

Supporting materials

Electronic and spin structures of the CaMn_4O_x clusters in the S_0 state of the oxygen evolving complex of photosystem II Domain-based local pair natural orbital (DLPNO) coupled-cluster (CC) calculations using optimized geometries and natural orbitals (UNO) by hybrid density functional theory (HDFT) calculations

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SI Chemical physics of strongly correlated electron systems

SI.1 Hubbard model for strongly correlated electron systems

3d transition metal complexes such as manganese oxides (Mn_xO_y) have been generally regarded as strongly correlated electron systems (SCES), where four degrees of freedom play important roles as illustrated in Scheme I. First of all, fundamental concepts and theoretical models for SCES in Scheme I in the text are therefore revisited for explanation and understanding of structure and reactivity of the CaMn_4O_x cluster in OEC of PSII. This physical viewpoint provides a systematic understanding of chemical behaviors of 3d electrons in various metalloenzymes such as oxygen evolving complex (OEC) of PSII.

Historically, the orbital symmetry conservation rule by Woodward and Hoffmann^{s1},^{s2} was the guiding principle for theoretical investigation of chemical reactions in late 1960's and early 1970's. The Hückel^{s3} and extended Hückel^{s4} methods have been used for elucidation of spatially symmetry-adapted molecular orbitals (MO). Since then, the Woodward-Hoffmann rule based on the Hückel MO (HMO) and extended Hückel MO (EHMO) has been applied for elucidation and predictions of various types of concerted reactions of closed-shell systems characterized with weak electron correlations. The concept of the orbital symmetry conservation is consistent with the so-called Noether's theorem relating with the symmetry and conservation law in the mathematical physics^{s5}.

On the other hand, HMO and EHMO obtained by neglecting the electron repulsion effects are not sufficient enough for MO-descriptions of symmetry-forbidden radical reactions because of lack of spin concepts. In early 1970's, we searched appropriate MO-models including the electron repulsion effects explicitly for diradicals with the singlet and triplet spin states, and found that Hubbard^{s6}, Kanamori^{s7} and Gutzwiller^{s8} already proposed effective model Hamiltonians involving the electron repulsion effects with different spins. The Hubbard Hamiltonian was written in the second quantization notation including electron spin σ in the field of the solid state physics.

$$H = \sum_{i,j,\sigma} -t_{ij}(C_{i,\sigma}^+ C_{j,\sigma} + C_{j,\sigma}^+ C_{i,\sigma}) + \sum_{i,j} U_{i,j} n_{i,\sigma} n_{j,\tau} \quad (\text{s1})$$

where $C_{i,\sigma}^+$ denotes the operator which create an electron with $\sigma(\tau) = \uparrow, \downarrow$ at site i , and t_{ij} is the transfer integral for electron delocalization. The corresponding annihilation operator is $C_{i,\sigma}$, and the $n_{i,\sigma} = C_{i,\sigma}^+ C_{i,\sigma}$ is the spin density operator for spin σ on the i -th site. These fermion operators obey the canonical anti-commutation relations.

$$\{C_{i,\sigma}^+, C_{j,\tau}\} = \delta_{ij}\delta_{\sigma\tau}, \{C_{i,\sigma}^+, C_{j,\tau}^+\} = \{C_{i,\sigma}, C_{j,\tau}\} = 0 \quad (\text{s2})$$

The transfer integrals of the on-site (t_{ii}) and nearest sites (t_{ij}) are chemically referred to as the Coulomb integral ($-\alpha_{ii}$) and resonance integral ($-\beta_{ij}$) in the HMO model.^{s3, s4} The on-site (U_{ii}) and inter-site (U_{ij}) Coulomb repulsion integrals play important roles in the Hubbard model.

SI.2 Broken-symmetry solution of the Hubbard model for diradicals

The Hubbard model was introduced for theoretical investigation of strongly correlated electrons systems (SCES) with narrow energy bands in the solid state physics.^{s6-s8} On the other hand, we used the Hubbard model for molecules with narrow orbital energy gaps, for which the electron repulsion effect (U) plays an important role.^{s9, s10} In 1973, the Hubbard model for the two-center two-electron system [2e, 2o] was first solved analytically to understand the essential role of the electron delocalization against the electron repulsion in chemical bonding.^{s9, s10} To this end, the one (order) parameter is defined to express the magnitude of the chemical bonding.

$$x = t/U = -\beta/U \quad (\text{s3a})$$

The normalized total energy of the restricted Hartree-Fock (RHF) solution (E_{RHF}) for the closed-shell bond of the homo-polar [2e, 2o] system is given by

$$E_{\text{RHF}} = \frac{E(\text{RHF}) - 2\alpha}{U} = -2x + \frac{1}{2} \quad (\text{s4a})$$

where α denotes the aforementioned Coulomb integral for the HMO model. On the other hand, the spin-polarized unrestricted Hartree-Fock (UHF) solution emerges in the weak covalent bonding region as follows.

$$E_{\text{UHF}} = \frac{E(\text{UHF}) - 2\alpha}{U} = -2x^2 \quad (x \leq 1/2) \quad (\text{s4b})$$

The bifurcation point from RHF to UHF is given by $x = 1/2$, where the HOMO-LUMO energy gap (-2β) becomes equivalent to the on-site repulsion integral U . This means chemically a conversion from a closed-shell covalent bond; M–M to an open-shell singlet diradical bond; $\uparrow \bullet \text{M} \dots \text{M} \bullet \downarrow$. One of such examples is the dissociation of $(\text{OC})_5\text{Mn} - \text{Mn}(\text{CO})_5$ into $(\text{OC})_5\text{Mn} \bullet + \bullet \text{Mn}(\text{CO})_5$. Therefore, the small HOMO-LUMO energy gap obtained by the HMO model is also regarded as a chemical index for conversion from the non-radical covalent bond to the diradical bond. The

HOMO-LUMO mixing procedure^{s10} in eq. (s5) was proposed to obtain the UHF molecular orbitals (MO) in the instability region ($x \leq 1/2$) as shown in Fig. S1.

$$\psi^+ = \cos \theta \phi_{HOMO} + \sin \theta \phi_{LUMO} \quad (s5a)$$

$$\psi^- = \cos \theta \phi_{HOMO} - \sin \theta \phi_{LUMO} \quad (s5b)$$

where the mixing parameter (θ) was determined by the UHF MO calculations. The UHF MOs obtained by the mixing are often spatially symmetry-broken because the HOMO and LUMO have the different spatial symmetry. The orbital bifurcation point shifts to a weak bond region than that of UHF in the case of the hybrid UHF and unrestricted Kohn-Sham (UKS)-type density functional theory (DFT) methods because of the reduction of the repulsion integral. The unrestricted UHF, UDFT and related methods permitting eq. (s5) are now referred to as the broken-symmetry (BS) methods.

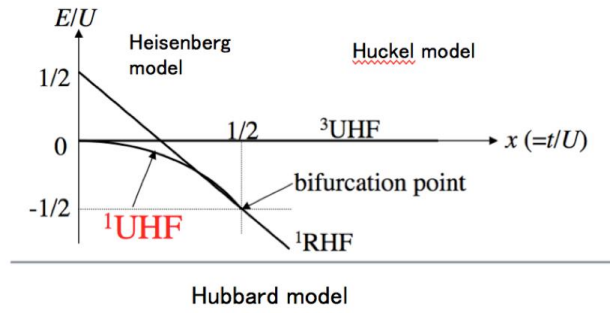


Fig. S1 The renormalized total energy curves by the RHF (non-radical) and UHF solutions (diradical) on the basis of the Hubbard model^{s9, s10}. The HOMO-LUMO mixing occurs in the region ($x < 1/2$), providing local spins for which spin Hamiltonian (Heisenberg) model is often employed.

In 1980's, we applied the Hubbard model for elucidation of characteristic variation of the nature of the transition metal (M) oxo (O) bonds (M=O) with the changes of the covalent bonding parameter (x) and ionic parameter (y) defined by^{s11}

$$y = (\alpha_M - \alpha_O)/U \quad (s3b)$$

where α_M and α_O denote the Coulomb integrals for the transition metal and oxygen sites, respectively. The strong covalent $d\pi$ - $p\pi$ bond (M=O) was emerged for the large x ($\gg 1/2$) and small ionic region ($y \sim 0$). On the other hand, the orbital bifurcation via the $d\pi$ - $p\pi$ HOMO and $d\pi$ - $p\pi^*$ LUMO mixing occurs in the small x ($< 1/2$) and small y (~ 0)

region, providing the metal-oxide diradical ($M\bullet\cdots\bullet O$) bond, where the $d\pi$ and $p\pi$ electrons are largely localized on the metal and oxygen sites, respectively (see Fig. S5 later). The oxygen site exhibited the oxyl-radical character responsible for the radical reactivity.^{s11} One of such examples was the high-valent Mn-oxo ($Mn(IV)\bullet\cdots\bullet O$) bond at that time. The inter-site one-electron transfer (OET) was induced with the increase of the ionic parameter (y), providing the zwitterionic (ZW) bond ($M^+\cdots^-O$) ($y \sim -1$) or ($M^-\cdots^+O$). The former ZW bond was realized in the case of early transition-metal oxo bonds such as $Ti(IV)^+O^-$, which were responsible for the ionic reactivity. Therefore, photo-induced back charge transfer was necessary for generation of the oxyl radical character: $Ti(III)\bullet\cdots\bullet O$ responsible for the radical reactivity in the excited state. Thus, the Hubbard model was effective for theoretical understanding of structure and reactivity of the transition-metal oxo bonds.

SI. 3 Resonating broken-symmetry method and necessity of spin projection

The broken-symmetry (BS) solution is often related to the true phase transition of infinite systems in the solid state physics. However, the BS solution is only responsible for strong electron correlations in the case of finite systems such as the $CaMn_4O_x$ cluster. Indeed, the concept of resonance plays an important role for recovery of the broken symmetry (BS) in finite systems without phase transition. For example, the UHF-I solution with the $\uparrow\bullet M\cdots M\bullet\downarrow$ spin configuration is degenerated in energy to the other UHF solution; UHF-II with the $\downarrow\bullet M\cdots M\bullet\uparrow$ spin configuration. Therefore, the quantum mechanical resonance between them occurs, affording the pure singlet and triplet diradical states. The normalized energy for the pure singlet diradical state, namely singlet projected UHF (PUHF), is given by^{s10, s12}

$$E_{PUHF} = \frac{E(UHF) - 2\alpha}{U} = \frac{-4x^2}{1+4x^2} \quad (s6)$$

The normalized pure triplet energy is zero, $E_{\text{triplet}} = 0$, indicating the no bond state. On the other hand, the 2×2 configuration interaction (CI) corresponds to the full CI for the $[2e, 2o]$ model. The normalized total energy for the singlet state is given by

$$E_{CI} = \frac{1}{2} (1 - \sqrt{16x^2 + 1}) \quad (s7)$$

Therefore, the PUHF energy is almost equivalent to that of the CI in the weak bond region, namely diradical region.

$$E_{PUHF} \approx E_{CI} \approx -4x^2 \quad (\text{s8})$$

The magnitude of the UHF energy is reduced to the one half of the PUHF energy (see eq. (s4b)) because of the contamination of the triplet configuration with $E_{\text{triplet}} = 0$, indicating the necessity of spin projection, namely recovery of broken symmetry (BS).^{s9-s12} This is the reason why we perform the spin projection for the BS solution. Thus, the simple Hubbard model has been useful for elucidation and understanding of characteristic behaviors of RHF, UHF, PUHF and CI descriptions of the chemical bond for homo-polar [2e, 2o] systems.^{s12}

SI.4 Heisenberg models for exchange-coupled systems

The Hubbard model provides local electrons with spins in the instability region in Fig. S1. Therefore, it is often transformed into the Heisenberg spin Hamiltonian model for theoretical description of spin degree of freedom, namely effective exchange interactions between local spins, in strongly correlated electron systems (SCES) in Scheme I. To this end, the Hubbard Hamiltonian is transformed into the spin Hamiltonian model^{s13, s14} based on the second quantization formula of the spin operator S_i .

$$H_{ij} = -2J_{ij}S_i \cdot S_j \quad (\text{s9})$$

where J_{ij} is the effective exchange integral given by the Hubbard Hamiltonian in eq. (s1). The total energies of the singlet and triplet states of the binuclear open-shell systems on the Heisenberg model are given by

$${}^1E_{\text{spin}} = {}^1\langle H_{ij} \rangle = \frac{3}{2}J_{ij}, \quad {}^3E_{\text{spin}} = {}^3\langle H_{ij} \rangle = -\frac{1}{2}J_{ij} \quad (\text{s10})$$

The energy gap between the singlet and triplet states is given by

$${}^1E_{\text{spin}} - {}^3E_{\text{spin}} = 2J_{ij} \quad . \quad (\text{s11})$$

where equation (s11) for the J value is often referred to as the chemist's notation. The J value was often expressed by the perturbation method as follows:

$$J_{ij} = \frac{{}^1E_{\text{spin}} - {}^3E_{\text{spin}}}{2} = \frac{-4x^2 - 0}{2} = \frac{-2t_{ij}^2}{U} \quad (\text{s12})$$

where $U = U_{ii} = U_{jj}$. The J -value becomes zero at the dissociation limit ($t_{ij} = 0$) of the covalent bond.

The Hubbard models for transition metal complexes are often transformed into the Heisenberg spin Hamiltonian. To this end, the above [2e, 2o] model can be

generalized in the case of A- and B-electrons at the sites a and b, where A(B)-electrons are parallel at the a(b) site because of the Hund rule, namely the local high-spin configuration by the on-site exchange integral (K_{ii}). One of such examples is the quadruple Cr-Cr bond: $L_4Cr \equiv CrL_4$ described with 8-electrons and 8-orbitals [8e, 8o] model. The effective exchange integrals defined by each orbitals (i, j) are approximated by the orbital averaged exchange integrals by neglecting the K_{ii} term as follows.

$$H_{ab} = -2 \sum_i \sum_j J_{ij} S_i \cdot S_j = -2J_{ab} S_a \cdot S_b \quad (s13a)$$

where

$$S_a = \sum_i S_i \ (i = 1, 2, \dots, A), \ S_b = \sum_j S_j \ (j = 1, 2, \dots, B) \quad (s13b)$$

Therefore, the Heisenberg models for polyradical species^{s15, s16} are generally given by

$$H = - \sum_{a>b} 2J_{ab} S_a \cdot S_b \quad (s14)$$

where J_{ab} is the orbital-averaged effective exchange integral between the spin sites a and b with total spin operators S_a and S_b .

SI. 5 Derivations of computational schemes of the effective exchange integrals

In early 1980s, J_{ab} value in eq. (s14) was often regarded as an empirical parameter, which was to be determined so as to reproduce the magnetic properties of molecule and molecular assemblies.^{s13, s14} Therefore, it was a challenge to discover practical and convenient methods for theoretical computations of the J values. Since then, several computational schemes of the J values have been proposed. To this end, the exchange split energy for the dimers are given by^{s11}

$$^{2i+1}E(HB) = -J_{ab}[i(i+1) - S_A(S_A+1) - S_B(S_B+1)] \quad (s15)$$

where S_A and S_B are the magnitude of spin operators S_a and S_b , respectively, and i is the magnitude of the total spin operator S_{total} .

$$i = S_A - S_B, S_A - S_B + 1, S_A - S_B + 2, \dots, S_A + S_B \quad (s16)$$

Therefore, energy levels of spin multiplettes are necessary to obtain J -values.

First of all, we calculated the effective exchange integrals within the spin-projected unrestricted Hartree-Fock (PUHF) approximation. To this end, the singlet state ($S=0$) is first examined. The UHF molecular orbitals in eq. (s5) were generally extended for the singlet ground state of the multi-electron systems as^{s13, s11}

$$\psi_n^+ = \cos \theta_n \phi_n + \sin \theta_n \phi_n^* \ (n = 1, 2, \dots) \quad (s17a)$$

$$\psi_n^+ = \cos \theta_n \phi_n - \sin \theta_n \phi_n^* \ (n = 1, 2, \dots) \quad (s17b)$$

where ψ_n^+ and ψ_n^- are the n -th bonding and antibonding approximated natural orbitals. The singlet UHF solution is described by a superposition of the $(n+1)$ PUHF solutions as

$$^1\Psi = |\psi_1^+ \alpha \psi_1^- \beta \psi_2^+ \alpha \psi_2^- \beta \cdots \psi_n^+ \alpha \psi_n^- \beta| = \sum_{i=0}^n C(2i+1)^{2i+1} \Phi(\text{PUHF}) \quad (\text{s18})$$

where $C(2i+1)$ and $^{2i+1}\Phi(\text{PUHF})$ are the expansion coefficient and the PUHF wave function for the $(2i+1)$ spin state, respectively. The total energy and total spin eigenvalue of the UHF solution can be rewritten with those of the $(n+1)$ PUHF solutions as

$$^1E(\text{UHF}) = \sum_{i=0}^n C^2(2i+1)^{2i+1} E(\text{PUHF}) \quad (\text{s19a})$$

$$^1\langle \hat{S}^2 \rangle(\text{UHF}) = \sum_{i=0}^n C^2(2i+1)^{2i+1} i(i+1) \quad (\text{s19b})$$

$$\sum_{i=0}^n C^2(2i+1) = 1 \quad (\text{s19c})$$

The spin contamination is negligible for the highest spin state $(2i+1)$ since

$$^{2i+1}E(\text{UHF}) \approx ^{2i+1}E(\text{PUHF}) \quad (\text{s20a})$$

$$^{2i+1}\langle \hat{S}^2 \rangle(\text{UHF}) = ^{2i+1}\langle \hat{S}^2 \rangle(\text{PUHF}) \quad (\text{s20b})$$

In order to calculate the J_{ab} value, the ^1UHF (eq. s19a) and $^{2i+1}E(\text{UHF})$ (eq. s20a), the energy levels are formally rewritten by using the Heisenberg energy levels given by eq. (s15)

$$\begin{aligned} ^1E(\text{UHF}) &= \sum_{i=0}^n C^2(2i+1) \left\{ -J_{ab} \left[i(i+1) - 2 \binom{n}{2} \binom{n}{2} + 1 \right] \right\} \\ &= -J_{ab} ^1\langle \hat{S}^2 \rangle(\text{UHF}) + J_{ab} n \left(\frac{n}{2} + 1 \right) \end{aligned} \quad (\text{s21a})$$

$$^{2i+1}E(\text{UHF}) = -J_{ab} n(n+1) + J_{ab} n \left(\frac{n}{2} + 1 \right) \quad (\text{s21b})$$

The effective exchange integral J_{ab} is obtained from eq. (s21a) and (s21b) as follows.

$$J_{ab} = \frac{^1E(\text{UHF}) - ^{2i+1}E(\text{UHF})}{n(n+1) - ^1\langle \hat{S}^2 \rangle(\text{UHF})} = \frac{^1E(\text{UHF}) - ^{2i+1}E(\text{UHF})}{^{2i+1}\langle \hat{S}^2 \rangle(\text{UHF}) - ^1\langle \hat{S}^2 \rangle(\text{UHF})} \quad (\text{s22a})$$

The spin projected UHF (PUHF) combined with the Heisenberg model can be applied to the unrestricted Hartree-Fock-Slater (UHFS) and Kohn-Sham (KS) density functional theory (DFT) methods, and hybrid HF and DFT (HDFT) methods such as UB3LYP since these methods are based on the single Slater determinant. Therefore, these methods are often referred to as the broken-symmetry (BS) method because of the use of BS orbitals in eq. (s17). The eq. (s22a) can be generalized to lowest-spin (LS) and the highest-spin (HS) states as follows.^{s11}

$$J_{ab} = \frac{LS_E(X) - HS_E(X)}{HS\langle \hat{S}^2 \rangle(X) - LS\langle \hat{S}^2 \rangle(X)} \quad (X = \text{BS, MR-CI, etc.}) \quad (\text{s22b})$$

Equations of (s22a) and (s22b) can be used for beyond BS methods such as MR CI because of the spin projection. Therefore, we have derived a general equation for the computation of J values with the BS HF solutions followed by quantum resonance: the AP procedure.^{s11} The denominators in eq. (s22b) were different among several equations proposed by other groups^{s17-s23}: details of derivations of other formula are given in our papers.

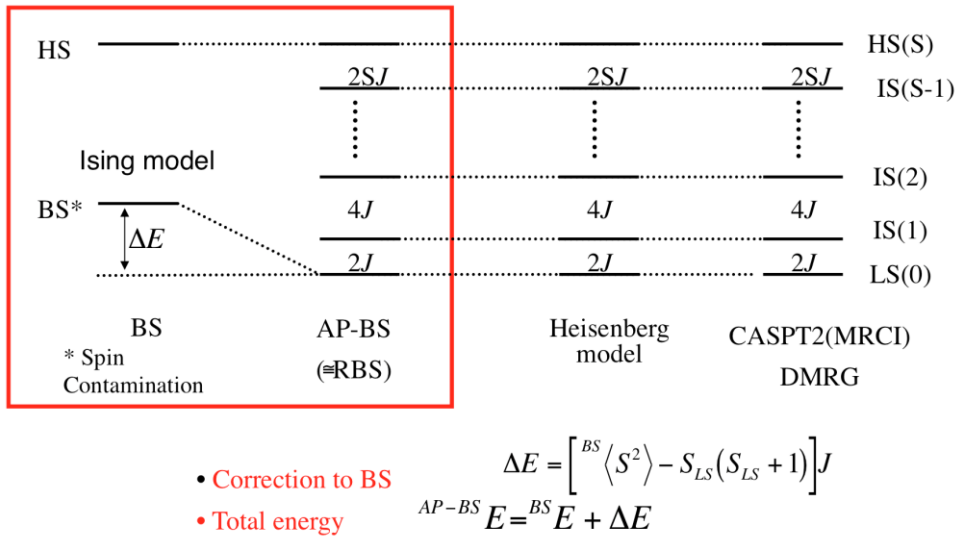


Fig. S2 Energy levels by the Heisenberg model, BS, AP-BS and CI.

