#### Supporting Information for: ,,Hyperfine Tensors for a model system for the oxygen evolving complex of photosystem II: calculation of the anisotropy shift that occurs beyond the strong exchange limit"

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# Contents

1	Molecular model for the oxygen evolving complex	$\mathbf{S2}$
	1.1 Cartesian Coordinates	S2
	1.2 Description and view of the molecular structure	S2
<b>2</b>	Spin Hamiltionan parameters	$\mathbf{S2}$
	2.1 Isotropic (Heisenberg) exchange coupling	S3
	2.2 Local hyperfine tensors	S3
	2.3 Scaling of local hyperfine tensors	S5
	2.4 Local zero field splitting tensors	S5
3	Spin projection coefficients for the strong exchange limit	$\mathbf{S7}$
4	Relative importance of zero field splitting at $\mathrm{Mn}^{\mathrm{III}}$ and $\mathrm{Mn}^{\mathrm{IV}}$	$\mathbf{S7}$
<b>5</b>	Coefficients $\Pi_{ik}$ (manuscript Eq. 9) calculated for the coupling constants	5
	from [S2]	<b>S</b> 9
6	References	$\mathbf{S9}$

# 1 Molecular model for the oxygen evolving complex

### 1.1 Cartesian Coordinates

The cartesian coordinates have been obtained from the supporting information of [S1]. This model is a simplification of the original Siegbahn model where coordinating amino acid residues have been reduced (e.g. the aspartate carboxylate side chain to acetate, histidine to imidazole).

Note that the mangenese atoms Mn1, Mn2, Mn3 and Mn4 are the atoms No. 6, 11, 13, 15 in the cartesian coordinate file deposited in the supporting information of [S1].

### **1.2** Description and view of the molecular structure

The following figure shows the  $C_{17}H_{37}CaMn_4N_3O_{24}$  molecular model system used in the present work. It consists of the  $CaMn_4$  core, five bridging oxygen atoms, an imidazole molecule, three bridging and three singly coordinating acetates, two hydroxyl ions (deprotonated water) coordinated to one of the Mn atoms, four water molecules not coordinated to manganese but bound via hydrogen bonds to the core, and one acetamide molecule hydrogen-bonded to one of these water molecules. The molecular model carries a single negative charge.



## 2 Spin Hamiltionan parameters

The many-spin Hamiltonian contributions regarded in this work are

$$\hat{H}_{MS} = \sum_{i,j} J_{ij} \vec{s}_i \cdot \vec{s}_j + \sum_i \vec{s}_i \cdot \mathbf{D}_i \cdot \vec{s}_i + \sum_{i,N} \vec{s}_i \cdot \mathbf{A}_{i,N} \cdot \vec{I}_N$$
(S1)

where the indices i, j run over the four spin centers and the index N runs over the hyperfine nuclei.  $\vec{s_i}$  is the single-center spin operator associated with spin center i, and  $\vec{I_N}$  is the nuclear spin of nucleus N. In the present case, the four spin centers are the four manganese ions and the four nuclei are the four manganese nuclei. Two-center contributions to zero field splitting (anisotropic exchange and spin-dipolar interactions) have not been regarded. Note that different conventions are used to write the isotropic Heisenberg coupling (first term), such that possibly the sign of the  $J_{ij}$  has to be reversed and/or a factor of 2 applied if these coupling constants are compared with other work.

#### 2.1 Isotropic (Heisenberg) exchange coupling

In the present work, we have used to sets of  $J_{ij}$  values from litarature sources. Both have been calculated using density functional theory and the TPSSh functional. The exchange coupling constants are documented in Table 4 of the manuscript which is repeated here for convenience. We also document the energy gap  $\Delta$  between the ground (doublet) and the first excited (quartet) state.

	$J_{12}$	$J_{13}$	$J_{14}$	$J_{23}$	$J_{24}$	$J_{34}$	$\Delta E$
Ref. [S1]	-18	-8	66	4	-44	-6	4
Ref. $[S2]$	-18	-20	68	16	-30	-6	11

#### 2.2 Local hyperfine tensors

In our previous work [S3] we have extensively described how to calculate the sixteen  $\mathbf{A}$  tensors that result for four spin centers and four magnetic nuclei from a set of *broken* symmetry calculations. The hyperfine tensors stem from quasirelatistic ZORA calculations. Starting from a scalar-relativistic calculation, the hyperfine tensors have been obtained by a second-order perturbational treatment where spin orbit coupling is the perturbation.

