncollinear spins that can be treated self-consistently, and this brings a new element into the description of the magnetic coupling. Although the collinear weighted-average BS method in recent years has provided practical case-by-case workarounds for some specific systems, we anticipate that noncollinear spins may be a more powerful method for theoretical modeling of transition-metal chemistry, and the collinear model of open-shell states should be used with caution, especially in cases where the spin systems are strongly coupled.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Optimized geometry of **1s**; full citation of ref 42. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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