SI.6 Derivations of general projection procedures for poly-nuclear systems

The projection scheme for two site models in eq. (s22a) was generalized to multi-sites systems^{s24}. To this end, the denominator in eq. (s22a) was expressed by the spin correlation function.

$$\begin{aligned} {}^{HS}\langle S^2 \rangle_{BS} &= {}^{HS}\langle (S_a + S_b)^2 \rangle_{BS} = \langle S_a^2 \rangle_{BS} + \langle S_b^2 \rangle_{BS} + {}^{HS}\langle S_a \cdot S_b \rangle_{BS} \\ &= S_A(S_A + 1) + S_B(S_B + 1) + {}^F\langle S_a \cdot S_b \rangle_{BS} \end{aligned} \quad (\text{s23a})$$

$$\begin{aligned} {}^{LS}\langle S^2 \rangle_{BS} &= {}^{LS}\langle (S_a + (-S_b))^2 \rangle_{BS} = \langle S_a^2 \rangle_{BS} + \langle (-S_b)^2 \rangle_{BS} + {}^{LS}\langle S_a \cdot -S_b \rangle_{BS} \\ &= S_A(S_A + 1) + S_B(S_B + 1) + {}^{AF}\langle S_a \cdot -S_b \rangle_{BS} \end{aligned} \quad (\text{s23b})$$

where the ferromagnetic (F) and antiferromagnetic (AF) spin correlation functions are defined by^{s24}

$${}^F\langle S_a \cdot S_b \rangle_{BS} = |S_A||S_B|, \quad {}^{AF}\langle S_a \cdot -S_b \rangle_{BS} = -|S_A||S_B| - S_B T^2 \quad (\text{s24})$$

The ferromagnetic (F) spin correlation (SC) function is given with the simple product of

spins. The anti-ferromagnetic (AF) SC function is simply expressed by the $-|S_A||S_B|$ as in the case of the classical spin model if the average orbital overlap (T) between the spin polarized orbitals in eq. (s18) is zero. However, the T -value is not zero in the case of AF pair in general. Therefore, the denominator in eq. (s22a) is expressed by

$$^{HS}\langle S^2 \rangle_{BS} - ^{LS}\langle S^2 \rangle_{BS} = 2^{LS}\langle S^2 \rangle_{BS} - 2^{AF}\langle S_a \cdot S_b \rangle_{BS} = 4|S_A||S_B| + 2S_B T^2 \quad (s25a)$$

where the second term corresponds to the quantum orbital overlap correction.

The spin projection scheme based on the SC function is easily extended to the multi-site spin systems. To this end, the total energy of the broken-symmetry (BS) solution for the total spin configuration X is formally expressed as follows.

$$^X E_{BS} = E_{const} - \sum_{a>b} 2J_{ab} \langle S_a \cdot S_b \rangle_{BS} \quad (s26)$$

On the other hand, the total spin angular momentum obtained by the BS solution is given by

$$\begin{aligned} ^X \langle S^2 \rangle_{BS} &= ^X \langle (\sum S_a)^2 \rangle_{BS} = \sum \langle S_a^2 \rangle + 2 \sum \langle S_a \cdot S_b \rangle_{BS} \\ &= \sum S_a(S_a + 1) + 2 \sum \langle S_a \cdot S_b \rangle_{BS} \end{aligned} \quad (s25b)$$

The total energy $^X E_{BS}$ and total spin angular momentum $^X \langle S^2 \rangle_{BS}$ obtained by several BS solutions ($X = 1, 2, \dots$) are used to determine the effective exchange integrals (J_{ab}) and SC functions ($\langle S_a \cdot S_b \rangle_{BS}$). The J_{ab} -values obtained by the F and AF SC functions are formally expressed by^{s21}

$$J_{ab} = \frac{^{LS}E_{BS} - ^{HS}E_{BS}}{2^F \langle S_a \cdot S_b \rangle_{BS} - 2^{AF} \langle S_a \cdot S_b \rangle_{BS}} \quad (s27)$$

The equation (s27) was successfully applied to the investigation of the magnetism of Ni₉ and Fe₇Mo cluster.^{s24} The J_{ab} -values in Table 4 in the text were obtained using eq. (s27).

SI.7 Importance of electron correlation effects for 3d metal oxides

In 1980s, the 3d transition metal oxo (M=O)^{s11}, metal peroxo (M–O–O) and metal hydroperoxide compounds^{s25-s29} were investigated as active catalytic sites for oxygenation reactions as illustrated in Fig. S3. On the other hand, 3d transition metal oxides were investigated as magnetic materials at that time. Surprisingly, Bednorz and Müller^{33, s30} discovered the high- T_c superconductivity of the copper oxides such as Ca-doped Ln_{2-x}Ca_xCuO₄ solid, which was investigated as catalysts for oxygenation reactions. The precursor compound Ln₂CuO₄ was the antiferromagnetic (AF) insulator characterized by the spin correlation functions observed by the neutron diffraction

experiments.^{34, s31} On the other hand, EHMO and pure DFT indicated that the Ln_2CuO_4 was normal metal without the band gap in contradiction to the experiments. The electron repulsion effect (U) could not be neglected for Ln_2CuO_4 .^{s32} In fact, the pure DFT (LSD) plus on site U model (LSD + U) was crucial for Ln_2CuO_4 .^{35, s12, s32} Thus, the electron repulsion effect plays an important role for some of 3d transition metal oxides, which are often referred to as the strongly correlated electron systems (SCES) in general.

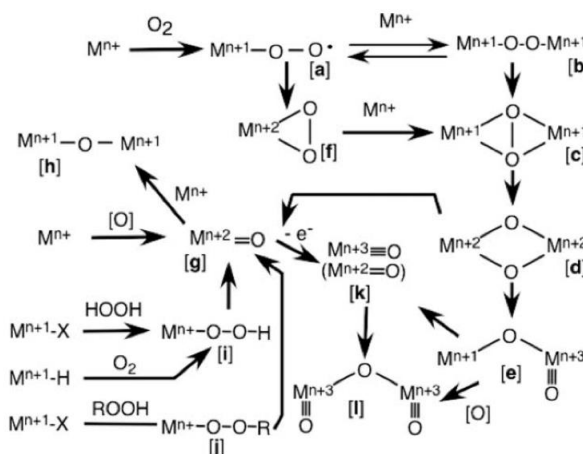


Fig. S3 3d transition metal oxides for oxygenation reactions. The structure and reactivity of metal-oxo [g, k], metal-hydro-peroxide [i, j], etc. were investigated in refs. s25-s29.

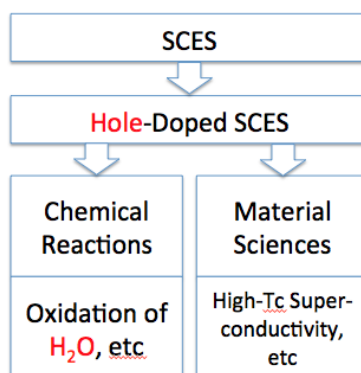


Fig. S4 Hole-doped SCES play important roles in both chemical reactions such as water oxidation and material sciences such as high- T_c superconductivity.

Figure S3 summarizes several kinds of 3d transition metal oxygen compounds, which are characterized as SCES in our theoretical viewpoint in Scheme I. The hole-doped copper oxides exhibit dual characteristics: (a) oxygenation catalysts and (b)

high- T_c superconductivity. The doped holes play important roles for emergence of both phenomena. Thus, important chemical reactivity and properties are expected for other 3d transition metal oxygen compounds. In this paper, the catalytic site for water oxidation in OEC of PSII is regarded as the Ca-doped manganese oxide, CaMn_4O_x , as shown in Fig. 1 in the text. From this theoretical viewpoint, catalytic activity for water oxidation and colossal magneto resistance of the Ca-doped Mn-oxides can be understood on the common physical basis.³²

Figure S5 illustrates the broken-symmetry (BS) orbitals for the high-valent $\text{M}=\text{O}$ bond (**k** in Fig. S3) by the HOMO-LUMO mixing in eq. (s5), which are mainly localized on the M- and O-site respectively, indicating the oxyl-radical property^{s11}: $\bullet\text{M}-\text{O}\bullet$. This finding was our starting point for our theoretical investigations of oxygenation reactions by 3d transition metal oxides. On the other hand, the HOMO-LUMO mixing for the $\text{M}-\text{O}-\text{M}$ bonds (**h** in Fig. S3) provide the BS orbitals for the $\bullet\text{M}-\text{O}-\text{M}\bullet$ open-shell configuration as shown in Fig. S7. BS methods are applicable to elucidation of structure and reactivity of other transition metal oxides, which are characterized as SCES in Scheme I. Thus, the systematic view in Figs. S3 and S4 may be applicable for design of new catalysts consisted of 3d electron systems.

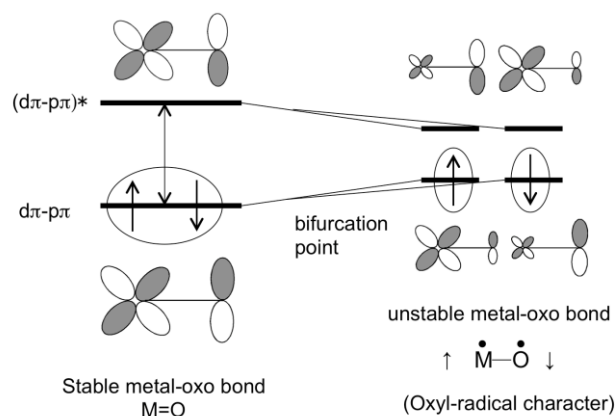


Fig. S5 The HOMO-LUMO mixing for the $\text{M}=\text{O}$ species with small energy gap provides the broken-symmetry (BS) orbitals which are mainly localized on the M- and O-sites, respectively, in accord with the oxyl-radical character $\bullet\text{M}-\text{O}\bullet$.^{s11}

References

- s1 R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 1965, **87**, 2046.

- s2 R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed.*, 1969, **8**, 781.
- s3 E. Hückel, *Z. Physik*, 1931, **70**, 204.
- s4 R. Hoffman, *J. Chem. Phys.*, 1963, **39**, 1397.
- s5 E. Noether, *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, Mathematisch-Physikalische Klasse 1918, 235.
- s6 J. Hubbard, *Proc. R. Soc. Lond. A*, 1963, **276**, 238.
- s7 J. Kanamori, *Prog. Theor. Phys.*, 1963, **30**, 275.
- s8 M.C. Gutzwiller, *Phys. Rev. Lett.*, 1963, **10**, 159.
- s9 K. Yamaguchi, T. Fueno and H. Fukutome, *Chem. Phys. Lett.*, 1973, **22**, 461.
- s10 K. Yamaguchi, *Chem. Phys. Lett.*, 1975, **33**, 330.
- s11 K. Yamaguchi, Y. Takahara and T. Fueno, in *Applied Quantum Chemistry*, ed. V.H. Smith Jr., H.F. Schaefer III and K. Morokuma, D. Reidel Pub. Com., Lancaster, 1986, 155.
- s12 K. Yamaguchi, in *Self-Consistent Field: Theory and Applications*, ed. R. Carbó and M. Klobukowski, Elsevier, Amsterdam, 1990, 727. (ref. 87 in the text)
- s13 W. Heisenberg, *Z. Physik*, 1928, **49**, 619.
- s14 K. Yamaguchi, *Chem. Phys. Lett.*, 1974, **28**, 93.
- s15 K. Yamaguchi, Y. Yoshioka and T. Fueno, *Chem. Phys.*, 1977, **20**, 171.
- s16 S. Yamanaka, K. Kanda, T. Saito, Y. Umena, K. Kawakami, J.-R. Shen, N. Kamiya, M. Okumura, H. Nakamura and K. Yamaguchi, *Adv. Quant. Chem.*, 2012, **64**, 121 (ref. 75 in the text).
- s17 A. P. Ginsberg, *J. Am. Chem. Soc.*, 1980, **102**, 111.
- s18 L. Noodleman and E. R. Davidson, *Chem. Phys.*, 1986, **109**, 131.
- s19 S. Yamanaka, T. Kawakami, H. Nagao and K. Yamaguchi, *Chem. Phys. Lett.*, 1994, **231**, 25.
- s20 E. Ruiz, P. Alemany, S. Alvarez and J. Cano, *J. Am. Chem. Soc.*, 1997, **119**, 1297.
- s21 T. Soda, Y. Kitagawa, T. Onishi, Y. Takano, Y. Shigeta, H. Nagao, Y. Yoshioka and K. Yamaguchi, *Chem. Phys. Lett.*, 2000, **319**, 223.
- s22 F. Neese, *Coord. Chem. Rev.*, 2009, **253**, 526.
- s23 N. J. Mayhall and M. Head-Gordon, *J. Chem. Phys.*, 2014, **141**, 134111.
- s24 M. Shoji, K. Koizumi, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura and K. Yamaguchi, *Chem. Phys. Lett.*, 2006, **432**, 343.
- s25 K. Yamaguchi, *J. Mol. Struct. THEOCHEM*, 1983, **103**, 101.

- s26 K. Yamaguchi, in *Singlet Oxygen Vol. III*, ed. A.A. Friemer, CRC Press, Boca Raton, 1985, Chapter 2, 119.
- s27 K. Yamaguchi, Y. Takahara and T. Fueno, in *The Role of Oxygen in Chemistry and Biochemistry*, ed. W. Ando and Y. Moro-oka, Elsevier, Amsterdam, 1988, 263.
- s28 K. Yamaguchi, Y. Takahara, T. Fueno, I. Saito and T. Matsuura, in *Medical, Biochemical and Chemical Aspects of Free Radicals*, ed. O. Hayashi, E. Niki, M. Kondo, T. Yoshikawa, Elsevier, Amsterdam, 1989, 993.
- s29 K. Yamaguchi, K. Takada, Y. Otsuji and K. Mizuno, in *Organic Peroxides*, ed. W. Ando, John Wiley & Sons, Chichester, 1992, 1.
- s30 J. G. Bednorz and K. A. Müller, *Z. Physik B*, 1986, **64**, 189. (ref. 33 in the text)
- s31 K. Yamaguchi, Y. Takahara, T. Fueno and K. Nasu, *Jpn. J. Appl. Phys.*, 1987, **26**, L1362.
- s32 K. Yamaguchi, M. Nakano, H. Namimoto and T. Fueno, *Jpn. J. Appl. Phys.*, 1988, **27**, L1835.

SII Electronic and spin structures of 3d transition-metal complexes

SII.1 Application of the computational scheme to binuclear 3d dimer

In early 1980s, the EPR spectroscopy was performed for the Mn dimer in the rare gas matrix^{s33}, demonstrating that the effective exchange interaction (J) was -9 cm^{-1} at the long interatomic distance (3.4 Å). The MCD spectroscopy^{s34} was also performed for the Mn dimer, reporting -10 cm^{-1} in consistent with the EPR result.^{s33} These experimental results were regarded as the reliable reference results for examination of scope and applicability of eq. (s22b).^{s11} We performed the ab initio UHF calculations of the J_{ab} values for the Mn dimer by using the eq. (s22a) as shown in Fig. S6. The calculated J_{ab} values for the direct exchange-coupled systems were -32 and $-7\text{ (cm}^{-1}\text{)}$ at 3.0 and 3.5 (Å) , respectively, in consistent with the experimental results.^{s33, s34} Thus, the HS-LS energy gaps were reasonably obtained, although the potential curves for both states were insufficient at the UHF level of theory because of the lacking of dynamical correlation corrections.

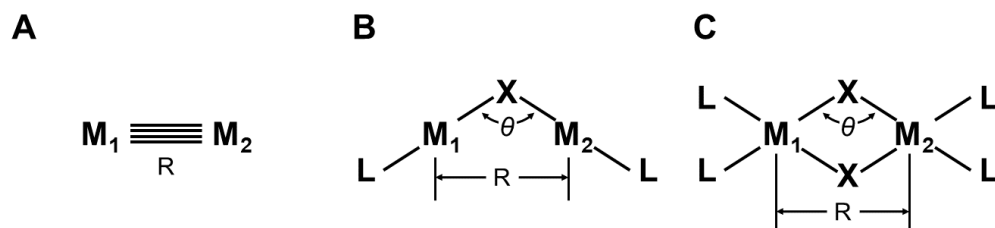


Fig. S6 Computational models for (A) direct exchange coupling between transition metals, (B) superexchange coupled dinuclear complex LM_1XM_2L and (C) superexchange coupled dinuclear complex $L_2M_1X_2M_2L_2$.

SII.2 Application of the computational scheme to binuclear 3d complexes

Next step, we examined applicability of eq. (s22a) to obtain the J -values of the super-exchange coupled systems; $M-O-M$. The $d\pi$ - $p\pi$ - $d\pi$ bond of the $M-O-M$ by the Hubbard model is regarded as the three-center four-electron $[4e, 3o]$ bond. Therefore, the HOMO and LUMO are given by the anti-symmetric non-bonding and symmetric anti-bonding orbitals as illustrated in Fig. S7.^{s35} The HOMO-LUMO energy gap is usually smaller than the on-site repulsion (U) integral for 3d transition metal $M=O=M$ systems such as Cr(III) ion. The HOMO-LUMO mixing occurs, providing the broken-symmetry orbitals in eq. (s5), which are mainly localized on the left- and

right-metal ions, respectively, in consistent with the 1,3-metal radical configuration; $\bullet\text{M}-\text{O}-\text{M}\bullet$ expressed by the Heisenberg model.

The ab-initio UHF/MIDI basis set was applied to obtain the J -values for the super-exchange coupled M–O–M systems as shown in Table S1.^{s35} The J -values for the Cr(III)–O–Cr(III) complexes were calculated to be largely negative in sign, indicating the strong antiferromagnetic interaction as shown in Table S1. However, the calculated J -value was -187 cm^{-1} for the $\text{NH}_3\text{Cr(III)-O-Cr(III)NH}_3$, indicating the reduction of the super-exchange interaction with coordination of NH_3 ligand. The magnitude of the J -value for Cr(III)–O–Cr(III) was indeed reduced to about one third with the coordination of the NH_3 ligand (see also Table S2). It was compatible with the observed J -value for the $(\text{NH}_3)_5\text{Cr(III)-O-Cr(III)(NH}_3)_5$,^{s36} indicating the applicability of the computational procedure for elucidation of the nature of the exchange-coupled binuclear complexes.^{s35}

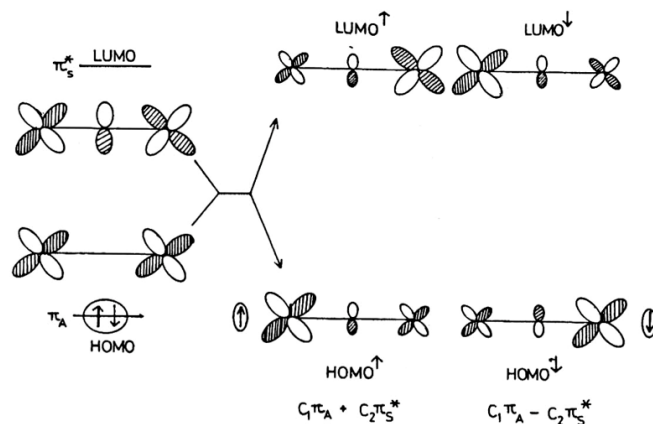


Fig. S7 The spin polarized molecular orbitals obtained by the HOMO-LUMO mixing for the M=O=M systems with 1,3-diradical characters $\bullet\text{M}-\text{O}-\text{M}\bullet$.

The J -values calculated for the Mn(II)–O–Mn(II) indicated the spin crossover from the antiferromagnetic (AF) and ferromagnetic (F) state with the increase of the Mn–O distance. The calculated J -value for $\text{NH}_3\text{Mn(III)-O-Mn(III)NH}_3$ was -60 cm^{-1} , indicating the AF interaction in consistent with magnetic behaviors of many Mn oxides. Interestingly, the Mn(III)–O–Mn(III) unit has been elucidated in the CaMn_4O_5 cluster in OEC of PSII.^{s16} The J -values calculated for the Fe(III)–O–Fe(III) also indicated the spin crossover from the AF and F state with the increase of the Fe–O distance. The linear Ni(II)–O–Ni(II) unit exhibited the AF interaction. The linear (180 degree)

Cu(X)–O–Cu(X) (X = II, III) unit indicated the large negative value, indicating the extremely strong AF interaction.