Note: The tensor  $\mathbf{A}(S = i, Nuc = N)$  describes the interaction of the electron at spincenter No. *i* with the nucleus No. *N*.

$$\mathbf{A}(S=1, Nuc=1)$$

3.57993	-6.17350	-102.11375	
0.23888	-26.16656	-6.20942	
-105.80934	0.16155	3.61918	

 $\mathbf{A}(S=2, Nuc=1)$ 

3.87440	0.74965	0.62803
0.76327	3.51285	0.73748
0.63083	0.72720	3.86843

$\mathbf{A}(S=3, Nuc =$	= 1)	
0.26645	0.02185	-0.03822
0.02485	0.64365	0.11294
-0.03625	0.11153	0.28993
$\mathbf{A}(S=4, Nuc =$	= 1)	
22.07128	-0.03315	1.17808
-0.01767	23.94872	0.70368
1.18405	0.68987	26.00653
$\mathbf{A}(S=1, Nuc =$	= 2)	
0.71991	0.65430	0.26469
0.63972	2.31901	0.79217
0.26353	0.80101	0.95479
$\mathbf{A}(S=2, Nuc =$	= 2)	
-124.03790	-4.06633	-0.88283
-4.00314	-136.37095	4.96329
-0.84500	4.93705	-127.53669
$\mathbf{A}(S=3, Nuc =$	= 2)	
12.89017	-1.62700	-1.25727
-1.60884	14.34435	-0.75498
-1.30698	-0.72920	13.17352
$\mathbf{A}(S = 4, Nuc =$	= 2)	
17.31643	1.98780	-0.34667
1.97931	17.26710	-2.48198
-0.34273	-2.46177	16.01267
$\mathbf{A}(S=1, Nuc =$	= 3)	
0.47142	0.19418	0.09756
0.19487	1.99905	0.28386
0.09842	0.28659	0.47126
$\mathbf{A}(S=2, Nuc =$	= 3)	
19.29185	-2.48501	-1.19536
-2.53712	19.15407	-2.96006
-1.17094	-3.00237	19.75238
$\mathbf{A}(S=3, Nuc =$	= 3)	
-139.60965	5.34856	2.14159
5.25835	-138.67622	0.95844
2.17776	1.08670	-137.02486

$\mathbf{A}(S=4, Nuc =$	= 3)	
-0.17255	-0.03069	0.04261
-0.03072	0.38353	-0.11659
0.04746	-0.12208	-0.11139
$\mathbf{A}(S=1, Nuc =$	= 4)	
12.18029	-0.27508	0.96293
-0.28831	13.37203	-0.53669
0.96009	-0.49756	15.66709
$\mathbf{A}(S=2, Nuc =$	= 4)	
7.94862	0.58669	0.82466
0.59882	8.85589	-1.30135
0.81922	-1.28530	6.95062
$\mathbf{A}(S=3, Nuc =$	= 4)	
-0.01626	-0.07381	0.03371
-0.07058	0.52706	-0.11190
0.03318	-0.11338	0.03698
$\mathbf{A}(S=4, Nuc =$	= 4)	
-136.41711	-3.83641	-1.93987
-3.79783	-139.72396	-4.85755
-1.89900	-4.80052	-136.93667

### 2.3 Scaling of local hyperfine tensors

There is ample evidence that density functional calculations considerably underestimate hyperfine coupling. Usually the isotropic part of local hyperfine tensors as obtained from a calculation are scaled, from calculation on mononuclear manganes complexes a scaling factor of 1.45 has been suggested [S4].

The tensors reported in the preceeding subsection are unscaled. Its isotropic part has been scaled by 1.45 before using them in the spin Hamiltonian. This means that if  $\lambda$  is the mean value of the diagonal elements of the unscaled tensor, scaling is accomplished by adding 0.45  $\lambda$  on each of the three diagonal elements.

### 2.4 Local zero field splitting tensors

Associated with each of the four spin centers (manganese ions) there is a local "on-site" zero field splitting tensor  $\mathbf{D}^{ii}$ .

 $\mathbf{D}^{11}$  (spin-orbit part), (D = -2.38, E = 0.02)

0.77674	0.18797	-0.02790
0.18797	-1.57139	0.05422
-0.02790	0.05422	0.79465

 $D^{11}$  (spin-dipolar part), (D = -0.40, E = 0.00) 0.12346 0.02433 0.00059 0.02433 -0.26779 -0.00058 0.00059 -0.00058 0.14433  $\mathbf{D}^{11}$  (total), (D = -2.78, E = 0.03)0.90020 0.21231 -0.02731-1.83918 0.21231 0.05364 0.05364 -0.02731 0.93898  $D^{22}$  (spin-orbit part), (D = -0.51, E = 0.16) -0.05021 0.01268 0.16886 0.01268 0.14752 -0.25520 -0.25520 0.16886 -0.09731  $D^{22}$  (spin-dipolar part), (D = -0.10, E = 0.03) -0.01816 0.01556 0.02721 0.01556 0.04375 -0.04676 0.02721 -0.04676 -0.02559  $\mathbf{D}^{22}$  (total), (D = -0.61, E = 0.19)-0.06838 0.02824 0.19607 0.19127 0.02824 -0.30196 0.19607 -0.30196 -0.12290 $D^{33}$  (spin-orbit part), (D = 0.32, E = 0.07) -0.02656 -0.16497 -0.07123 -0.164970.09519 -0.01141-0.07123-0.01141 -0.06863  $D^{33}$  (spin-dipolar part), (D = 0.07, E = 0.01) 0.00672 -0.03963 -0.00490 -0.03963 0.01258 -0.00536 -0.00490-0.00536 -0.01930  $\mathbf{D}^{33}$  (total), (D = 0.39, E = 0.08)-0.01984-0.20460 -0.07613 -0.20460 0.10777 -0.01677-0.07613 -0.01677 -0.08793  $D^{44}$  (spin-orbit part), (D = -0.47, E = 0.06) -0.046120.21185 -0.00051 0.21185 -0.129070.09153