The J -values calculated for the Cu(II)(OH)₂Cu(II) complex indicated the strong Cu–O–Cu angle (θ) dependence as illustrated in (C) of Fig. S6.^{s35} The J -values were considered to be positive for the Cu(II)(OH)₂Cu(II) complex with smaller angles (< 100 degree) because of contribution of the charge-transfer configuration Cu(I)–O(•)Cu(II) where the orthogonal 2p-orbital and 3d-orbital interaction was feasible for the ferromagnetic (F) super-exchange interaction. The calculated J -values were indeed positive for the Cu(II)(OH)₂Cu(II) complex with smaller angles (< 100 degree). On the other hand, the calculated J -values are negative for the Cu(II)(OH)₂Cu(II) complex with larger angles (>110 degree) because of contribution of the charge-transfer configuration Cu(I)–O(•)Cu(II) where the non-zero 2p-orbital and 3d-orbital interaction is feasible for the antiferromagnetic (AF) super-exchange interaction. The same mechanism was found to be operative for the Cu(II)(OH)₂Ni(II) complexes.

The J -values for the Fe(III)S₂Fe(III) unit^{s35, s37, s38} were calculated to be antiferromagnetic (AF) in consistent with the experiments.^{s39} Thus, early BS calculations combined with the Heisenberg model were found to be useful and practical for theoretical elucidation of binuclear transition metal complexes, which were regarded as model complexes for active sites of several metalloenzymes. Recently, BS hybrid UHF and UDFT (UHDFT) methods such as UB3LYP have been conveniently used for elucidation and computation of the sign and magnitude of J -values for multi-nuclear transition-metal complexes involved in metalloenzymes. On the other hand, beyond UHDFT calculations are now feasible for elucidation of scope and applicability of various DFT methods to strongly correlated electron systems (SCES) as shown in this paper, providing the reference data for selection of appropriate DFT method for QM/MM calculations of large systems involving the SCES core like in the case of OEC of PSII. In this paper, the BS UB3LYP computational method combined with eq. (s22) was used for the CaMn₄O₅ cluster in OEC of PSII.

Table S1 The J values for binuclear transition metal complexes by the broken symmetry methods^{a)}

Systems	Conf.	J_{ab} (R(M–O), Angle θ) ^{a)}			
Cr(III)...Cr(III)	d ³ -d ³	–2565 (1.7)	–677 (2.0)	–10.3 (2.5)	6.4 (3.0)
Cr(III)OCr(III)	d ³ -d ³	–6204 (1.0)	–1987 (1.25)	–671 (1.5)	–377 (1.7)
XCr(III)OCr(III)X	d ³ -d ³	–187 (1.7)	–79 (1.8)	–10 (1.9)	
Mn...Mn	d ⁵ -d ⁵	–32(3.0)	–7(3.5)		
Mn(II)OMn(II)	d ⁵ -d ⁵	–3534 (1.0)	–156 (1.5)	7 (2.0)	
XMn(II)OMn(II)X	d ⁵ -d ⁵	–24 (1.71)			
XMn(III)OMn(III)X	d ⁴ -d ⁴	–60 (1.71)			
Fe(III)OFe(III)	d ⁵ -d ⁵	–4913 (1.0)	–264 (1.5)	–71 (1.6)	279 (1.8)
		326 (1.9)			
Ni(II)ONi(II)	d ⁸ -d ⁸	–14754 (1.0)	–831 (1.5)	–525 (1.7)	
XNi(II)ONi(III)X	d ⁸ -d ⁸	–174 (1.7)			
Cu(II)OCu(II) ^{b)}	d ⁹ -d ⁹	–36453 (1.0)	–4621 (1.6)	–5433 (1.8)	
Cu(III)OCu(III) ^{b)}	d ⁸ -d ⁸	–19616 (1.0)	–5671 (1.6)	–5688 (1.8)	
Cu(II)(OH) ₂ Cu(II)	d ⁹ -d ⁹	554(2.85, 97)	207(2.98, 103)		
		–175(3.15, 110)	–170(3.12, 110)		
H ₂ Cu(II)(OH) ₂ Ni(II)H ₂	d ⁹ -d ⁸	–24(2.85,95.6)	–170(3.15,110)		
Fe(III)Fe(III)	d ⁵ -d ⁵	–16(2.70, 75)			
Fe(III)S ₂ Fe(III)	d ⁵ -d ⁵	–926(2.70, 75)			
(H ₂)Fe(III)S ₂ Fe(III)(H ₂)	d ⁵ -d ⁵	–175(2.70, 75)			

^{a)} results from ref. s11, ^{b)} results from ref. s35.

SII.3 Extended Hubbard model for 3d transition metal oxides

As shown in Fig. S7, the BS magnetic orbitals for Cr(III)–O–Cr(III) have the tails on the oxygen site, indicating an important role of the oxygen dianion for the super-exchange interaction. This means the necessity of the extended Hubbard model including the O-site explicitly.^{s32} The extended Hubbard model in eq. (s1) was applied to elucidate the electronic structures of the 3d transition metal μ -oxo unit M–O–M (M = Mn, Fe, Cu, ...), for which the necessary α_{ii} , β_{ij} and U_{ij} parameters in eq. (s1) were determined using the spectroscopic results and the computational results in Table S1.^{s32}

Figure S8 shows the orbital energies ($\alpha_{ii} = \varepsilon_{dd}$) of transition metal ions, orbital energy difference between the metal and oxygen site (O^{2-}). The charge transfer (CT) excitation energy is given with the extended Hubbard model^{s32, s40} as

$$\Delta_{pd} = (\varepsilon_{dd} - \varepsilon_{pp}) + (U_{dd} - U_{dd}) \approx (\varepsilon_{dd} - U_{dd}) - \varepsilon_{pp} \quad (s28)$$

where the on-site repulsion integral (U_{pp}) is often neglected. The CT excitation energy becomes positive in sign even if the orbital energy gap $\delta = \varepsilon_{dd} - \varepsilon_{pp}$ is negative in sign because of on-site repulsion integral (U_{dd}). Therefore, transition metal oxides are often classified into three types on the basis of relative magnitude of U_{dd} and Δ_{pd} : (i) CT insulator ($U_{dd} > \Delta_{pd}$), (ii) intermediate case ($U_{dd} \sim \Delta_{pd}$) and (iii) Mott-Hubbard insulator ($U_{dd} < \Delta_{pd}$).^{s40}

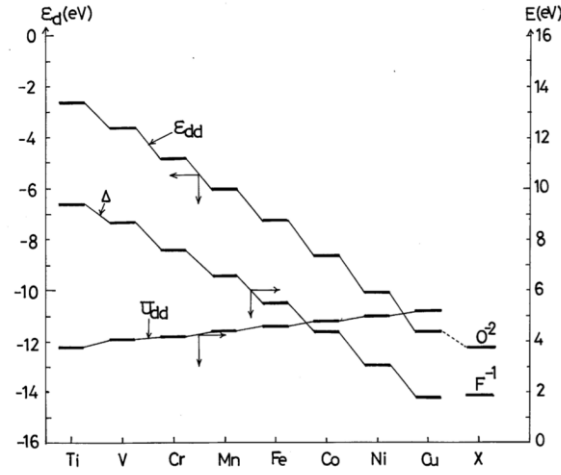


Fig. S8 Variations of the orbital energy (ε_{dd}) and for on-site repulsion integral (U_{dd}) for 3d metal ions, orbital energy gap (Δ) between M and O sites.

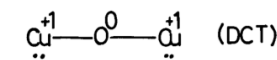
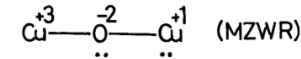
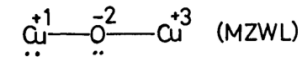
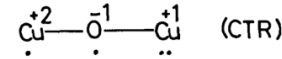
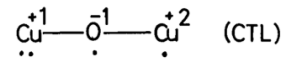
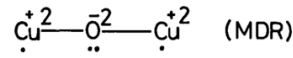


Fig. S9 The VB configurations of the Cu–O–Cu unit for full VB CI calculations.

The full VB CI calculations using six VB configurations were performed to obtain the energy levels and hole populations as shown in Fig. S9. The effective exchange integral for the M–O–M unit was calculated by eq. (s11), where total energies of the singlet and triplet states obtained by the full valence-bond (VB) configuration interaction (CI) method. Figure S10 shows the energy levels for the Cu–O–Cu $d\pi$ - $p\pi$ - $d\pi$ bond before and after CI using two different parameter sets. Table S2 summarizes the calculated J values for M–O–M systems by FVB-CI (the method I). On the other hand, the effective exchange integrals for M–O–M systems are given by

$$J_{dd} = -\frac{2t_{pd}^4}{\Delta_{pd}} \left[\frac{1}{\Delta_{pd}^2} + \frac{1}{U_{dd}\Delta_{pd}} \right] = -2T_{dd}^2 \left[\frac{1}{\Delta_{pd}} + \frac{1}{U_{dd}} \right] \approx -\frac{2T_{dd}^2}{\Delta_{pd}} \left(T_{dd} = \frac{t_{pd}^2}{\Delta_{pd}} \right) \quad (\text{s29})$$

where the U_{dd}^{-1} term is approximately neglected.^{s40} The effective J values are mainly resulted from the CT interaction between M and O sites. The effective J values obtained with eq. (s29) are given in parentheses. The estimated J values by the one-third of the J values for naked M–O–M units by UHF^{s35} are given in the method II, together with the experimental values in Table S2. Table S3 shows the FVB-CI coefficients for M–O–M systems.

From Table S3, the magnitude of the J value for the Cu–O–Cu by FVB-CI was larger than 1000 cm^{-1} , indicating very strong super-exchange interactions. The corresponding J value by the perturbation method was too large as shown in Table S3, indicating its breakdown because of the small Δ_{pd} in eq. (s29). In fact, the charge-transfer (CTL(R)) configuration for the Cu–O–Cu unit, $\text{Cu(I)}-\text{O}^{1-}\bullet-\text{Cu(II)}\bullet$ and $\bullet\text{Cu(II)}-\text{O}^{1-}-\text{Cu(I)}$, are the main configurations in the case of the parameter set ($t_{pd} = 0.9$, $\Delta_{pd} = 0.4$). Thus, the hole delocalization is very important for the Cu–O–Cu unit. On the other hand, the metal diradical configuration (MDR) $\bullet\text{M}-\text{O}^{2-}-\text{M}\bullet$ was the main configuration for M–O–M units, indicating the applicability of the perturbation equation (s29) to estimation of the J values for M–O–M systems as shown in Table S2. The CTL(R) configurations were the next main configurations for other M–O–M systems, indicating important roles of the CT interactions between M and O sites for the super-exchange interactions.

The hole-doped $\text{Cu(II)}-\text{O}-\text{Cu(II)}$ is formally expressed by the trapped valence configuration $\text{Cu(III)}-\text{O}-\text{Cu(II)}$. However, the CT from O^{2-} to Cu(III) occurs to afford the $\text{Cu(II)}-\text{O}\bullet-\text{Cu(II)}$, which exhibits the oxyl-radical character responsible for oxygenation reactions in the field of chemical reactions.^{s11} On the other hand, in the

two dimensional (2D) CuO_2 plane of the $\text{Ln}_2\text{Cu(II)O}_4$ solid, one hole doping induces the loss of $4J$ attractive interactions, indicating the loss of total $8J$ for separated independent two holes in the plane. However, only the $7J$ is lost if two holes form a pair, indicating a possibility that the remained J may contribute the Cooper pair formation for the high- T_c superconductivity. Thus, hole doping is a common physical origin of the oxyl-radical reactivity and emergence of characteristic functions such as superconductivity and magneto-resistance in SCES as shown in Fig. S4.

The J -values for the M–O–M systems in Tables S1 and S2 were applied to estimate the transition temperature for the superconductivity on the basis of the electron correlation (cooperative charge and spin fluctuations) model as shown in Table S4. At the moment, the high- T_c superconductivity was not observed for the hole-doped nickel oxides. However, nickel oxides developed for the purpose may be used for effective Ni-cluster catalysts for oxygenation reactions, where short-range electron correlation plays an important role in consistent with the strategy in Fig. S4. On the other hand, the hole-doped Co-oxide planes indicated the low-temperature superconductivity.^{s41} However, compact shapes of clusters are necessary for hole-hole interaction, indicating the utility of cubane-like clusters which are often characterized as the spin frustration systems. In fact, Lewis and Nocera^{s42} proposed a similar strategy for conversion of SCES into effective catalysts for water oxidation. To this end, they indeed proposed use of spin frustration systems examined in the next section.

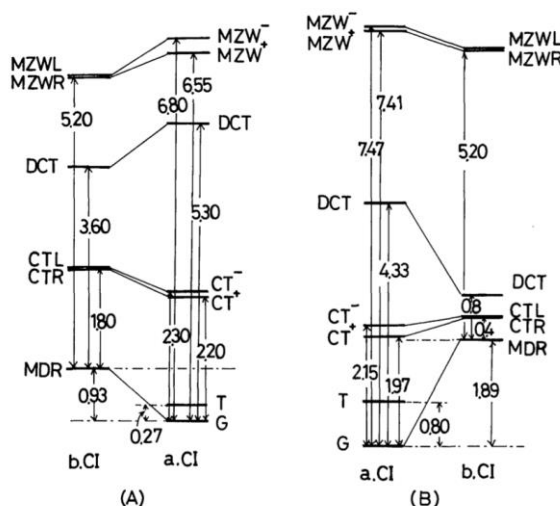


Fig. 8 The energy levels for two different parameter sets (A) and (B) of the Cu–O–Cu systems by the before and after full VB CI calculations.

Table S2 The calculated J-values by the full VB CI method.

System	t	Δ	J_{MM} -values (cm^{-1}) ^{a)}		
			I	II	Exp.
CuOCu	0.9	1.8	−1082(−2443)	−1110	−925
	0.9	0.4	−3233(−3330) ^{b)}		
NiONi	0.7	3.1	−174(−211)	−177	−139
	0.7	1.8	−528(−530)		
CoOCo	0.7	4.4	−89(−87)		
FeOFe	0.6	5.5	−26(−28)	−24	−21
MnOMn	0.7	6.6	−18(−18)	−14	−10
CuFCu	0.75	3.7	−148(−173)	−117	−132
NiFNi	0.65	5.0	−43(−46)	−20	−36
CoFCo	0.65	6.3	−26(−27)		
FeFFe	0.5	7.4	−6(−6)		
MnFMn	0.5	8.5	−5(−5)	−0.2	−3

Table S3 FVB-CI coefficients for M-O-M systems.

System	t	Δ	1D_i (singlet)				3D_i (triplet)	
			MDR	CTL(R)	DCT	MZWL(R)	MDR	CTL(R)
CuOCu	0.9	1.8	0.782	0.403	−0.226	−0.084	0.888	0.325
	0.9	0.4	0.484	0.509	−0.481	−0.091	0.760	0.460
NiONi	0.7	3.1	0.944	0.224	−0.068	−0.042	0.960	0.198
	0.7	1.8	0.852	0.346	−0.104	−0.062	0.915	0.286
CoOCo	0.7	4.4	0.972	0.161	−0.035	−0.032	0.978	0.148
FeOFe	0.6	5.5	0.987	0.111	−0.017	−0.020	0.989	0.105
MnOMn	0.7	6.6	0.991	0.092	−0.012	−0.017	0.992	0.089
CuFCu	0.75	3.7	0.955	0.203	−0.056	−0.039	0.966	0.182
NiFNi	0.65	5.0	0.982	0.132	−0.024	−0.023	0.985	0.124
CoFCo	0.65	6.3	0.989	0.105	−0.015	−0.020	0.990	0.100
FeFFe	0.5	7.4	0.995	0.068	−0.007	−0.010	0.996	0.067
MnFMn	0.5	8.5	0.996	0.059	−0.005	−0.009	0.997	0.058

Table S4 The J-model for superconductivity.

System	J_{ab} (cm^{-1})	T_c (K)	Experiment (K)
CuOCu	−1110	159.6	160 (HgCuO ₂)
NiONi	−174	25.0	—
CoOCo	−89	12.8	5 (NaCoO ₂)
MnOMn	−18	2.59	—
CuFCu	−148	21.3	—
NiFNi	−43	6.18	—
MnFMn	−5	0.719	—

SII. 4 Non-collinear spin structures for spin frustration systems

In 1970s, radical clusters with equilateral triangle and tetrahedral structures were important and interesting targets since they were transition structures for

exchange-forbidden radical insertion reactions as shown in Fig. S9.^{s43} The potential curves are obtained by the in-house GSO-DFT program package as shown in Fig. S10. The non-collinear spin structures were also attracted from the viewpoint of spin frustrations.^{s44, s45} Therefore, the Hubbard models for the three-center three-electron [3e, 3o] system with the equilateral triangle geometry and four-center four-electron [4e, 4o] system with the tetrahedral geometry were analytically solved at that time for elucidation of quantum spin effects.^{s12} The HOMO-SOMO-LUMO mixing was necessary for the equilateral [3e, 3o] system because of the degeneracy between SOMO and LUMO energy levels, providing the general spin orbitals (GSO) consisted of both up (α)- and down (β)-spin components for canting (two dimensional (2D)) spin states^{s46}, for example,

$$\psi_{GSO} = c_1\phi_{HOMO}\alpha + c_2\phi_{SOMO}\alpha + c_3\phi_{LUMO}\beta \quad (s30)$$

where c_i denotes the mixing coefficient determined by GSO Hartree-Fock (HF) calculations. Figure S11A illustrates variation of relative energies of spin-restricted open-shell (O) Hartree-Fock (RHF), axial (one-dimensional) spin density wave (ASDW = UHF), projected ASDW (PSDW) and spin-optimized (SO) SCF solution, which is equivalent to the full CI in the [3e, 3o] system. The GSO HF solution in eq. (s30) is an approximation of the spin optimized (SO)-SCF (full CI) solution, indicating the necessity of the resonating GSO CI treatment (see Fig. S12). The situation was the same for the tetrahedral [4e, 4o] system with the 3D spin configuration as shown in Fig. S11B.

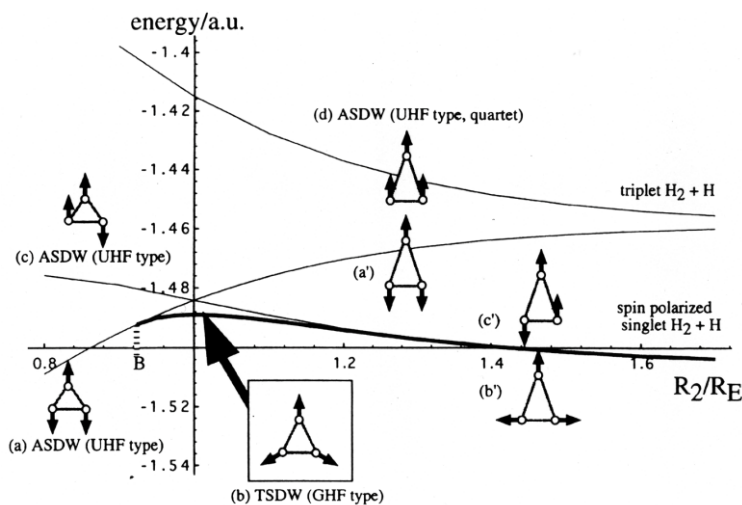


Fig. S9 Potential curves for the radical insertion reactions in the case of the H_3 radical.

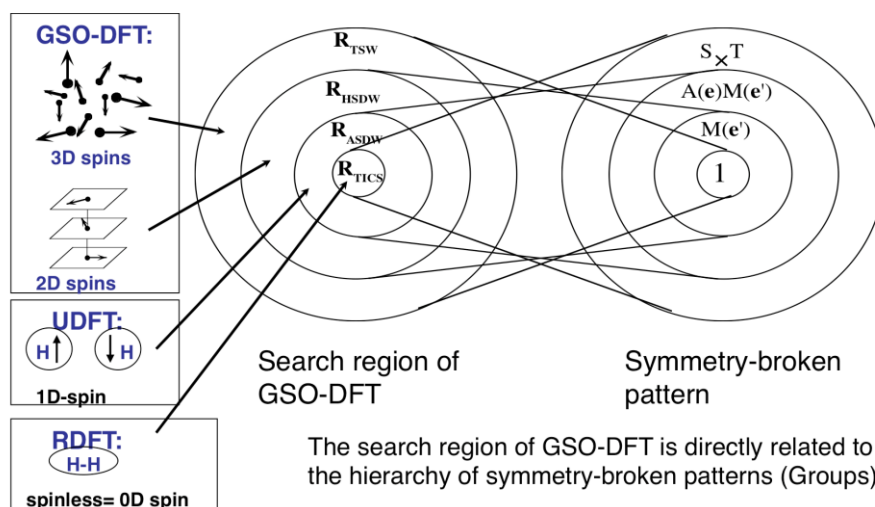


Fig. S10 Magnetic group theoretical classification of molecular spin orbitals (GSO).