-0.00051

0.09153

S6

0.17520

 $D^{44}$  (spin-dipolar part), (D = -0.07, E = 0.02)

-0.01104	0.03349	0.00811
0.03349	-0.00885	0.01981
0.00811	0.01981	0.01989

 $\mathbf{D}^{44}$  (total), (D = -0.54, E = 0.08)

-0.05717	0.24534	0.00761
0.24534	-0.13792	0.11134
0.00761	0.11134	0.19509

## 3 Spin projection coefficients for the strong exchange limit

Spin projection coefficients are documented for two sets of coupling constants  $J_{ij}$  documented in Sec. 2.1, taken from [S1] and [S2]. The spin projection coefficients calculated for the coupling constants from [S1] are (of course) identical to those reported in that work.

Source of $J_{ij}$	$P_1$	$P_2$	$P_3$	$P_4$
[S1]	1.477	-0.987	1.368	-0.857
[S2]	1.728	-0.893	1.113	-0.947

# 4 Relative importance of zero field splitting at $Mn^{III}$ and $Mn^{IV}$

Here we report the effective hyperfine tensors arising with multiplet mixing taken into account through leading (second) order perturbation theory, using the isotropic exchange coupling constants from [S2]. We report four sets of results, where we have (a) scaled down all ZFS tensors to zero, (b) scaled down the Mn<sup>III</sup> ZFS tensor ( $\mathbf{D}^{11}$ ) to zero but left the three Mn<sup>IV</sup> ZFS tensors ( $\mathbf{D}^{22}$ ,  $\mathbf{D}^{33}$ ,  $\mathbf{D}^{44}$ ) unmodified, (c) scaled down the three Mn<sup>IV</sup> tensors to zero but left the Mn<sup>III</sup> ZFS tensor unmodified, and (d) left all ZFS tensors unmodified. Note that the results from case (a) duplicate those of the strong exchange limit (left panel in Table 5 of the manuscript) while case (d) corresponds to the full perturbative treatment (central panel in Table 5 of the manuscript). The full set of data is presented here to demonstrate that cases (a) and (b) produce a similar anisotropy pattern, so so cases (c) and (d). This means that zero field splitting at the Mn<sup>III</sup> center dominates the anisotropy transfer.

(a). All ZFS tensors zero					
Mn	$A_{\rm iso}^{\rm eff}$	$T_1^{\rm eff}$	$T_2^{\rm eff}$	$T_3^{\rm eff}$	
1	-232	-52	-39	91	
2	169	-7	-2	9	
3	-246	-9	-2	11	
4	214	-5	-3	8	

	(b). Only	ZFS a	t Mn <sup>IV</sup>	•
Mn	$A_{\rm iso}^{\rm eff}$	$T_1^{\rm eff}$	$T_2^{\rm eff}$	$T_3^{\rm eff}$
1	-234	-55	-40	95
2	169	-11	2	10
3	-246	12	2	-15
4	214	-10	-2	12

(c). Only ZFS at Mn <sup>III</sup> .							
Mn	$A_{\rm iso}^{\rm eff}$	$T_1^{\rm eff}$	$T_2^{\rm eff}$	$T_3^{\rm eff}$			
1	-219	-20	-12	32			
2	172	-62	-59	121			
3	-246	57	53	-110			
4	214	-44	-36	80			

(d). All four ZFS tensors included.							
Mn	$A_{\rm iso}^{\rm eff}$	$T_1^{\rm eff}$	$T_2^{\rm eff}$	$T_3^{\rm eff}$			
1	-220	-24	-12	36			
2	171	-57	-53	111			
3	-246	54	45	-99			
4	214	-41	-35	76			

# 5 Coefficients $\Pi_{ik}$ (manuscript Eq. 9) calculated for the coupling constants from [S2]

Coefficients  $\Pi_{ik}$  (see Eq. 9) determining the tensorial spin projection coefficients within second-order perturbation theory (using Heisenberg exchange coupling constants from [S2]).

$\mathbf{k} =$	1	2	3	4
i=1	-0.554	-0.432	-0.640	-0.186
i=2	0.636	0.556	0.855	0.216
i=3	-0.487	-0.436	-0.683	-0.167
i=4	0.404	0.312	0.468	0.137

### 6 References

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