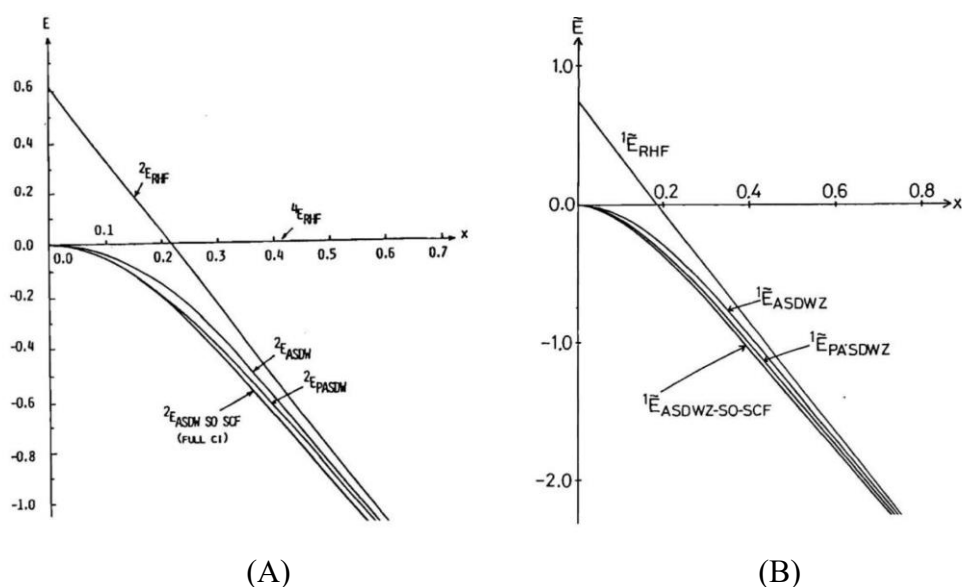


Fig. S11 The normalized energies of several solutions for the Hubbard models of triangular [3e, 3o] and tetrahedral [4e, 4o] systems.^{s12}

The Hubbard models for the [3e, 3o] and [4e, 4o] systems in Fig. S11 were often transformed into the corresponding Heisenberg models with three- and four-sites spin systems.^{s11} The Heisenberg spin Hamiltonian models for these systems were typical spin frustration systems because of degeneracy of different axial (one dimension; 1D) spin triangular or tetrahedral structures in energy. The 3×3 and 8×8 full CI constructed of the degenerated spin structures are necessary for quantum spin Hamiltonians of the [3e, 3o] and [4e, 4o] systems, respectively. The corresponding

resonating BS (RBS) CI calculations using three ASDW(UHF) and HSDW(GSO) solutions in Fig. S12 are also essential for these quantum systems^{s43-s46} as shown in Fig. S13. Recently, triangular and Kagome lattices consisted of equilateral triangles are accepted from the viewpoint of quantum spin liquid states.^{s44, s45, s47} The RBS CI methods for spin frustration systems were examined in details previously.^{s48}

The non-collinear spin structures described by eq. (s29) were also obtained for spin-frustrated systems with classical spins of Cr, Mn, etc. (spin size $> S = 1$). Figure S14 illustrates the non-collinear spin structures of the equilateral Cr_3 ($S = 6/2$ for Cr) and tetrahedral Cr_4 clusters obtained by the GSO-DFT calculations in Fig. S10.^{s49}

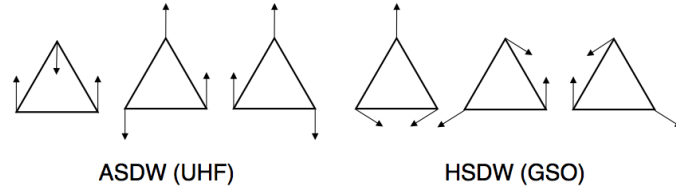


Fig. S12 Three axial (1D) and helical (2D) spin configurations for the $[3e, 3o]$ systems.

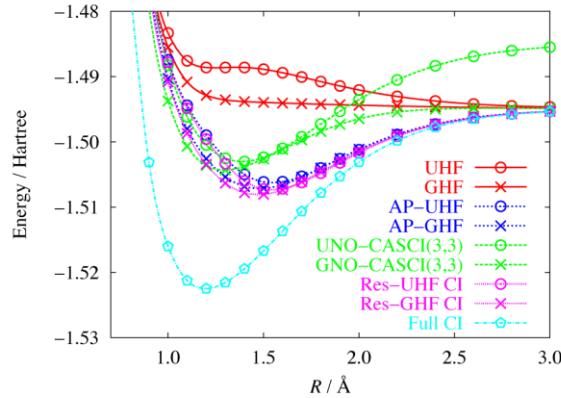


Fig. S13 Potential curves of the H_3 radical by RBS CI methods.

The effective exchange integrals (J) for these Cr clusters are also obtained using eq. (s27) as shown in Table S5. The J -values are negative in sign, indicating the direct antiferromagnetic (AF) interactions in consistent with the equilateral triangle spin structure as shown in Fig. S14. The tetrahedral spin structures were also obtained for the Cr_4 cluster with the tetrahedral geometry. The non-collinear spin structures are obtained for clusters of clusters such as the trigonal bipyramidal structure as shown in in Table S6. The Cr_5 cluster with the noncollinear structure (H) was the ground state because of the direct antiferromagnetic interactions between the Cr atoms.^{s49} The

trigonal bipyramidal structure of the Fe₅ cluster was a precursor of the so-called Masaoka catalyst for water oxidation.^{s52}

The GSO DFT calculations were performed for the Co(IV)₃ and Co(IV)₇ model clusters of the 2D lattice of the CoO₂ superconductors as shown in Fig. S15. The triangular spin structure and triangular spin lattice were obtained for these model clusters as shown in Fig. S16. The antiferromagnetic (negative) J -values were obtained for the lattice as shown in Table S7, providing reasonable transition temperature (T_c) for the superconductivity.^{s41} According to the working hypothesis in Fig. S4, the CoO₂ may be a candidate for catalysts of water oxidation (see also Table S4).

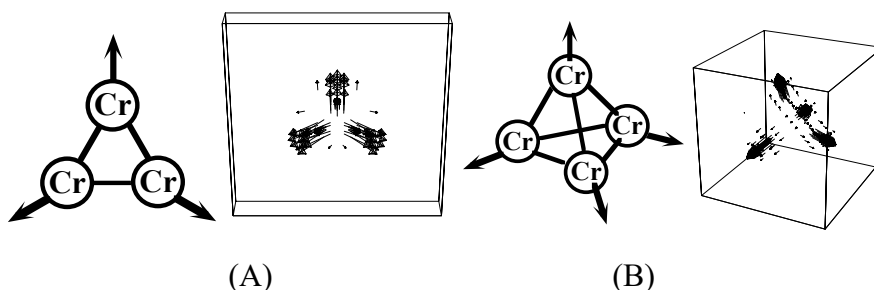


Fig. S14 GSO-DFT calculations of (A) the triangular Cr₃ system and (B) the tetrahedral Cr₄ systems. The spin density plots obtained by GSO-DFT are shown for illustrations.

Table S5 The effective exchange integrals (J) (cm⁻¹) for Cr clusters by the GSO-HF, GSO-HFS and GSO-DFT methods.

	GHFS	GSO-SVWN5	GHF
Cr ₂	-279.6	-430.8	-162.8
Cr ₃ (D _{3h})	-270.3	-401.7	-113.7
Cr ₄ (T _d)	-210.7	-360.4	-99.73

Table S6 The Cr₅ cluster with the 1D (ASDW) and 3D (torsional spin wave (TSW1, TSW2) spin structures and the magnitude of the spin moment by GSO-DFT method.

Spin structure	ΔE (a.u.)	M_{api}	M_{cant}
F (ASDW)	-0.24873	2.53	2.69
G (TSW1)	-0.38346	2.35	2.35
H (TSW2)	-0.40048	2.44	2.37

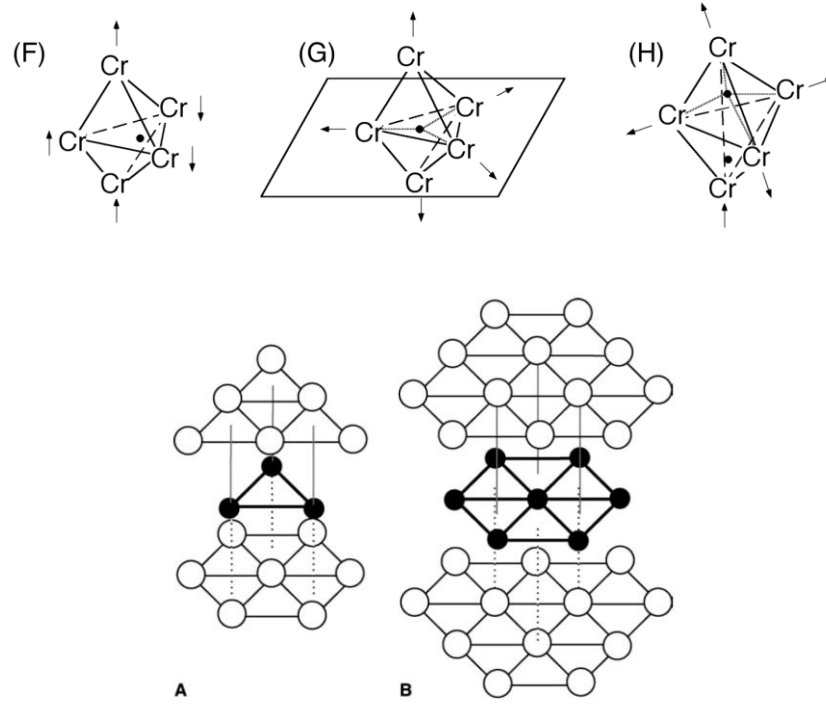


Fig. S15 Geometrical structures of (A) Co(IV)₃ and (B) Co(IV)₇ clusters for the CoO₂ superconductors.

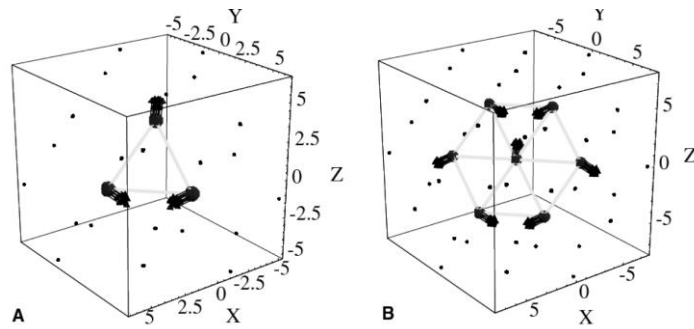


Fig. S16 Non-collinear spin structures of (A) Co(IV)₃ and (B) Co(IV)₇ clusters for the CoO₂ superconductors.

Table S7 The calculated J -values and T_c for the CoO_2 superconductors.The effective exchange integral (J) values of $\text{Co}_{4+}^{3(2e^-)}_{13}$ and $\text{Co}_{4+}^{7(2e^-)}_{24}$ clusters by ab initio GSO methods

	$\text{Co}_{4+}^{3(2e^-)}_{13}$		$\text{Co}_{4+}^{7(2e^-)}_{24}$	
	$J \text{ (cm}^{-1}\text{)}^a$	$T_c \text{ (K)}^b$	$J \text{ (cm}^{-1}\text{)}^a$	$T_c \text{ (K)}^b$
GHF	-3.21	0.46	-5.46	0.79
GSO-BLYP	-3.91	0.56	-16.4	2.35
GSO-B3LYP	-2.64	0.38	-10.7	1.54

 T_c values estimated via J -model are also listed.^a The estimation value of J of $\text{Na}_{0.5}\text{CoO}_2(\text{H}_2\text{O})_{1.3}$ is 56 cm^{-1} ([31]).^b The experimental value of T_c of $\text{Na}_{0.35}\text{CoO}_2(\text{H}_2\text{O})_{1.3}$ is 5 K ([13]).

SII.5 Hole- and electron-doping SCES for water oxidation

The triangular, cubane-type and trigonal bipyramidal transition metal complexes exhibit spin frustrations. Indeed, the non-collinear spin structures were obtained for triangular transition metal complexes; M_3X and M_3X_4 ($\text{M} = \text{Cu, Mn, Fe, ...}$; $\text{X} = \text{O, S, ...}$) with spin frustrations. On the other hand, the tetrahedral-type spin structures were resulted for cubane-type transition-metal complexes; M_4X_4 ($\text{M} = \text{Mn, Fe, Co, ...}$; $\text{X} = \text{O, S, ...}$) with antiferromagnetic (180 degree) super-exchange interactions. Indeed, the tetrahedral spin state was also the ground singlet state of the cubane-like $\text{Mn(II)}_4\text{O}_4$ cluster with the super-exchange interactions.^{s50} On the other hand, the highest spin structures were often obtained for the cubane-type clusters such as the CaMn_3O_4 cubane in the CaMn_4O_5 cluster in OEC of PSII because of the ferromagnetic 90 degree super-exchange interactions as in the case of $\text{Cu(OH)}_2\text{Cu}$ in Table S1.^{s16} The relative stabilities between the low-spin (LS) and high-spin (HS) configurations for these complexes were determined with the sign of the J -values as shown in Tables S1, S5 and S6. The magnetic susceptibility experiments were also applied to elucidation of spin states of multinuclear complexes; adamantane-type transition metal complexes; M_4X_6 ($\text{M} = \text{Mn, Fe}$; $\text{X} = \text{O, S}$), trigonal bipyramidal complex $\text{Fe(III)}_5\text{O}$. The Heisenberg models were used for elucidation of magnetic properties of such complex exchange-coupled systems. Details of theoretical descriptions are given in other papers.^{s15, s40, s51}

The triangular, cubane and trigonal bipyramidal structures with spin frustrations have structural characteristics for formation of binuclear sites with appropriate spatial distances, which undergo catalytic actions such as water oxidation. For example, as mentioned above, trigonal bipyramidal Fe_5 cluster catalysts by Masaoka et al. has the triangular Fe_3O cluster with two Fe=O bonds for the O-O bond formation.^{s52} On the other hand, the formal Mn(III)_5 cluster was converted into Ca-doped Mn_4 cluster in the

case of OEC of PSII as illustrated in Fig. 1 in the text. GSO-DFT calculations elucidated the equilateral triangle spin structure for regular cubane-type CaMn_3O_4 cluster of the London model for OEC of PSII.^{s53} Thus, compact hole-doped 3d metal clusters with spin frustrations have structural flexibility for formation of active sites for oxygenation reactions in Fig. S4, indicating candidates for effective catalysts for oxygenation reactions such as water oxidation. The remained metal sites act effectively as hole-doped sites for multi-electron oxidation reactions without sacrificial reagents. The molecule-based magnets with spin frustrations are now interesting from the viewpoint of emergence of specific catalytic reactivity in appropriate reaction conditions as shown in Fig. S4.

Iron-sulfur cubane-type clusters, Fe_4S_4 , involved in the photosystem I (PSI) are typical SCES systems in Scheme I from our theoretical viewpoint.^{s54, s55} Figure S17 illustrates the non-collinear spin structures of triangular and cubane-type iron-sulfur clusters, and cyclic iron-sulfur clusters.^{s54} Possible variations of spin and valence structures of the iron-sulfur clusters with capture of electrons are shown in Fig. S18.^{s55} P-cluster model Fe_8S_7 cluster, dimer of the Fe_4S_4 cluster, and clusters of Fe_4S_4 clusters in many biological systems are also regarded as SECS in Scheme I.^{s56} The electron-doped FeMoco cluster, $\text{Fe}_7\text{MoS}_9\text{C}$, is the well-known native catalyst for reduction of nitrogen molecule into ammonia.^{s57} Thus, the electron-doped SCES play important roles for electron transfers and reduction reactions in chemistry. The extended iron-sulfur clusters are also important in material science as illustrated in Fig. S19.

Combinations of hole- and electron-doped SCES provide hybrid systems for oxidation of water molecule and reduction of carbon dioxide or nitrogen molecule as illustrated in Fig. S20.^{s58} The native photosynthesis system in Fig. S21 can be also regarded as a hybrid system consisted of the hole-doped CaMn_4O_x and electron-doped Fe_4S_4 clusters. Thus, hole- and electron-doped SCES systems consisted of 3d transition metals (Mn, Fe, Cu, ...) are important and interesting for developments of artificial catalytic systems consisted of abundant atoms in the earth as shown in Figs. S4 and S19. Scheme I in the text is our guiding principle for theoretical investigation of the CaMn_4O_x cluster and bio-inspired catalysts for oxidation or reduction reactions as illustrated in Figs. S4 and S19.

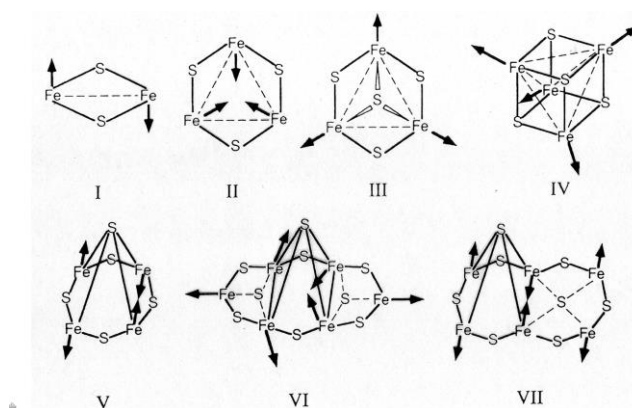


Fig. S17 Non-collinear spin structures of the iron-sulfur clusters.

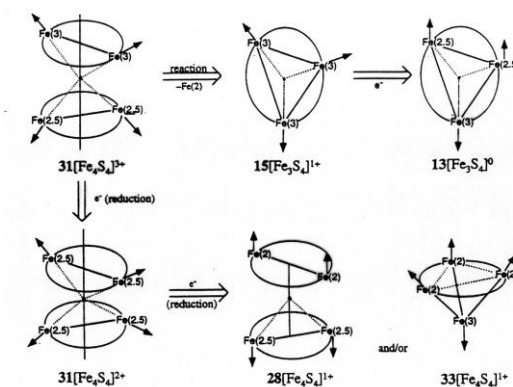


Fig. S18 Charge and spin fluctuations of iron-sulfur clusters.^{s55}

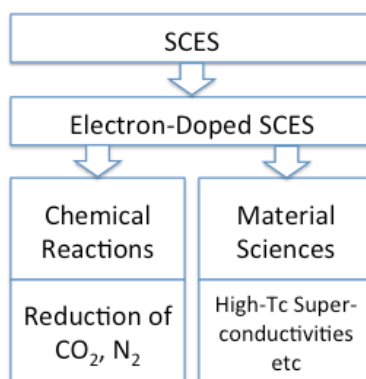


Fig. S19 Electron-doped SCES play important roles in both chemical reactions such as reduction reactions by iron-sulfur clusters and material sciences such as high- T_c superconductivity.⁴⁹

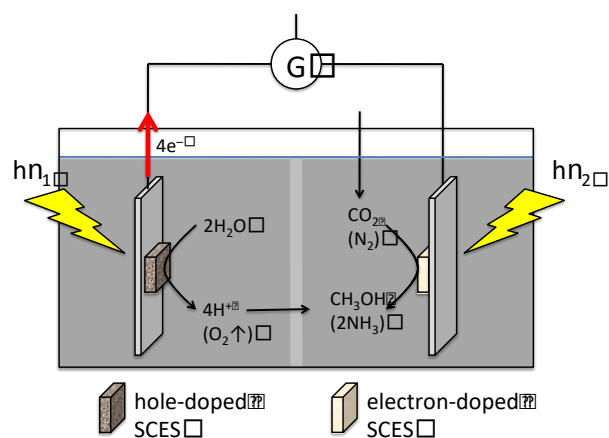


Fig. S20 Combination systems of hole- and electron-doped SCES systems for oxidation of water and reduction of CO₂, etc.⁴⁹

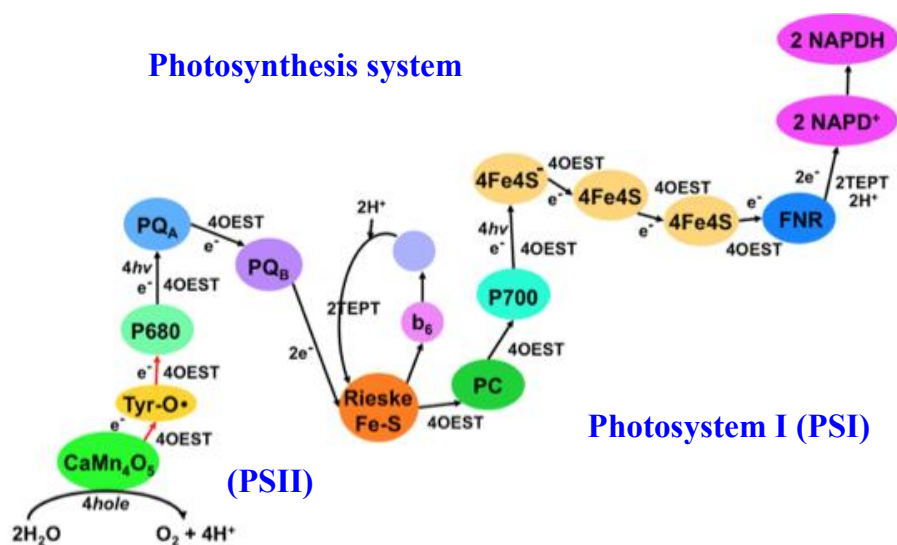


Fig. S21 Native photosynthesis system consisted of the hole-doped CaMn₄O_x cluster in PSII and electron-doped 4Fe-4S clusters in photosystem I (PSI)

SII.6 Beyond HDFT methods for SCES

The above collinear and non-collinear HF and HDFT solutions for the CaMn_4O_x cluster in PSII and Fe-S clusters in PSI are obtained on the basis of the independent particle model described with single Slater determinant approximation. However, the independent particle model may be regarded as a first step for theoretical approach to SCES in the Scheme I in the text. The dynamical electron correlation effects indeed play important roles for quantitative investigations of relative energies of the several possible structures as shown in present DLPNO-CCSD(T) calculations of CaMn_4O_x cluster in the S_0 state of PSII. Furthermore, for the next step, multi-configuration (MC) zero-order (ZO) references are often necessary for beyond HDFT calculations of these complex transition-metal complexes as illustrated in Fig. 7 in the text. For the successive multi-reference (MR) calculations^{51, 85, s12}, the first order density matrix of the HDFT solutions is diagonalized to obtain the approximated natural orbitals (UNO) and occupation numbers, which are used for construction of the MC ZO references as shown in Fig. 7 in the text. The UNO (DLPNO) MRCC calculations of the low-spin states of the CaMn_4O_x cluster in OEC of PSII will be performed in future.

References

- s33 R. J. Van Zee, C. A. Baumann, and W. Weltner, Jr., *J. Chem. Phys.*, 1987, **74**, 6977.
- s34 J.-C. Rovoal, J. C. Emampour, K. J. Zeringue and M. Vala, *Chem. Phys. Lett.*, 1982, **92**, 313.
- s35 K. Yamaguchi, T. Tsunekawa, Y. Toyoda and T. Fueno, *Chem. Phys. Lett.*, 1988, **141**, 371.
- s36 H. Kobayashi, T. Haseda, E. Kanda and M. Mori, *J. Phys. Soc. Jpn.*, 1960, **15**, 1646.
- s37 K. Yamaguchi, T. Fueno, N. Ueyama, A. Nakamura and M. Ozaki, *Chem. Phys. Lett.*, 1989, **164**, 210.
- s38 Y. Kitagawa, T. Saito, M. Ito, M. Shoji, K. Koizumi, S. Yamada, T. Kawakami, M. Okumura and K. Yamaguchi, *Chem. Phys. Lett.*, 2007, **442**, 445.
- s39 R. H. Holm, *Acc. Chem. Res.*, 1977, **10**, 427.
- s40 M. Shoji, Y. Nishiyama, Y. Maruno, K. Koizumi, Y. Kitagawa, S. Yamanaka, T. Kawakami, M. Okumura and K. Yamaguchi, *Int. J. Quant. Chem.*, 2004, **100**, 887.
- s41 S. Yamanaka, R. Takeda, M. Shoji, K. Koizumi, Y. Kitagawa and K. Yamaguchi, *Polyhedron*, 2005, **24**, 2784.

- s42 N. L. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15729.
- s43 K. Yamaguchi, *Chem. Phys. Lett.*, 1975, **30**, 288.
- s44 P. W. Anderson, *Mater. Res. Bull.*, 1973, **8**, 153.
- s45 P. W. Anderson, *Science*, 1987, **235**, 1196.
- s46 K. Yamaguchi, Y. Yoshioka and T. Fueno, *Chem. Phys. Lett.*, 1977, **46**, 360.
- s47 L. Savary and L. Balentz, *Rep. Prog. Phys.*, 2017, **80**, 016502.
- s48 R. Takeda, S. Yamanaka and K. Yamaguchi, *Int. J. Quant. Chem.*, 2007, **107**, 3219.
- s48 T. Kawakami, R. Takeda, S. Nishihara, T. Saito, M. Shoji, S. Yamada, S. Yamanaka, Y. Kitagawa, M. Okumura and K. Yamaguchi, *J. Phys. Chem. A*, 2009, **113**, 15281.
- s49 S. Yamanaka, R. Takeda, T. Kawakami, K. Nakata, T. Sakuma, T. Takada and K. Yamaguchi, *J. Magn. Magn. Mater.*, 2004, **272-276**, e235.
- s50 S. Yamanaka, R. Takeda and K. Yamaguchi, *Polyhedron*, 2003, **22**, 2013.
- s51 H. Nagao, M. Nishino, Y. Shigeta, T. Soda, Y. Kitagawa, T. Onishi, Y. Yoshioka and K. Yamaguchi, *Coord. Chem. Rev.*, 2000, **198**, 265.
- s52 M. Okamura, M. Kondo, R. Kuga, Y. Kurashige, T. Yanai, S. Hayami, V. K. K. Praneeth, M. Yoshida, K. Yoneda, S. Kawata and S. Masaoka, *Nature*, 2016, **530**, 465.
- s53 K. N. Ferreira, T. M. Iverson, K. Maghlaoui, J. Barber and S. Iwata, *Science*, 2004, **303**, 1831. (ref. 19 in the text)
- s54 K. Yamaguchi, T. Fueno, M. Ozaki, N. Ueyama and A. Nakamura, *Chem. Phys. Lett.*, 1990, **168**, 56.
- s55 K. Yamaguchi, S. Yamanaka, M. Nishino, Y. Takano, Y. Kitagawa, H. Nagao and Y. Yoshioka, *Theoret. Chem. Acc.*, 1999, **102**, 328.
- s56 M. Shoji, K. Koizumi, Y. Kitagawa, S. Yamanaka, M. Okumura, K. Yamaguchi, Y. Ohki, Y. Sunada, M. Honda and K. Tatsumi, *Int. J. Quant. Chem.*, 2006, **106**, 3288.
- s57 K. Miyagawa, M. Shoji, H. Isobe, S. Yamanaka, T. Kawakami, M. Okumura and K. Yamaguchi, *Mol. Phys.*, DOI: 10.1080/00268976.2020.1760388.
- s58 K. Yamaguchi, Y. Kitagawa, H. Isobe, M. Shoji, S. Yamanaka, M. Okumura, *Polyhedron*, 2013, **57**, 138. (ref. 52 in the text)

SIII Electronic structures of the CaMn_4O_x cluster

SIII.1 Low- and high-oxidation scenarios for the CaMn_4O_x cluster in OEC of PSII

In our theoretical view point in Scheme I, the CaMn_4O_x cluster in OEC of PSII is a typical SCES, where spin, charge, orbital and molecular motion (vibration etc.) plays important roles. In fact, valence states of Mn complexes often entail difficult and complex problems in chemistry. As introduced in the text, two different scenarios have been proposed for the CaMn_4O_x cluster in OEC of PSII: (α) the low-oxidation scenario (LOS)^{s59}; and (β) high-oxidation scenario (HOS). For example, the LOS and HOS scenarios provide the $\text{Ca(II)Mn(II)Mn(III)}_3\text{O}_x$ and $\text{Ca(II)Mn(IV)Mn(III)}_3\text{O}_x$ clusters in the S_0 state of OEC of PSII. Figure S22 illustrates valence states of the CaMn_4O_x cluster for Kok cycle assuming the HOS scenario.

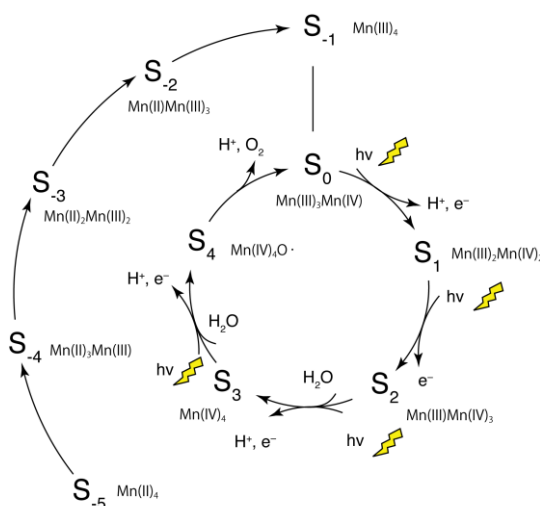


Fig. S22 An extended Kok cycle for water oxidation of oxygen evolving complex (OEC) of photosystem II (PSII). The original Kok cycle for OEC of PSII is consisted of five steps ($S_0 \sim S_4$). However, pre- S_0 steps ($S_{-1} \sim S_{-5}$) are discussed on the basis of the DFT computational results in relation to radiation damage of the CaMn_4O_5 cluster by the high-resolution XRD structure.

From the viewpoint of HOS in Fig. S22, the Mn-Mn distances revealed by the high-resolution (HR) XRD structure¹¹ were too long. In fact, the $\text{Mn}_{1(d)}\text{-Mn}_{2(c)}$, $\text{Mn}_{2(c)}\text{-Mn}_{3(b)}$, $\text{Mn}_{3(b)}\text{-Mn}_{4(a)}$, $\text{Mn}_{1(d)}\text{-Mn}_{3(b)}$ and $\text{Mn}_{1(d)}\text{-Mn}_{4(a)}$ distances revealed by the HR XRD structure were about 2.8 (2.7), 2.9 (2.8), 3.0 (2.7), 3.3 (3.2) and 5.0 (Å), respectively, where the corresponding values by EXAFS are given in parentheses. The

Mn_{3(b)}-Mn_{4(a)} distance by HR XRD was longer by 0.3 Å than the EXAFS value. Therefore, several groups claimed that the HR XRD structure¹¹ was the X-ray damaged S₋₃ (II, II, III, III) or S₋₂ (II, III, III, III) structures from the HOS scenario as shown in Fig. S22. On the other hand, the observed Mn-Mn distances by HR XRD were reasonable from the viewpoint of the LOS scenario.^{s59}

We have performed the full geometry optimization of the two electron reduced structures S_{-1ccca}(3333) and S_{-1acca}(3333) to elucidate the Mn-Mn distances as shown in Table S8.^{s58} The optimized Mn_{3(b)}-Mn_{4(a)} distances by QM(UB3LYP/ECP)/MM calculations^{52, 70} were about 3.1 and 2.7 (Å) for these structures, respectively, as shown in Table S8, indicating variations with the protonation conditions of the O₍₅₎ site. In fact, the short (2.7 Å) Mn_{3(b)}-Mn_{4(a)} distance by EXAFS was reproduced even for the assumed S₁- structure with the (3333) valence state under the assumption of O₍₅₎ = O²⁻. On the other hand, it became 3.1 Å for the double protonated state: O₍₅₎ = H₂O. The optimized Mn-Mn distances for the S₁ structure: S_{1bbca} by UB3LYP-D3 were 2.71 (2.7), 2.78 (2.8), 2.89 (2.9), 3.26 (3.2) and 5.04 (4.9) (Å), respectively, where the modified Mn-Mn distances obtained by reduction of 0.1 Å (possible experimental uncertainty of the Mn-Mn distances at the 1.9 Å resolution of XRD) from the HR XRD results are given in parentheses. The optimized Mn-Mn distances for S_{1bbca} with the (3443) valence state were consistent with the modified Mn-Mn distances within the experimental uncertainty. The X-ray damage-free Mn-Mn distances for the S₁ state by the Okayama XFEL structure (4UB6) were 2.68, 2.70, 2.89, 3.20 and 4.93 (Å), respectively, in consistent with the modified XRD structure. Thus, the protonation state of the O₍₅₎ was an important factor for determination of the Mn_{3(b)}-Mn_{4(a)} distance, indicating that the S₋₃ and/or S₋₂ structures were hardly conceivable for HR XRD.¹¹

SI.2 EPR results for the CaMn₄O_x cluster in the S₁ state of OEC of PSII

The EPR spectroscopy is effective for elucidation of valence states of Mn ions and protonation states of the CaMn₄O_x cluster in OEC of PSII.^{s60-s68} The parallel EPR spectroscopy elucidated the temperature-dependent para- magnetism for the S₁ state of the OEC of PSII, elucidating the small energy gap (about 2 cm⁻¹) between the ground singlet (*S* = 0) and excited triplet state (*S* = 1).^{s69} But the EPR spectra were not observed in the CH₃OH-containing S₁ sample, indicating an important environmental (polar) effect. Both spin and charge degrees of freedom in Scheme I were important

for theoretical analysis of the EPR structures of the CaMn_4O_x cluster in OEC of PSII. The four Mn spin sites provide eight different axial spin structures: three low spin, four intermediate spin and one high-spin configuration as illustrated in Fig. S23.⁶⁸ On the other hand, the $\text{Mn(III)}_2\text{Mn(IV)}_2$ valence state in the HOS scenario provides six different trapped valence configurations in the S_1 state as shown in Fig. S24.^{s70} Therefore, total $8 \times 6 = 48$ broken-symmetry (BS) solutions were feasible in the S_1 state.^{s70}

We have constructed 48 BS solutions assuming the HR XRD structure with $\text{O}_{(5)} = \text{O}^{2-}$, namely $S_{1\text{acca}}$ structure.^{s70} The lowest energy configuration for the XRD structure was found to be $S_{1\text{acca}}$ with the (3443) structure.^{s16} However, the ground spin state was calculated to be $S = 3$ in contradiction to the EPR result ($S = 0$) as shown in Fig. S25, indicating necessity of further refinements of the HR XRD structure¹¹. The full geometry optimizations of the eight different spin states of the $S_{1\text{acca}}$ with the (3443) structure were performed to elucidate relative energies including the zero-point energy (ZPE) corrections.^{s70} The total energies and total spin angular momentums for the eight spin structures were used to determine the effective exchange integrals (J) for the S_1 state using eq. (s27) under the adiabatic + ZPE correction procedure. The exact diagonalization of the spin Hamiltonian matrix provided the ground singlet state ($S = 0$) with the nearly degenerated (2 cm^{-1}) excited triplet ($S = 1$) state in accord with the EPR observation.

The optimized geometry for the $S_{1\text{acca}}$ with the (3443) structure provided a short (about $2.7 \text{ \AA}$) $\text{Mn}_{3(\text{b})}\text{-Mn}_{4(\text{a})}$ distance in compatible with the EXAFS³¹ and Berkeley XFEL¹² results. We have performed full geometry optimizations for the eight spin configurations of the proton-shifted $S_{1\text{bbca}}$ with the (3443) structure to elucidate the effective exchange integrals (J). The exact diagonalization of the spin Hamiltonian matrix provided the ground singlet state for the $S_{1\text{bbca}}$ with the (3443) structure, but the energy gap between the ground singlet and excited triplet states was larger than 15 cm^{-1} in consistent with no observation of the temperature-dependent paramagnetism in the polar condition.^{s70} As mentioned above, the optimized geometry for the $S_{1\text{bbca}}$ with the (3443) structure was compatible with the XFEL structure by Okayama group.⁸² Thus, the intra-cluster proton-shift between W2 and $\text{O}_{(5)}$ sites was feasible, depending on the environmental conditions in the S_1 state.

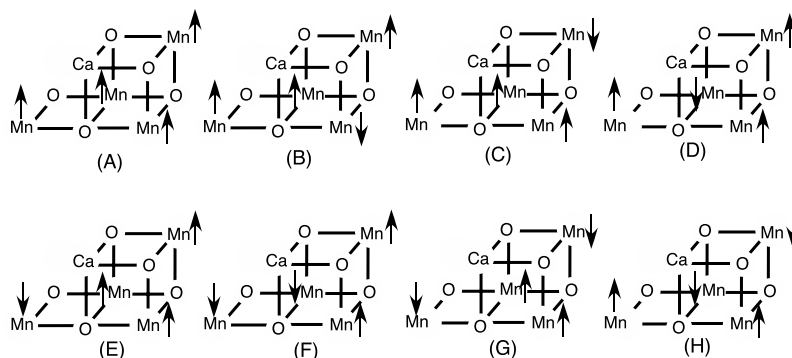


Fig. S23 Eight spin configurations for the CaMn_4O_x cluster in OEC of PSII.

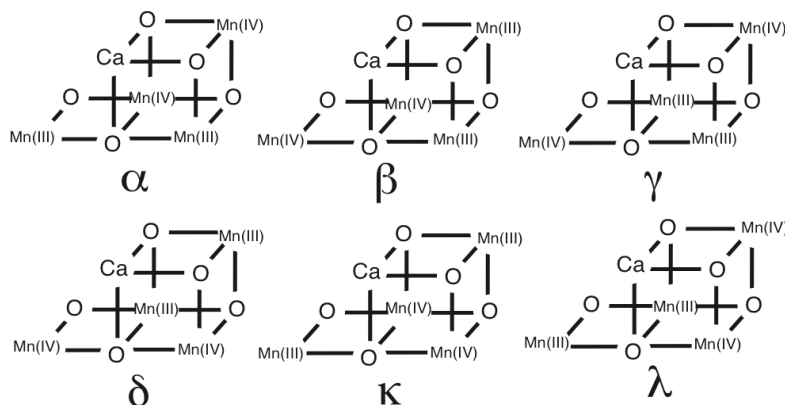


Fig. S24 Six trapped valence configurations in the S_0 state.

SIII.3 EPR results for the CaMn_4O_x cluster in the S_0 state of OEC of PSII

The EPR spectra detected the $S = 1/2$ spin state for the CH_3OH -containing sample^{8,9} in the S_0 state in a sharp contrast to the disappearance of the EPR spectra in the S_1 state. The eight spin configurations in Fig. S23 were equally feasible for the S_0 state. On the other hand, four different trapped valence configurations were conceivable for the S_0 state with the Mn(IV)Mn(III) valence state.⁷⁸ The $8 \times 4 = 32$ different spin-charge configurations were feasible for the S_0 state. The corresponding 32 BS UB3LYP solutions for the $S_{0\text{acca}}$ state were constructed assuming the HR XRD structure. Figure S26A shows the energy levels before spin projection for the ground and lower-energy excited state. On the other hand, Figure 26B illustrates the energy levels after spin projection. Qualitative tendency for the energy levels was not changed because of the local nature of the Mn spins. From Figures S26A and S26B, the $S_{0\text{acca}}$ state with the (3343) valence state was one of the most plausible structure, for which the $S = 1/2$ spin state ($\uparrow\downarrow\uparrow\downarrow$) was the ground state in accord with the EPR result.^{8,9} However, full

geometry optimizations of the S_0 intermediates were not performed at that time.⁷⁰ In this paper, we revisited the S_0 state as shown in the text.

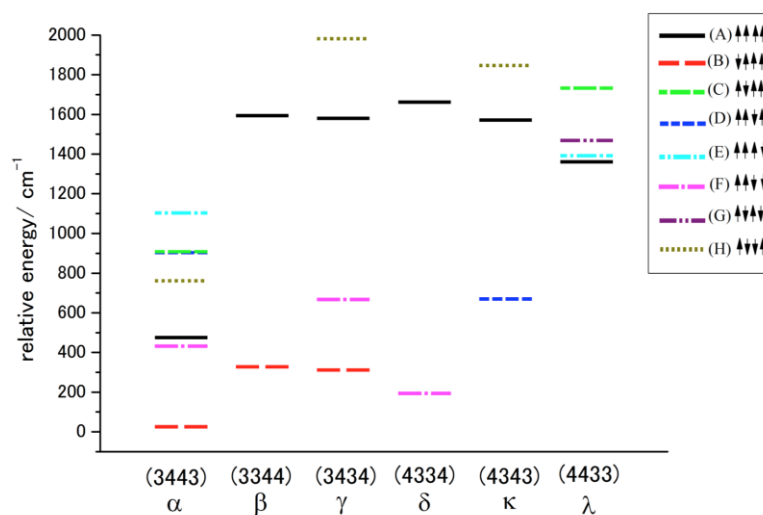


Fig. S25 The energy levels for the ground and lower-excited states of the CaMn₄O₅ cluster in the S_1 state of OEC of PSII obtained by UB3LYP.⁷⁵

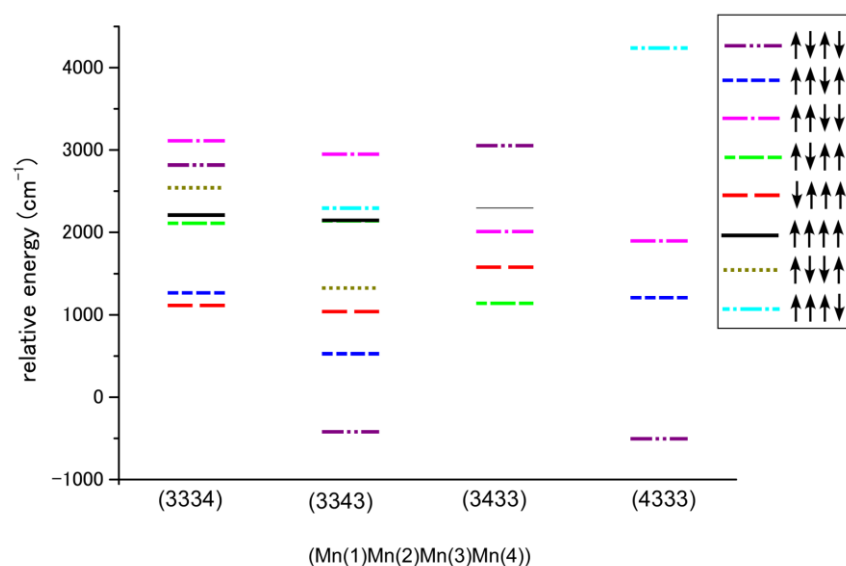


Fig. S26A The energy levels for the ground and lower-excited states of the CaMn₄O₅ cluster before spin projection in the S_0 state of OEC of PSII obtained by UB3LYP.⁷⁵

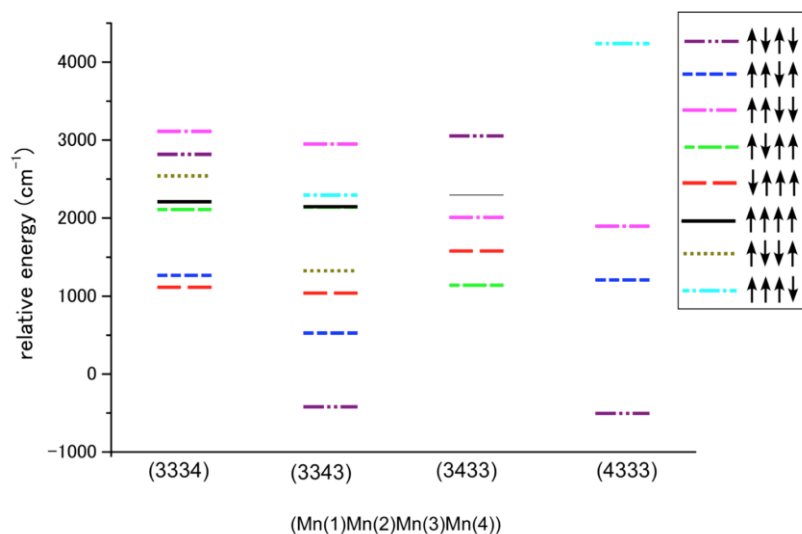


Fig. S26B The energy levels for the ground and lower-excited states of the CaMn_4O_5 cluster after spin projection in the S_0 state of OEC of PSII obtained by UB3LYP.⁷⁵

Krewald et al.⁷⁰ already performed the full geometry optimizations of several S_0 intermediates under the assumption of the 4H^+ configuration like in the case of $S_{0\text{acca}}$. They found that the $S_{0\text{acca}}$ state with the (3343) valence was the most stable among the S_0 intermediates as shown in Table S8. However, the optimized $\text{Mn}_{1(\text{d})}\text{-Mn}_{2(\text{c})}$, $\text{Mn}_{2(\text{c})}\text{-Mn}_{3(\text{b})}$, $\text{Mn}_{3(\text{b})}\text{-Mn}_{4(\text{a})}$, and $\text{Mn}_{1(\text{d})}\text{-Mn}_{3(\text{b})}$ distances were 2.90 (2.76), 2.96 (2.86), 2.74 (2.85) and 3.39 (3.27) (Å), where the corresponding values by Berkeley XFEL were given in parentheses. The optimized short $\text{Mn}_{3(\text{b})}\text{-Mn}_{4(\text{a})}$ distance (2.74 Å) with the assumption $\text{O}_{(5)} = \text{O}^{2-}$ was different from the XFEL value (2.85 Å)¹², and the ground spin state ($S = 7/2$) was also different from the EPR result ($S = 1/2$).^{8,9}

Krewald et al.⁷⁰ performed the full geometry optimization of the proton-shifted structure, $S_{0\text{bbca}}$ state with the (3433) valence structure, indicating the small energy gap (0.6 kcal/mol) as compared with the $S_{0\text{acca}}$ state with the (3343) valence structure. Thus the valence structure of the CaMn_4O_x cluster was variable, depending on the protonation of the $\text{O}^{(5)}$ site in accord with the Scheme I in the text. The ground spin state for the proton-shifted structure was $S = 1/2$ in accord with the EPR results. However, the optimized $\text{Mn}_{1(\text{d})}\text{-Mn}_{2(\text{c})}$, $\text{Mn}_{2(\text{c})}\text{-Mn}_{3(\text{b})}$, $\text{Mn}_{3(\text{b})}\text{-Mn}_{4(\text{a})}$, and $\text{Mn}_{1(\text{d})}\text{-Mn}_{3(\text{b})}$ distances for the (3433) valence structure were 2.79 (2.73), 2.81 (2.80), 2.96 (3.00) and 3.37 (3.19) (Å), respectively, where the corresponding values by our large-scale QM/MM calculations assuming the HS state were given in parentheses.^{s65} The optimized

Mn_{3(b)}-Mn_{4(a)} distances by both methods were about 3.0 Å, which is longer by 0.1 Å than the XFEL result.¹²

Krewald et al.⁷⁰ further performed the full geometry optimizations of several S₀ intermediates under the assumption of the 5H⁺ configuration as shown in Table S8. They found that the S_{0bbcb} state with the (3433) valence was the most stable among the S₀ intermediates as shown in Table S8. The same result was obtained in the present calculations. The ground spin states by their and our DFT calculations were $S = 5/2$ and $S = 7/2$, respectively, in contradiction to the EPR result ($S = 1/2$). The optimized Mn_{1(d)}-Mn_{2(c)}, Mn_{2(c)}-Mn_{3(b)}, Mn_{3(b)}-Mn_{4(a)}, and Mn_{1(d)}-Mn_{3(b)} distances were 2.78 (2.79), 2.81 (2.76), 3.15 (3.08) and 3.43 (3.31) (Å), where the corresponding values by the present calculations were given in parentheses. The optimized Mn_{3(b)}-Mn_{4(a)} distances (3.1 ~ 3.2 Å) were different from the XFEL value (2.85 Å).¹²

Krewald et al.⁷⁰ performed the geometry optimization of the S_{0bbca} state with the (3433) valence structure, indicating the small energy gap (2.6 kcal/mol) as compared with the S_{0bbcb} state with the (3433) valence structure as shown in Table S8. The optimized Mn_{1(d)}-Mn_{2(c)}, Mn_{2(c)}-Mn_{3(b)}, Mn_{3(b)}-Mn_{4(a)}, and Mn_{1(d)}-Mn_{3(b)} distances were 2.80 (2.78), 2.80 (2.78), 2.94 (2.89) and 3.38 (3.33) (Å), where the corresponding values by the present calculations were given in parentheses. The optimized Mn_{3(b)}-Mn_{4(a)} distances (2.89 Å) by ours was compatible with the XFEL value (2.85 Å).¹²

Judging from all the computational results⁷⁰ examined above, the S_{0bbca} with the (3433) valence structure resulted from the assumption of the 4H⁺ configuration is consistent with the $S = 1/2$ spin state observed for the CH₃OH-containing samples by the EPR method.^{8, 9} On the other hand, the S_{0bbca} with the (3433) valence structure obtained from the assumption of the 5H⁺ configuration is consistent with the S₀ structure observed by the Berkeley XFEL method.¹² Thus, full geometry optimizations of all the conceivable important intermediates in the S₀ and S₁ states by UB3LYP and/or UB3LYP-D3 were found to be crucial for reliable theoretical investigations of the EPR, EXAFS and XFEL experimental results. Through investigations at the HDFT level of theory were desirable before the successive time-consuming beyond HDFT calculations such as DLPNO-CCSD(T). The natural orbitals (UNO) of the UB3LYP solutions were also useful as starting orbitals for UCC SD(T) calculations of the CaMn₄O_x cluster since the UHF calculations were often

hardly converged for complex 3d transition metal clusters.^{51, s71}

Table S8 The observed and calculated Mn-Mn distances.

Systems	State	Mn ₁ -Mn ₂	Mn ₁ -Mn ₃	Mn ₁ -Mn ₄	Mn ₂ -Mn ₃	Mn ₃ -Mn ₄	RE
XFEL: S ₀ ^{a)}	1/2	2.76	3.27	4.97	2.86	2.85	
XRD (3WU2) ^{b)}		2.8 (2.7)	3.3 (3.2)	5.0 (4.9)	2.9 (2.8)	3.0 (2.9)	
XFEL: S ₁ ^{a)}		2.77	3.24	4.86	2.85	2.73	
XFEL: S ₁ ^{c)}		2.60	3.16	4.97	2.72	2.89	
Mn ₅ : B(O ₅ =OH ⁻)	S ₀ ^{d)}	2.72	3.50	5.43	2.83	3.00	
C _a : S ₀ bcca(3442)	S ₀ ^{d)}	2.71	3.44	5.34	2.81	3.00	
Mn ₅ : S ₁ (O ₅ =O ²⁻)	S ₁ ^{d)}	2.76	3.48	4.77	2.78	2.69	
S ₁ acca(3443)	S ₁ ^{d)}	2.74	3.23	4.71	2.77	2.69	
Mn ₅ : S ₂ (O ₅ =O ²⁻)	S ₂ (R) ^{d)}	2.76	3.32	4.71	2.79	2.72	
S ₂ acca(3444)	S ₂ (R) ^{d)}	2.75	3.39	5.06	2.76	2.70	
Mn ₅ : S ₂ (O ₅ =O ²⁻)	S ₂ (L) ^{d)}	2.73	2.87	4.24	2.79	2.91	
S ₂ acca(4443)	S ₂ (L) ^{d)}	2.71	2.86	5.19	2.75	3.18	
S ₋₁ ccca(3333) ^{e)}	0/2	2.78	3.44	5.32	2.82	3.07	
S ₋₁ acca(3333) ^{e)}	0/2	2.82	3.46	5.04	2.82	2.74	
S ₀ bcca(3433) ^{f)}	15/2	2.74	3.40	5.13	2.78	2.91	
S ₀ bbca(3433) ^{g)}	15/2	2.73	3.18	4.95	2.80	3.00	
S ₀ bcca(3433) ^{g)}	15/2	2.73	3.26	4.92	2.77	2.92	
S ₀ ccca(3433) ^{g)}	15/2	2.73	3.39	5.20	2.77	3.10	
S ₀ bbca(3442) ^{b)}	15/2	2.71	3.44	5.34	2.81	3.00	
S ₀ bbca(3433) ^{e)}	1/2	2.77	3.31	5.19	2.81	3.04	
S ₀ bbca(3433) ^{e)}	15/2	2.75	3.33	4.90	2.80	2.71	
S ₀ bbca(3433)(⊥) ^{h)}	1/2	2.79	3.37		2.81	2.96	0.6
S ₀ abcb(3433)(⊥) ^{h)}	1/2	2.76	3.61		2.90	2.86	5.5
S ₀ bbca(3433)(=) ^{h)}	1/2	2.79	3.17		2.81	3.03	5.1
S ₀ bbca(3343)(=) ^{h)}	7/2	2.87	3.34		2.90	2.93	3.7
S ₀ acca(3343)(⊥) ^{h)}	7/2	2.90	3.39		2.96	2.74	0.0
S ₀ abcb(3343)(⊥) ^{h)}	7/2	2.90	3.28		2.90	2.87	7.0
S ₀ accb(3433)(⊥) ⁱ⁾	7/2	2.77	3.59		2.86	2.87	5.9

S ₀ bcca(3433)($\perp$) ⁱ	9/2	2.80	3.38	2.80	2.94	2.6
S ₀ bbcb(3433)($\perp$) ⁱ	5/2	2.78	3.43	2.81	3.15	0.0
S ₀ accb(3343)(=) ⁱ	15/2	2.89	3.33	2.93	2.87	7.0
S ₀ bcca(3343)(=) ⁱ	7/2	2.87	3.33	2.91	2.94	4.1
S ₀ cbca(3433)(=) ⁱ	1/2	2.79	3.38	2.82	3.12	12.3

a) XEFL results from ref. 12, b) XRD results from ref. 11, c) XFEL results from ref. 82, d) computational results from ref. 52, e, f) computational results from ref. 83, g) computational results from ref. 80, h) computational results based on the 4H⁺ model from ref. 70, i) computational results based on 5H⁺ model from ref. 70.

References

- s59 R. Pace, L. Jin and R. Stranger, *Dalton Trans.*, 2012, **41**, 11145. (ref. 22 in the text)
- s60 A. Boussac, J. L. Zimmermann and A. W. Rutherford, *Biochemistry*, 1989, **28**, 8984.
- s61 S. L. Dexheimer and M. P. Klein, *J. Am. Chem. Soc.*, 1992, **114**, 2821.
- s62 R. D. Britt, J. M. Peloquin and K. A. Campbell, *Annu. Rev. Biophys.*, 2000, **39**, 463.
- s63 W. Lubitz, E. J. Reijerse and J. Messinger, *Energy Environ. Sci.*, 2008, **1**, 15. (ref. 21 in the text)
- s64 D. R. J. Kolling, N. Cox, G. M. Ananyev, R. J. Pace and G. C. Dismukes, *Biophys. J.*, 2012, **103**, 313. (ref. 23 in the text)
- s65 D. A. Pantazis, *ACS Catal.*, 2018, **8**, 9477. (ref. 27 in the text)
- s66 W. Lubitz, M. Chrysina and N. Cox, *Photosynth. Res.*, 2019, **142**, 105. (ref. 28 in the text)
- s67 N. Cox, D. A. Pantazis and W. Lubitz, *Annu. Rev. Biochem.*, 2020, **89**, 795. (ref. 29 in the text)
- s68 H. Mino and H. Nagshima, *J. Phys. Chem. B*, 2020, **124**, 128.
- s69 T. Yamauchi, H. Mino, T. Matsukawa, A. Kawamori and T. Ono, *Biochemistry*, 1997, **36**, 7520.
- s70 H. Isobe, M. Shoji, S. Yamanaka, H. Mino, Y. Umena, K. Kawakami, N. Kamiya, J.-R. Shen and K. Yamaguchi, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11911.
- s71 T. Saito, H. Yasuda, S. Nishihara, S. Yamanaka, Y. Kitagawa, T. Kawakami, M. Okumura and K. Yamaguchi, *Chem. Phys. Lett.*, 2011, **505**, 11.

SIV Structural data of optimized geometries for all models

SIV.1 S₀(3442) (C)

Table S9 Mulliken charge and spin densities of CaMn₄O₅ cluster of S₀(3442)(C) states calculated by B3LYP.

	C _a : S ₀ bcca(3442)		C _b : S ₀ accb(3442)	
	Charge	Spin	Charge	Spin
Ca	1.568	0.005	1.552	0.005
Mn ₁	0.918	3.940	1.000	3.952
Mn ₂	0.830	3.056	0.812	3.048
Mn ₃	0.954	2.866	0.960	3.057
Mn ₄	0.999	4.865	1.026	4.874
O ₁	-0.925	-0.001	-0.901	-0.013
O ₂	-0.633	-0.017	-0.619	-0.015
O ₃	-0.668	-0.034	-0.624	-0.059
O ₄	-0.695	0.251	-0.676	0.007
O ₅	-0.864	-0.010	-0.952	0.080

Ca: S₀bcca(3442)

H	-3.94629911	-0.94063430	-4.89579174
C	-4.13124574	-0.81548939	-3.82918955
C	-2.83785872	-0.51849884	-3.09908959
O	-2.64784414	-1.02325078	-1.97164512
O	-2.01900807	0.25856377	-3.68995179
H	-4.61922486	-1.69886118	-3.42237317
H	-4.79919137	0.04124703	-3.70688780
H	4.09313560	-3.70338749	-0.76861121
C	3.58662466	-3.68746271	0.19741086
C	2.63324770	-2.52107128	0.24337433
O	1.73625299	-2.41630630	-0.62033081
O	2.80967649	-1.67942558	1.19119543
H	3.00829215	-4.60892696	0.28193734
H	4.31817761	-3.63685572	0.99890342
H	5.57678166	2.39303107	-0.51128781
C	4.71984841	2.11643361	0.07623201
C	4.06793228	0.93273109	0.23094521
N	4.05421547	3.01905636	0.87542604
C	3.03531449	2.39269271	1.47721854
N	3.01722771	1.11930205	1.11137537
H	2.33440861	2.86304971	2.14176370
H	4.26448247	-0.02512765	-0.21479368
H	4.28424122	3.99474685	0.98629210
H	2.16224072	5.11829179	0.01683216
C	1.79026221	5.00124649	-0.99800926
C	0.98745857	3.72909069	-1.15533718
O	0.54597639	3.20983155	-0.07509701
O	0.79143151	3.28387435	-2.30684349
H	2.61533853	5.01515042	-1.70867373

H	1.13153390	5.84250747	-1.22800446
H	0.58521013	-1.46827908	6.34865465
C	1.10641920	-0.57688321	5.99621845
C	0.86492612	-0.41857752	4.51613203
O	-0.35056487	-0.31905272	4.15705843
O	1.85426548	-0.39304432	3.73702917
H	2.16859241	-0.65809589	6.21261150
H	0.68394303	0.28098065	6.52166858
H	-3.89141929	-3.28400113	3.62578366
C	-4.10928021	-3.03910658	2.58684741
C	-2.96209193	-2.27120684	1.97499532
O	-2.57895835	-2.52976418	0.82350299
H	-4.99604619	-2.40114696	2.57390061
O	-2.46670897	-1.35583501	2.73424549
H	-4.31135404	-3.94239647	2.01588191
H	-3.94129069	3.83049813	2.71666497
C	-3.03445189	3.60662616	3.28179328
C	-2.25553190	2.55674997	2.53704459
O	-2.14428053	1.41443520	3.06604809
O	-1.77237888	2.89973997	1.41750709
H	-3.29952755	3.26288946	4.27799103
H	-2.44454367	4.52141706	3.33942056
Ca	-0.81464171	-1.66891658	-0.61951915
Mn	1.57920538	-0.23214963	1.62674323
Mn	-1.07412976	-0.07722876	2.27261147
Mn	-0.79801501	1.74086919	0.13929379
Mn	-0.66445451	1.63716281	-2.83549491
O	0.08634938	-1.34475313	1.61809751
O	-1.78927941	0.26742540	0.65120244
O	0.28928205	1.11998116	1.81448669
O	-1.75674335	2.26934838	-1.18576742
O	0.22830635	0.54057199	-1.02524074
H	1.16910706	0.75239380	-1.06184850
O	-0.71097311	-4.19270256	-0.36827103
H	-0.27450855	-4.73840220	-1.03420003
H	-1.59412366	-4.56356747	-0.24140324
O	-0.41075672	-2.58943981	-2.87420568
H	-0.27272105	-2.07123690	-3.68747385
H	0.19929166	-3.34229653	-2.95132539
O	0.59031201	-1.47061866	-5.26278514
H	1.37703957	-2.07020094	-5.23790267
H	0.19731622	-1.55239561	-6.13938141
O	1.79072302	-4.28285561	-2.55011056
H	1.98255034	-5.15267811	-2.18200562
H	1.83814145	-3.64142157	-1.79427510
O	2.70817868	-3.12530491	-4.88956149
H	2.46659791	-3.59130806	-4.05986283
H	3.49642634	-2.61236550	-4.67471639
O	1.03672156	0.90066505	-4.07401241
H	0.88674081	0.07688970	-4.59664133
H	1.46534462	1.53176518	-4.66384047
O	-1.33219447	3.15212308	-4.40513162
H	-1.23233378	4.05811754	-4.08256716
H	-2.26961261	3.05727087	-4.62258433
O	0.40433064	-3.95832201	2.32787971
H	0.31008620	-2.98532105	2.23637433
H	0.09839067	-4.26857804	1.46179663

Cb: S₀acch(3442)

H	-3.80712937	-0.18238482	-4.86465358
C	-4.09423329	-0.33624123	-3.82526248
C	-2.93996756	-0.02022809	-2.90100104
O	-2.80408272	-0.68965589	-1.84585421

O	-2.17644716	0.93681898	-3.23558788
H	-4.44667775	-1.35490042	-3.67626909
H	-4.91405136	0.35077700	-3.59927604
H	3.94949453	-1.91431908	-3.05476573
C	4.05272440	-1.92748670	-1.97101456
C	2.80470601	-1.38908546	-1.32044553
O	1.68550896	-1.65364564	-1.80579054
O	2.97929281	-0.68596997	-0.26645111
H	4.16983365	-2.96691027	-1.65375525
H	4.93159217	-1.36679606	-1.66329652
H	4.00491672	4.50155750	-0.07198096
C	3.54968409	3.66487540	0.42674865
C	3.09418649	2.46786064	-0.03676627
N	3.31238423	3.65649388	1.78278630
C	2.72668067	2.49581563	2.10960946
N	2.58429539	1.75125539	1.02589078
H	2.40620164	2.22611565	3.09998679
H	3.08067351	2.07539884	-1.03752130
H	3.52662972	4.40019673	2.42872501
H	0.83946446	5.18688869	1.84412903
C	0.34202430	5.32424964	0.88664602
C	-0.10850602	4.00039119	0.31678639
O	-0.43586322	3.11080630	1.16729303
O	-0.16683644	3.86566370	-0.92716634
H	0.99781827	5.83681482	0.18624358
H	-0.54600739	5.94075636	1.04778573
H	2.47686912	-2.95899444	5.03613012
C	2.62820192	-1.88073701	4.96567117
C	1.91209210	-1.35754329	3.74399212
O	0.64992580	-1.58596446	3.71944474
O	2.55919021	-0.75293386	2.86169745
H	3.69120621	-1.65821082	4.91631612
H	2.19469009	-1.42789102	5.85881046
H	-2.28259753	-5.17297637	2.80493131
C	-2.79459752	-4.69682876	1.97012209
C	-2.02825494	-3.48667407	1.49590829
O	-1.96750218	-3.21862304	0.28501813
H	-3.77340344	-4.36286474	2.32312638
O	-1.49148048	-2.78779221	2.43447976
H	-2.93620555	-5.40117933	1.15354920
H	-4.29416263	1.38786259	4.28845986
C	-3.28084232	1.26392745	4.67417475
C	-2.38132498	0.83171920	3.54504331
O	-1.81419201	-0.30155641	3.65749596
O	-2.25788267	1.62476844	2.57225037
H	-3.28001340	0.53557811	5.48082655
H	-2.94682815	2.23400138	5.04425823
Ca	-0.71520683	-1.54597765	-1.01876871
Mn	1.60188151	-0.03091661	0.94464672
Mn	-0.60644416	-1.07373331	2.26438449
Mn	-1.11283342	1.25018595	0.89374358
Mn	-0.87656337	2.07586105	-1.95736826
O	0.60626731	-1.61406615	0.98570017
O	-1.75364167	-0.46794339	0.97917763
O	0.21321384	0.60633878	2.11226367
O	-2.43571526	1.89423064	-0.28968827
H	-2.98579922	1.13330253	-0.52981481
O	-0.01021302	0.81766697	-0.48429912
O	-0.15296658	-4.03908039	-1.49011094
H	-0.02822446	-4.43094854	-2.36318707
H	-0.91825897	-4.47099122	-1.08356032
O	-0.77077423	-1.88642054	-3.54010811
H	-0.47909164	-1.10806915	-4.05501522
H	-0.17197516	-2.59252680	-3.82749784
O	0.50988134	0.06816798	-5.13669160

H	1.26334630	-0.49993145	-5.43797962
H	0.01917904	0.32832499	-5.92537153
O	1.62127182	-3.41995808	-3.82818356
H	2.10303295	-4.23756702	-3.65761379
H	1.72860081	-2.84940001	-3.02483202
O	2.49553641	-1.65629194	-5.75745742
H	2.28063311	-2.35968587	-5.10495496
H	3.36989591	-1.33284197	-5.50972757
O	0.88550805	1.99006067	-3.30082128
H	0.79848633	1.32384368	-4.02789610
H	1.16769386	2.81364049	-3.71698294
O	-1.87673037	3.77675426	-3.18213485
H	-2.00211575	4.54925844	-2.61469304
H	-2.76280720	3.48902297	-3.43949030
O	1.87221310	-3.99857226	0.60562002
H	1.34150204	-4.18743181	-0.18403689
H	1.50666091	-3.13264528	0.88832560

SIV.2 S₀(2443) (D)

Table S10 Mulliken charge and spin densities of CaMn₄O₅ cluster of S₀(2443)(D) states calculated by B3LYP.

	D _a : S ₀ bcca(2443)		D _b : S ₀ accb(2443)	
	Charge	Spin	Charge	Spin
Ca	1.557	0.009	1.549	0.010
Mn ₁	0.939	4.846	0.987	4.848
Mn ₂	0.890	3.020	0.869	3.025
Mn ₃	0.874	3.038	0.870	3.092
Mn ₄	0.984	3.941	0.998	3.956
O ₁	-0.983	0.084	-0.989	0.074
O ₂	-0.610	-0.025	-0.614	-0.014
O ₃	-0.670	0.007	-0.642	-0.015
O ₄	-0.609	0.028	-0.655	0.043
O ₅	-0.816	0.012	-0.809	-0.089

D_a: S₀bcca(2443)

H	-3.37909911	-0.83116507	-5.20453193
C	-3.60428795	-1.01794476	-4.15467167
C	-2.46220137	-0.55548003	-3.28197680
O	-2.07535357	-1.24537688	-2.33327392
O	-1.95614551	0.58533026	-3.60753691
H	-3.81253065	-2.07291219	-3.99268941
H	-4.49158884	-0.43406695	-3.89762767
H	4.60028153	-1.07142089	-2.32057222
C	4.64982944	-1.38859503	-1.27791510
C	3.29641375	-1.19473180	-0.62702495
O	2.29453569	-1.74042356	-1.16586437
O	3.24869333	-0.49149390	0.41976233

H	4.90062210	-2.45119656	-1.27368567
H	5.42296225	-0.83110107	-0.75605729
H	4.00222991	4.78828470	1.01751568
C	3.51272910	3.94568736	1.47235894
C	3.35998030	2.65015070	1.07195884
N	2.86592883	4.03701148	2.68270690
C	2.35143142	2.82866442	2.97938972
N	2.63415286	1.96324956	2.02260855
H	1.78436996	2.61752066	3.86992247
H	3.70519042	2.16224476	0.17778164
H	2.80119520	4.85906545	3.26206289
H	0.85686793	5.30967724	0.80349060
C	0.62746987	5.19681530	-0.25231202
C	0.05238996	3.83505922	-0.53884688
O	-0.32951553	3.13614898	0.43898972
O	-0.02601255	3.48880669	-1.75576384
H	1.52131992	5.35481515	-0.85413593
H	-0.11070958	5.94692155	-0.54561661
H	0.59032006	-2.43224689	6.04886112
C	0.84014578	-1.37647888	5.93004727
C	0.72815886	-1.00879069	4.47104050
O	-0.42958608	-1.12931738	3.95757470
O	1.75595761	-0.61431616	3.86289675
H	1.84426832	-1.19138789	6.30337618
H	0.11461547	-0.80039970	6.50584210
H	-2.95462675	-4.83269940	2.72678083
C	-3.14602515	-4.54204465	1.69491445
C	-2.26084995	-3.38499237	1.29399672
O	-1.79455427	-3.33368368	0.13972391
H	-4.18659861	-4.21560434	1.62638205
O	-2.07606722	-2.50328200	2.20624222
H	-2.99775141	-5.38693589	1.02589541
H	-5.03332779	2.04124494	2.63283132
C	-4.16702566	1.94579191	3.28951684
C	-3.05109790	1.27436252	2.53374120
O	-2.62200435	0.16863434	2.93527159
O	-2.62480821	1.91229462	1.50903381
H	-4.43482710	1.37168413	4.17251171
H	-3.85504139	2.95139839	3.57360397
Ca	-0.18747122	-1.80676760	-0.92705989
Mn	1.76022641	-0.04311562	1.81820165
Mn	-1.02674741	-0.84281945	2.05400772
Mn	-1.19760072	1.28854017	0.34481914
Mn	-0.96071610	1.84133276	-2.47170297
O	0.40905000	-1.62342637	1.36174574
O	-1.77648459	-0.42241247	0.43090515
O	-0.19712111	0.81267352	1.86897240
O	-2.15796274	1.83116293	-1.15341015
O	0.15736455	0.69024685	-0.95597421
H	1.03956445	1.05512450	-0.80651333
O	0.57605881	-4.27142612	-0.82986721
H	-0.27771429	-4.67221418	-0.60636310
H	0.91109576	-4.73428028	-1.60742662
O	0.15654466	-2.58283950	-3.29670043
H	0.20431142	-1.86201895	-3.95150559
H	0.98581165	-3.07867125	-3.42169376
O	0.85339592	-0.53604009	-5.15906116
H	1.78078811	-0.88419644	-5.21793034
H	0.49517628	-0.55026784	-6.05501180
O	2.77236522	-3.45517420	-3.12965821
H	3.20469027	-4.26649901	-2.84145426
H	2.67298495	-2.87096399	-2.32775285
O	3.32246643	-1.63614347	-5.12350300
H	3.23422375	-2.32947806	-4.43261520
H	3.98907171	-1.02516339	-4.78749314

O	0.62319226	1.70286278	-3.78143802
H	0.69979379	0.89936389	-4.36993350
H	0.86923225	2.48243282	-4.29451700
O	-1.94525023	3.42476554	-3.86962575
H	-2.14105568	4.23896891	-3.38706578
H	-2.80257325	3.08327712	-4.15848798
O	1.60946303	-3.93868660	1.89063183
H	1.47113185	-4.30798419	1.00646683
H	1.13698794	-3.06998433	1.82232115

Db: S_{0accb}(2443)

H	-3.47376033	-0.33361493	-4.75521749
C	-3.94577803	-0.16430668	-3.78446140
C	-2.87344626	-0.08401258	-2.72661051
O	-2.84756080	-0.87124131	-1.77207855
O	-1.99282875	0.84299636	-2.90533398
H	-4.64632016	-0.96868939	-3.56785885
H	-4.47363684	0.79118529	-3.83567232
H	3.87815305	-0.90852199	-3.61427975
C	4.08855751	-1.25844951	-2.60183259
C	2.91735924	-0.92481415	-1.70110200
O	1.77143014	-1.31444233	-2.05331818
O	3.15364672	-0.27554272	-0.64447469
H	4.19634645	-2.34517467	-2.65033167
H	5.01172591	-0.81465801	-2.23477105
H	3.49848249	5.10139559	0.28628367
C	3.21618091	4.16747480	0.73944403
C	2.94538188	2.93856696	0.21152850
N	3.05031266	4.02986526	2.09668670
C	2.68791189	2.75925342	2.35069423
N	2.61774623	2.06868075	1.22853241
H	2.47403956	2.38432571	3.33735751
H	2.95597670	2.62252749	-0.81744392
H	3.17831873	4.74919766	2.79072315
H	0.51716650	5.13763877	2.04344941
C	-0.00846167	5.23132744	1.09513440
C	-0.40201627	3.87428511	0.57755739
O	-0.67293908	2.97898892	1.41755282
O	-0.47653283	3.72659890	-0.68178162
H	0.60402764	5.75911694	0.36668118
H	-0.92813194	5.80015017	1.26325011
H	2.61756612	-3.22608024	4.84613885
C	2.72950329	-2.13954318	4.85308074
C	2.03060200	-1.56231992	3.64539316
O	0.78593567	-1.83766607	3.55444871
O	2.68481929	-0.86663096	2.83393581
H	3.78484540	-1.87296899	4.85467774
H	2.24842678	-1.76357818	5.75908977
H	-1.85404100	-5.56215479	2.31626679
C	-2.37475416	-5.09044268	1.48293122
C	-1.74556685	-3.75940550	1.14191266
O	-1.72133378	-3.37162299	-0.04143078
H	-3.40910846	-4.90720533	1.78905788
O	-1.29377160	-3.09898781	2.14362093
H	-2.37824774	-5.74288547	0.61061392
H	-4.37063209	0.72965622	4.39038201
C	-3.34825725	0.63172095	4.76288811
C	-2.43292778	0.32809806	3.60446943
O	-1.79262486	-0.75372500	3.60806686
O	-2.38261456	1.21586122	2.68903481
H	-3.30048561	-0.15549218	5.51270364

H	-3.06224103	1.58943268	5.20278344
Ca	-0.53491739	-1.47039130	-1.11769279
Mn	1.92255610	0.01054290	1.01714912
Mn	-0.47723725	-1.31796977	2.10224852
Mn	-1.26153834	1.06143069	1.05920545
Mn	-1.12526662	2.08732935	-1.63298533
O	0.69594899	-1.71117143	0.82720628
O	-1.72859172	-0.66861360	0.90262792
O	0.12249765	0.45012564	2.10363972
O	-2.65592365	1.79910415	-0.08863660
H	-3.25400427	1.08149965	-0.33860956
O	-0.23636586	0.95908820	-0.54224432
O	0.21243918	-3.95148118	-1.77638052
H	-0.58338828	-4.29559159	-1.33800506
H	0.22375128	-4.29266725	-2.67832823
O	-0.76377250	-1.73643443	-3.64116746
H	-0.49949841	-0.90382924	-4.08574613
H	-0.11364022	-2.38647696	-3.94905583
O	0.29872321	0.46161023	-5.00334312
H	1.08323188	0.00120921	-5.40115297
H	-0.25963965	0.75002910	-5.73459298
O	1.73117111	-2.96352114	-4.14823819
H	2.28781523	-3.74314768	-4.04270681
H	1.83135342	-2.42231196	-3.31783479
O	2.34631343	-1.00159663	-5.93238539
H	2.22793238	-1.77737495	-5.33429332
H	3.20440896	-0.62546358	-5.70369949
O	0.57510047	2.26531512	-3.04886480
H	0.50023925	1.63670968	-3.81313804
H	0.71319184	3.14415230	-3.42182306
O	-2.21454744	3.51109171	-2.72006138
H	-2.44347865	4.29913082	-2.20497005
H	-3.04783301	3.14144692	-3.04828179
O	2.08714640	-3.95751727	0.39346924
H	1.61207950	-4.17927744	-0.42287350
H	1.61624743	-3.13624415	0.68103320

SIV.3 S₀(3433) (E)

Table S11 Mulliken charge and spin densities of CaMn₄O₅ cluster of S₀(3433)(E) states calculated by B3LYP.

	E _a : S ₀ bcca(3433)		E _b : S ₀ accb(3433)		E _c : S ₀ bccb(3433)	
	Charge	Spin	Charge	Spin	Charge	Spin
Ca	1.568	0.006	1.573	0.001	1.534	0.007
Mn ₁	0.958	3.956	0.971	3.958	0.950	3.960
Mn ₂	0.868	3.059	0.857	3.068	0.863	3.077
Mn ₃	1.060	3.922	1.059	3.949	1.079	3.936
Mn ₄	1.020	3.939	1.018	3.943	0.995	3.945
O ₁	-0.934	-0.018	-0.936	-0.009	-0.916	-0.015
O ₂	-0.688	0.022	-0.728	-0.026	-0.673	-0.022

O ₃	-0.728	-0.044	-0.733	0.026	-0.725	-0.037
O ₄	-0.678	-0.017	-0.698	0.039	-0.653	-0.044
O ₅	-0.936	0.086	-0.903	-0.035	-0.914	0.090

Ea: Sobcca(3433)

H	-3.75325022	-1.01772248	-4.94984084
C	-4.03075081	-0.84104692	-3.90999190
C	-2.80017538	-0.49313687	-3.10402216
O	-2.56062270	-1.08928807	-2.04250562
O	-2.06537092	0.43372999	-3.60379301
H	-4.52960997	-1.71664868	-3.50147896
H	-4.71580494	0.00936592	-3.89350108
H	4.10240151	-3.68599951	-0.93691282
C	3.89627454	-3.35976861	0.08047609
C	2.82695289	-2.29794919	0.10092004
O	1.89072510	-2.32773520	-0.72389394
O	2.94505425	-1.40949285	1.01663256
H	3.51489760	-4.21719357	0.64089255
H	4.80656645	-3.00929963	0.56105445
H	5.40042993	2.92507262	-0.46995449
C	4.56959612	2.56055033	0.10702622
C	3.98373679	1.33507464	0.18450958
N	3.87181409	3.36622612	0.97868331
C	2.89823158	2.64365851	1.54823486
N	2.94094789	1.40137420	1.08981748
H	2.18506187	3.02541698	2.25599893
H	4.22178985	0.42215313	-0.32967382
H	4.06134644	4.33927774	1.16353527
H	1.91019725	5.24246032	-0.19332287
C	1.64340221	4.94365801	-1.20327365
C	0.82161539	3.68031995	-1.20075753
O	0.36049154	3.28015374	-0.09221351
O	0.63213517	3.11057610	-2.31194942
H	2.53979006	4.80059262	-1.80574814
H	1.05113001	5.73387290	-1.67021501
H	0.77942660	-1.54231243	6.26840972
C	1.22248974	-0.59912800	5.94503654
C	0.95068315	-0.40549443	4.47254184
O	-0.27151821	-0.39243226	4.12851240
O	1.92987985	-0.26940166	3.69076718
H	2.29032140	-0.60198729	6.14924370
H	0.73923314	0.20157299	6.50711487
H	-3.45803432	-3.71184501	3.61398294
C	-3.78398378	-3.43410142	2.61196548
C	-2.75753958	-2.53910054	1.95928198
O	-2.41811843	-2.73078979	0.78086352
H	-4.71863593	-2.87736538	2.70924620
O	-2.31116634	-1.60031156	2.71817636
H	-3.95592292	-4.32178026	2.00775948
H	-4.33652215	2.55725826	3.85594263
C	-3.43193526	3.13074833	3.65105196
C	-2.52677358	2.34168664	2.73470282
O	-2.26763340	1.15084587	3.12909756
O	-2.08749399	2.87209619	1.69204071
H	-2.92009207	3.28863097	4.60233922
H	-3.68960242	4.09089879	3.21080552
Ca	-0.73319320	-1.75925764	-0.66230057
Mn	1.60246122	-0.08592692	1.53660486
Mn	-1.08210138	-0.16993013	2.25076218
Mn	-0.86334883	1.71265414	0.20898447

Mn	-0.70847452	1.57343114	-2.66963686
O	0.21095156	-1.31247909	1.55217708
O	-1.81408151	0.12725701	0.64744155
O	0.19627095	1.16289706	1.79472193
O	-1.78536781	2.08933191	-1.35543976
O	0.28978385	0.32819036	-1.29272689
H	1.24253932	0.34400883	-1.43700155
O	-0.38218194	-4.27731864	-0.26921069
H	0.08365220	-4.81815210	-0.91864372
H	-1.24168869	-4.69520971	-0.12712251
O	-0.44176157	-2.85457028	-2.88028288
H	-0.34276590	-2.28404394	-3.66565112
H	0.30155454	-3.48061338	-2.94769303
O	0.39935947	-1.39380944	-5.13181802
H	1.26609481	-1.87481699	-5.17410785
H	-0.00560674	-1.46491063	-6.00479282
O	2.02642359	-4.13101617	-2.67404275
H	2.31326833	-4.98647204	-2.33511108
H	2.04393766	-3.50268320	-1.90300479
O	2.70957161	-2.78137422	-4.97625450
H	2.56427268	-3.30832043	-4.15953937
H	3.46540840	-2.21289222	-4.78654660
O	0.61327886	1.06168895	-4.17646551
H	1.54137155	1.20787858	-3.95041230
H	0.54417208	0.13965788	-4.55372924
O	-1.57796599	3.18519672	-4.19242035
H	-1.55629819	4.05908702	-3.78123110
H	-2.51528597	2.97014079	-4.29038220
O	0.78621673	-3.84038522	2.35282383
H	0.61312659	-2.88225031	2.21383344
H	0.47242647	-4.21688069	1.51598234

Eb: S_{0accb}(3433)

H	-3.51063892	-1.10320623	-5.13385458
C	-3.88911843	-0.81429094	-4.15321288
C	-2.73700753	-0.47452542	-3.23176658
O	-2.74169498	-0.90292018	-2.05598282
O	-1.81856275	0.26066826	-3.72097024
H	-4.50531605	-1.60881655	-3.73803860
H	-4.50272999	0.07965870	-4.28851824
H	4.20842666	-3.43166518	-1.10220877
C	3.71766092	-3.50865312	-0.13130234
C	2.74042392	-2.37173239	0.03308333
O	1.85194451	-2.18553237	-0.82675592
O	2.88586082	-1.64614740	1.07643942
H	3.15936897	-4.44637191	-0.11719741
H	4.45992708	-3.51270231	0.66199657
H	5.85298317	2.54887973	0.34115949
C	4.88744877	2.23660992	0.69640060
C	4.32509726	1.00529926	0.84089144
N	3.93298589	3.13610898	1.11601597
C	2.84186538	2.46031316	1.49814764
N	3.04599418	1.15998207	1.34268502
H	1.92657868	2.90456342	1.84302345
H	4.72592008	0.03142096	0.62714396
H	4.02297681	4.14123935	1.12578127
H	1.89827658	5.26026107	0.24462561
C	1.52379466	5.19214398	-0.77435843
C	0.74474995	3.91646628	-0.98951875
O	0.19730871	3.40665778	0.04316669
O	0.65207352	3.45817649	-2.15126863
H	2.34260182	5.26243980	-1.48780641
H	0.84601159	6.03217886	-0.94674537

H	0.51873777	-1.98283499	6.26142067
C	1.04337003	-1.06225999	6.00075178
C	0.84373039	-0.78015037	4.53164623
O	-0.36367394	-0.64307161	4.15301701
O	1.85363010	-0.70002171	3.78591838
H	2.09955331	-1.15770316	6.23989077
H	0.60072467	-0.25419273	6.58506906
H	-3.85714182	-3.55900516	3.39041768
C	-4.06155161	-3.26494229	2.36175313
C	-2.92296896	-2.43920449	1.80927009
O	-2.55127706	-2.59930603	0.63493923
H	-4.96292101	-2.64730025	2.36394898
O	-2.42748719	-1.58934260	2.63750283
H	-4.23451556	-4.14121561	1.74101734
H	-4.20415994	3.47400156	2.91098981
C	-3.31661420	3.23443299	3.49892872
C	-2.43608933	2.31313690	2.69718769
O	-2.18599951	1.17097236	3.17996136
O	-2.00243255	2.75517253	1.59239382
H	-3.60840706	2.77953845	4.44165450
H	-2.78065963	4.16664635	3.68243022
Ca	-0.83531528	-1.52826605	-0.73229161
Mn	1.61923886	-0.27443114	1.66770490
Mn	-1.05790562	-0.23377226	2.28581822
Mn	-0.90361516	1.74844131	0.24282122
Mn	-0.51678303	1.61776012	-2.60807991
O	0.13293316	-1.40603121	1.50696033
O	-1.81061718	0.19711413	0.69837519
O	0.30817917	1.00488933	1.99829063
O	-2.00075911	2.36915684	-1.61881333
H	-2.79334500	1.82244820	-1.70212058
O	0.02412253	0.76357016	-1.11595928
O	-0.60811165	-4.06575756	-0.68431662
H	-0.17329393	-4.53633120	-1.40593524
H	-1.47932287	-4.46887862	-0.57380937
O	-0.37573754	-2.29370373	-3.04930952
H	-0.29043385	-1.71792818	-3.82686119
H	0.28251546	-2.99850684	-3.17675254
O	0.67566320	-0.99073934	-5.37947579
H	1.44544129	-1.60876443	-5.44638454
H	0.34673949	-0.82942326	-6.27087543
O	1.89063410	-3.89698995	-2.87146539
H	2.07846146	-4.78624978	-2.55019421
H	1.93983883	-3.29755836	-2.07842236
O	2.75720074	-2.71132402	-5.20462887
H	2.53930831	-3.18453096	-4.37161320
H	3.56569539	-2.21947171	-5.01712909
O	1.15984386	0.88800585	-3.58989101
H	1.69225766	0.39434261	-2.94983184
H	0.97679863	0.25377754	-4.33806397
O	-0.92186505	2.73239271	-4.35778134
H	-0.93980514	3.68670484	-4.19192505
H	-1.79931628	2.49754842	-4.69538247
O	0.53998919	-4.03829555	2.00119473
H	0.22935604	-4.29413865	1.11947243
H	0.41550809	-3.06272703	1.97820637

Ec: S0bbcb(3433)

H	-3.03970988	-1.83821743	-4.84433335
C	-3.59394493	-1.18641036	-4.16503164
C	-2.60833623	-0.53949430	-3.22514069
O	-2.55043908	-0.88081292	-2.03053762
O	-1.84918789	0.35102137	-3.75581260

H	-4.31960115	-1.77918043	-3.61352561
H	-4.09573009	-0.43081844	-4.76893806
H	3.97389302	-3.86305429	-0.74470280
C	3.74745409	-3.51467914	0.26130807
C	2.73418689	-2.40044421	0.22619314
O	1.80628673	-2.41144133	-0.60665839
O	2.89053708	-1.48497860	1.11258730
H	3.30015437	-4.34440527	0.81449428
H	4.65633445	-3.20519663	0.77111744
H	5.49573590	2.70293467	-0.54794162
C	4.64736323	2.39167626	0.03464980
C	4.05555456	1.17820512	0.20155164
N	3.92668801	3.27195387	0.81087977
C	2.93600858	2.60369152	1.41427820
N	2.98687893	1.32527759	1.06722117
H	2.20290250	3.04557079	2.06411331
H	4.30151469	0.22335260	-0.22538874
H	4.11158455	4.25794790	0.91630891
H	1.98213617	5.22570275	-0.31123694
C	1.54063718	5.02674950	-1.28446074
C	0.80341719	3.71576654	-1.28289826
O	0.35589668	3.30238367	-0.17070162
O	0.65221402	3.12450267	-2.38529512
H	2.30050806	5.03572410	-2.06294645
H	0.81462509	5.81377643	-1.50462210
H	0.63830238	-1.33407413	6.34644176
C	1.11741281	-0.42006681	5.99235830
C	0.88646325	-0.28596389	4.50824524
O	-0.33100861	-0.25247960	4.13743107
O	1.88124957	-0.21426666	3.74152205
H	2.17985364	-0.44503405	6.22076825
H	0.64574834	0.41939763	6.50542816
H	-3.28633049	-3.89829130	3.37693054
C	-3.82509117	-3.28392907	2.65192855
C	-2.83278542	-2.37330279	1.97195604
O	-2.50377774	-2.56779263	0.79296239
H	-4.56351849	-2.69834535	3.19889059
O	-2.37344826	-1.43326779	2.72637179
H	-4.31180308	-3.92869157	1.92422222
H	-4.49984749	2.77718416	3.33830182
C	-3.52730755	3.27142989	3.38752000
C	-2.53647548	2.46498959	2.58453192
O	-2.26016086	1.31132445	3.06620409
O	-2.06259207	2.94005153	1.52898290
H	-3.22324246	3.29517640	4.43406894
H	-3.61391138	4.28211768	2.99650027
Ca	-0.76079778	-1.73125322	-0.64056984
Mn	1.61382409	-0.09903208	1.58395981
Mn	-1.08586677	-0.06825956	2.27058559
Mn	-0.77735386	1.72495988	0.19097200
Mn	-0.49160138	1.49089498	-2.86737185
O	0.16381596	-1.26377726	1.60610207
O	-1.77453598	0.23956267	0.62290665
O	0.24319513	1.21548152	1.78705983
O	-1.76859013	2.04841478	-1.49678939
H	-2.55348093	1.48100726	-1.49544199
O	0.33099923	0.35755216	-1.27900836
H	1.28905607	0.30757369	-1.37632424
O	-0.52661264	-4.25116767	-0.23163300
H	-0.02801228	-4.77164083	-0.87833216
H	-1.38467194	-4.68180439	-0.12759107
O	-0.54434947	-2.80065673	-2.83719746
H	-0.29507458	-2.28506765	-3.64592873
H	0.00857660	-3.59413565	-2.87949774
O	0.38192423	-1.53567908	-5.03785208

H	1.24174362	-1.99872531	-4.99117277
H	0.54786282	-0.61404882	-4.72801770
O	1.66612004	-4.49230630	-2.30962536
H	2.18520572	-5.25092063	-2.01840572
H	1.81503594	-3.76815683	-1.64972871
O	2.66013722	-3.15729460	-4.61633186
H	2.36754186	-3.65514562	-3.82677197
H	3.42196812	-2.64423381	-4.32305074
O	0.76923965	1.00270170	-4.13343778
H	1.66583697	1.18091095	-3.82071222
O	-1.44108175	3.11608912	-4.33881703
H	-1.41517394	3.98562705	-3.91887603
H	-2.37868886	2.90635295	-4.44219539
O	0.58424215	-3.82806296	2.42330285
H	0.27926505	-4.18728501	1.57524102
H	0.46141856	-2.86363884	2.28608678

SIV.4 S₀(3343) (F)

Table S12 Mulliken charge and spin densities of CaMn₄O₅ cluster S₀(3343)(F) states calculated by B3LYP.

	F _a : S ₀ bcca(3343)		F _b : S ₀ accb(3343)		F _c : S ₀ bbcb(3343)	
	Charge	Spin	Charge	Spin	Charge	Spin
Ca	1.563	0.008	1.526	0.006	1.533	0.009
Mn ₁	0.894	3.940	0.959	3.959	0.889	3.953
Mn ₂	0.975	3.940	0.978	3.946	0.988	3.941
Mn ₃	0.928	3.029	0.938	3.076	0.931	3.022
Mn ₄	0.996	3.925	1.015	3.949	0.978	3.960
O ₁	-1.022	-0.015	-1.031	-0.018	-1.004	-0.019
O ₂	-0.687	-0.032	-0.703	-0.026	-0.691	-0.009
O ₃	-0.724	0.094	-0.721	0.054	-0.692	0.078
O ₄	-0.609	0.027	-0.653	0.038	-0.597	-0.044
O ₅	-0.816	0.008	-0.795	-0.077	-0.789	0.010

F_a: S₀bcca(3343)

H	-3.19489279	-1.68565639	-5.19919794
C	-3.46156349	-1.61195750	-4.14545255
C	-2.30202549	-1.07422092	-3.34082518
O	-2.04379197	-1.53630000	-2.22455886
O	-1.64554131	-0.12042752	-3.90717090
H	-3.78112597	-2.57853130	-3.76289767
H	-4.29056803	-0.90464476	-4.06089308
H	4.47171368	-3.33760886	0.54204764
C	3.78502796	-3.22093371	1.38117556
C	2.80706549	-2.10994696	1.09080901
O	2.14908658	-2.12809552	0.02146304

O	2.70088413	-1.19694357	1.97150488
H	3.22636302	-4.15323919	1.48353768
H	4.34244914	-3.03024390	2.29410565
H	5.93840220	2.77439247	1.56278314
C	4.89321743	2.52099912	1.55546668
C	4.23907488	1.34957666	1.78904805
N	3.91279266	3.44643525	1.27155952
C	2.71847733	2.84096138	1.33882631
N	2.88079044	1.56361358	1.64936061
H	1.77173273	3.30580373	1.13434645
H	4.62863160	0.38083579	2.04304966
H	4.05438404	4.42103461	1.05550605
H	2.10090350	5.04653394	-0.94786128
C	1.75820061	4.72350144	-1.92784797
C	0.90196875	3.48837683	-1.81870940
O	0.34747432	3.24378688	-0.71898083
O	0.78443374	2.77767470	-2.86622750
H	2.60336728	4.54040704	-2.58918036
H	1.15111586	5.51871788	-2.36756448
H	-0.46122690	-0.53729820	6.48202704
C	-0.02168521	0.38653802	6.10283411
C	-0.00522924	0.34241618	4.59511364
O	-1.13783896	0.18704510	4.03190560
O	1.09124942	0.46257051	3.99438622
H	0.98191339	0.51153922	6.50135254
H	-0.65653302	1.21154355	6.43017900
H	-3.48082140	-4.24855202	2.94770018
C	-4.01034027	-3.64668088	2.20417759
C	-3.05852348	-2.57767902	1.70727137
O	-2.38744055	-2.81374829	0.67118342
H	-4.87761322	-3.20109225	2.68903649
O	-2.98073649	-1.51555131	2.39666251
H	-4.32042407	-4.30044275	1.39105885
H	-4.75376265	3.32975229	2.13630463
C	-3.75678132	3.74745224	1.99374424
C	-2.81467325	2.64499155	1.59044269
O	-2.77616850	1.62111384	2.32282729
O	-2.11940641	2.83652418	0.54343997
H	-3.42575056	4.15038713	2.95268553
H	-3.78124614	4.53964474	1.25038371
Ca	-0.48461593	-1.84282267	-0.42059704
Mn	1.32043541	0.22448742	1.85496118
Mn	-1.54421047	0.03922415	2.08186917
Mn	-0.83264397	1.58698873	-0.25708561
Mn	-0.47582813	1.23264842	-3.10690028
O	-0.02223518	-1.04147340	1.78400473
O	-1.80347495	0.16134678	0.23221227
O	0.11335012	1.54094862	1.35842789
O	-1.66021758	1.82565626	-1.92539639
O	0.38819813	0.38750243	-1.21432953
H	1.31725968	0.62207526	-1.09237526
O	-0.02281479	-4.22595072	0.45263219
H	0.58282478	-4.80821239	-0.02171949
H	-0.88957555	-4.65421290	0.44040608
O	0.21462676	-3.23383476	-2.34348890
H	0.32596988	-2.80345697	-3.21169839
H	1.03665130	-3.74366269	-2.21800821
O	1.11634937	-2.10048726	-4.75298638
H	2.02907774	-2.46291810	-4.60409626
H	0.83691249	-2.39511949	-5.62835683
O	2.74362918	-4.10751302	-1.65860936
H	3.01673230	-4.88767492	-1.16312435
H	2.58503296	-3.38881582	-0.98800206
O	3.52574999	-3.11314753	-4.09941834
H	3.35298342	-3.49721459	-3.21155799

H	4.20896000	-2.44589829	-3.96344562
O	1.01966850	0.49527410	-4.31758057
H	1.91354549	0.79971604	-4.11357503
H	1.06526024	-0.48686716	-4.49836651
O	-1.21874645	2.52295675	-4.93518891
H	-1.28467671	3.45676174	-4.69598328
H	-2.12102026	2.24778095	-5.14698265
O	0.33433870	-3.31927259	3.17454072
H	0.28752223	-3.87995540	2.38561002
H	0.21467371	-2.42081830	2.78067593

Fb: S₀accb(3343)

H	-3.32269496	-1.49654655	-4.75616815
C	-3.82763869	-1.04383065	-3.90087875
C	-2.79246998	-0.62012924	-2.88977235
O	-2.79784787	-1.07736071	-1.73852558
O	-1.91666738	0.22058241	-3.32282312
H	-4.52546936	-1.75584647	-3.46768630
H	-4.36474687	-0.16608923	-4.26386142
H	4.35307477	-3.01453390	-1.48687324
C	3.93585301	-3.07094427	-0.48018313
C	2.88026408	-2.00659280	-0.31388770
O	1.89368708	-1.98658090	-1.08581313
O	3.06266584	-1.16421667	0.62678851
H	3.46217770	-4.04786379	-0.37445541
H	4.72793922	-2.96405029	0.25566535
H	5.50947721	3.24359821	-0.50698174
C	4.62066324	2.85275968	-0.04509437
C	4.16790440	1.57882908	0.12275510
N	3.66831880	3.66608554	0.52756582
C	2.68548947	2.89819136	1.01650860
N	2.95634052	1.62230685	0.78614481
H	1.79346629	3.25798056	1.49403520
H	4.60699396	0.64425671	-0.17488967
H	3.68610591	4.67381973	0.57200596
H	1.25573923	5.49628068	0.05785012
C	0.76369920	5.33046046	-0.89814642
C	0.13376645	3.96339027	-0.93772013
O	-0.28793467	3.47364431	0.13707252
O	0.04547816	3.39531462	-2.07105158
H	1.46773908	5.45448861	-1.71786952
H	-0.03233726	6.07113562	-1.00753955
H	1.64089221	-1.82418592	5.95544793
C	1.92882334	-0.81455940	5.65951063
C	1.41037145	-0.53564806	4.27046732
O	0.15493697	-0.69959891	4.10805666
O	2.21543028	-0.16156146	3.38389681
H	3.00964074	-0.70667050	5.70149560
H	1.46114755	-0.12008566	6.35984544
H	-2.60851926	-5.11255051	2.48568724
C	-3.28418281	-4.25492809	2.43678822
C	-2.48662879	-3.05569226	1.97000947
O	-2.18900570	-2.99023281	0.74708922
H	-3.71213062	-4.08842767	3.42289632
O	-2.14541672	-2.20334560	2.84065427
H	-4.06711916	-4.49102867	1.71663363
H	-4.20147726	2.18549009	4.18749061
C	-3.32559693	2.77388057	3.91146507
C	-2.44695460	1.95061218	3.00691094
O	-2.07871206	0.82147758	3.43895646
O	-2.13381592	2.45012776	1.88541658
H	-2.77443614	2.99528090	4.82702005
H	-3.63079593	3.69964854	3.43109053

Ca	-0.70564311	-1.65615311	-0.63046091
Mn	1.67548646	0.07984540	1.27528851
Mn	-0.92026304	-0.48988582	2.44381544
Mn	-1.05030162	1.56809204	0.44945254
Mn	-0.87653830	1.65035129	-2.42025348
O	0.44259072	-1.29706998	1.40670313
O	-1.80139669	-0.00642542	0.84955861
O	0.32449130	1.30824517	1.64405892
O	-2.38591149	2.05658385	-0.90088145
H	-3.05956730	1.36288185	-0.88762871
O	-0.12088661	0.80638164	-1.01542205
O	-0.17944779	-4.20612647	-0.50080500
H	-0.08882173	-4.78926398	-1.26347279
H	-1.04266010	-4.39109223	-0.09241512
O	-0.56823513	-2.51516194	-2.96634744
H	-0.37013983	-1.91150812	-3.70823625
H	0.08658460	-3.22906177	-3.06146964
O	0.50321968	-1.09457153	-5.14328632
H	1.32391136	-1.63180321	-5.27803440
H	0.05367170	-1.04392427	-5.99506614
O	1.82649032	-3.91121318	-2.93347165
H	2.14831950	-4.74517461	-2.57270675
H	1.91520076	-3.23824797	-2.20552836
O	2.70577592	-2.66351098	-5.20114623
H	2.50594952	-3.18588510	-4.39127711
H	3.50614106	-2.16554296	-4.99661701
O	0.82068753	1.23555539	-3.83852515
H	1.67142796	1.20488789	-3.38378598
H	0.73792276	0.38006762	-4.32948352
O	-1.76539203	2.80003229	-3.94122658
H	-1.86043137	3.74276303	-3.74002215
H	-2.64142212	2.47955378	-4.20142686
O	1.38956124	-3.78398661	1.91337584
H	1.01088573	-4.16735112	1.10762947
H	1.10408278	-2.84180438	1.84355817

Fe: S₀bbcb(3343)

H	-2.44923558	-2.64190383	-4.84092151
C	-3.07451043	-1.94390303	-4.27874316
C	-2.17528411	-1.12911874	-3.38528470
O	-2.09243685	-1.36394730	-2.17452494
O	-1.50416140	-0.20668411	-3.98934616
H	-3.79069978	-2.50838960	-3.68669900
H	-3.58583224	-1.30412137	-4.99665576
H	4.28032978	-3.54025556	0.68679952
C	3.59514335	-3.37887293	1.51962257
C	2.67132506	-2.23131566	1.20224351
O	2.01069893	-2.23796811	0.13666532
O	2.61268762	-1.29261977	2.06466057
H	2.99487980	-4.28314871	1.63526974
H	4.15519854	-3.19537931	2.43234268
H	6.11453033	2.40587422	1.53056891
C	5.05466700	2.22506010	1.50434027
C	4.30772839	1.14198795	1.85322176
N	4.15900373	3.16884712	1.05159123
C	2.92124883	2.66096426	1.13324325
N	2.97632976	1.42739746	1.61711270
H	2.02073064	3.16464066	0.83200821
H	4.61397723	0.19072303	2.24808419
H	4.38981261	4.08896619	0.70943999
H	2.07921135	5.08242780	-1.11981854
C	1.73802301	4.73248433	-2.09106743
C	0.93157870	3.47126941	-1.94619076

O	0.40201648	3.23318693	-0.83163532
O	0.82412751	2.73631209	-2.97633241
H	2.57892842	4.57016492	-2.76274797
H	1.09279423	5.49503551	-2.53446521
H	-0.51234754	-0.27298387	6.51137180
C	-0.02053238	0.60601302	6.09252459
C	-0.00910733	0.49680984	4.58971052
O	-1.14694036	0.34982332	4.03389937
O	1.08805275	0.56246933	3.98148175
H	0.98929452	0.69181241	6.48518586
H	-0.60631172	1.48033037	6.38150170
H	-3.78148410	-3.93688634	3.01355566
C	-4.22605445	-3.36292877	2.19627019
C	-3.19761207	-2.36191096	1.71525000
O	-2.52546957	-2.63343030	0.69119523
H	-5.10538743	-2.85332756	2.58823637
O	-3.06391157	-1.30621493	2.41096583
H	-4.50569011	-4.04995251	1.40023935
H	-4.63876785	3.53278706	2.03922442
C	-3.63754743	3.92491982	1.86095269
C	-2.71446011	2.78771762	1.52002995
O	-2.72172308	1.78506038	2.28202297
O	-1.97934961	2.93058418	0.49172221
H	-3.28915285	4.38163668	2.78950070
H	-3.65475651	4.67076979	1.07096269
Ca	-0.54293413	-1.82335174	-0.38103592
Mn	1.34262931	0.19952945	1.88377199
Mn	-1.56440175	0.14882492	2.10282848
Mn	-0.71210434	1.62301197	-0.23606317
Mn	-0.29456907	1.12651844	-3.27435794
O	-0.07821943	-0.97085139	1.83052288
O	-1.76827800	0.27198135	0.23346963
O	0.22290571	1.59750409	1.30611324
O	-1.62493061	1.79246184	-2.01176362
H	-2.41955644	1.24175802	-1.98031575
O	0.42967373	0.38856099	-1.21643026
H	1.37375796	0.55181040	-1.08933700
O	-0.26884106	-4.21192849	0.52748585
H	0.31946738	-4.83767177	0.08719736
H	-1.15413672	-4.59979578	0.50567041
O	0.07290927	-3.23813202	-2.27877146
H	0.29714063	-2.84247758	-3.15765777
H	0.80100407	-3.86111622	-2.11040258
O	0.97299694	-2.27118013	-4.65213810
H	1.87758312	-2.60070616	-4.47703685
H	1.02502342	-1.29145145	-4.56293586
O	2.48969518	-4.34246943	-1.47420959
H	2.82224831	-5.08368217	-0.95598924
H	2.38492121	-3.58485546	-0.84408163
O	3.47110946	-3.34871936	-3.88254623
H	3.21133841	-3.73513538	-3.02019596
H	4.08434562	-2.63760526	-3.66306995
O	1.04926171	0.42944564	-4.34617841
H	1.88600623	0.89877709	-4.23832519
O	-1.24585394	2.48240858	-4.93363535
H	-1.28030443	3.40771863	-4.65828814
H	-2.16411732	2.22223067	-5.08581833
O	0.13184334	-3.28487938	3.23501703
H	0.04702410	-3.83311126	2.43978554
H	0.07018560	-2.37855275	2.85470443