**Supporting Materials**

**Theory of Chemical Bonds in Metalloenzymes XXIV Electronic and Spin Structures of FeMoco and Fe-S Clusters by Classical and Quantum Computing**

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**SI Theoretical backgrounds**

**SI. 1 Developments of theoretical models for strong correlation electron systems**

In the supporting material, we revisit our historical developments of quantum mechanical computational methods for strongly correlated electron systems (SCES) in the permission of the editorial policy of this special issue for the molecular quantum mechanics (MQM) 2019 conference. First of all, we revisit theoretical backgrounds and computational models for chemical reactions. In early 1970th, the orbital symmetry conservation rules were developed for theoretical understanding of concerted reactions in organic chemistry [s1]. The Hückel and extended Hückel (EH) molecular orbital (MO) computations [s2] were often performed to elucidate approximate MOs with spatial symmetry (Pn; point group), which were effectively used for elucidation of concerted reaction pathways and prediction of possible concerted reactions.

On the other hand, local spins play important roles for radical reactions. Therefore, we employed spin Hamiltonian models, namely Heisenberg spin Hamiltonian for derivations of selection rules of radical reactions [67-69]. The permutation symmetry (*S*N) was used for derivations of exchange-allowed radical abstraction and exchange-forbidden radical insertion reactions based on the quantum Heisenberg (QHB) model [67]. The electron-exchange (permutation; *P*12) is expressed by the spin Hamiltonian model; , where Si is the spin operator for local spin at the i-site. The *P*12 values for the radical reaction index are indeed given by *S*12 = (2(–3/4) + 1/2) = –1 for singlet pair (namely local singlet diradical configuration for the bond formation and *S*12 = (2(1/4) + 1/2) =1 for triplet pair (namely local triplet diradical configuration for no bond formation) [67]. The radical abstraction and insertion reactions are, respectively, referred to as spin-symmetry-allowed and –forbidden on the basis of the classical Heisenberg (CHB) model [68, 69], where the magnetic symmetry for spin structures is expressed by the magnetic group (*M* = *T* × *S*) consisted of the time-reversal (*T*) symmetry for spin (axial vector) inversion and spin rotation (*S*).

Thus, four symmetry groups (*P*n, *S*N, *T*, and *R*) were employed for characterization of electronic and spin states of molecules by quantum mechanics [66]. These symmetries are usually conserved in the EHMO and restricted Hartree-Fock (RHF) MO models, indicating the symmetry-adapted (SA) property [s1, s2]. On the other hand, the RHF solutions often suffer several-type of instability conditions [s3] for molecules with strong correlation electron systems (SCES), being reorganized into the so-called broken- symmetry (BS) MO solutions [82], which are generally characterized by the magnetic double group (*G* = *T* × *S* × *P*n) [66, 75]. The spatial and spin symmetries are often non-conserved (namely broken) for the BS MO models. The symmetry-recovered MO models are also obtained by the projection procedures for BS MO models [66, 75] because of no-phase transition in finite quantum systems. As an example of our computational schemes for SCES, the potential energy curves of the H3 model with the equilateral triangular structure by several MO models were calculated on the basis of the Hubbard model [75], where the on-site Coulomb repulsion (U) for SCES was added to the Hückel model. In fact, the SA doublet spin state obtained by the projected BS solution was the ground state of the equilateral H3 radical [75].

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| (A) | | (B) |
| Figure S1 | (A) Potential energy curves for the dissociation reactions of the equilateral H3 radical and (B) calculated expectation values of the *S*2 spin operators. | |

Takeda et al. [87] revisited the dissociation reactions of the equilateral H3 radical as illustrated in Fig. S1. The potential curve by the ab-initio UHF solution with the collinear (one dimension; 1D) spin structure (see also Fig. 13A) was repulsive in nature. The potential curve by general Hartree-Fock (GHF) with triangular (two dimensional: 2D) spin structure (see also Fig. 13A) was still non-bonding. On the other hand, the resonating BS (RBS) configuration interactions (CI) of three degenerate BS solutions in energy (three UHF solutions or three GHF solutions) provided the potential curves responsible for the association of three hydrogen atoms into the H3 radical as shown in Fig. S1A. The approximated spin projection (AP) for UHF and/or GHF provided similar potential curves to the RBS CI curves as shown in Fig. S1A. The calculated S2 values were 0.75 for the pure doublet state by RBS CI as shown in Fig. S1B. On the other hand, they were larger than 0.75, indicating the spin contamination (quartet state with *S*=3/2) in the low-spin (LS) UHF and GHF solutions. Thus, BS calculations followed by AP for the LS state are applicable for the first step to SCES such as Fe3S4 cluster (see Fig. 13).

**SI. 2 Electronic and spin structures of transition-metal complexes**

In late 1970th, the temperature-dependent paramagnetism was already observed for the binuclear chromium complexes; L4Cr(II)Cr(II)L4 (L4=ligands) with a formal quadruple bond [s4], indicating the near degeneracy between the ground state and excited triplet state. The restricted (R) Hartree-Fock-Slater (HFS) solution [40, s5, s6], a precursor of present DFT model, for this compound indeed suffered the triplet instability, indicating the reorganization into the unrestricted (U) HFS solution obtained by the mixing of HOMO(dδ-dδ bonding MO) and LUMO(dδ-dδ anti-bonding MO) [83]. The resulting BS MOs are mainly localized on the left and right Cr(II) ions, respectively. These BS orbitals were occupied by the up (↑)- and down (↓)-spins, respectively, indicating anti-ferromagnetic spin coupling in consistent with the temperature- dependent paramagnetism responsible for thermal mixing between the ground singlet and excited triplet states [s4].

The temperature-dependent paramagnetism [59, 60] was also observed for the binuclear transition-metal oxygen complexes with formal three-center four-electron bonds; LpM=O=MLp (Lp=Ligands), where M denotes a 3d transition metal. The energy gap between the HOMO (dπ-pπ-dπ bonding) and LUMO (dπ-pπ-dπ anti- bonding) for the RHF solutions of these species was too small, inducing the HOMO- LUMO mixing which provides more stable UHF solutions, Lp•M-O-M•Lp (Lp=Ligands) with localized orbitals on the left and right metal-ions. The energy gaps between the LS and high-spin (HS) BS UHF solutions were used to calculate the effective exchange integrals (*J*ab) for the Heisenberg model for these species (see equation 7 in the text). Table S1 summarizes the calculated Jab values for several binuclear transition metal complexes (M-O-M) by LS (BS) and HS UHF solutions [79]. From Table S1, the sign of the Jab values were negative in sign, indicating the antiferromagnetic (AF) exchange interactions in compatible with the observed *J* values [59, 78, 79]. The magnitude of the AF effective exchange integrals decreases with the increase of the M-O distances. Moreover, the spin crossover from AF to ferromagnetic (FM) interaction was concluded for the M-O-M bonds (M=Mn(II), Fe(III)) with longer M-O bonds. Thus, the BS methods were applicable for the first step to SCES with AF and FM interactions.

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| Table S1 | The effective exchange integrals for binuclear M-O-M systems [79] |
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**SI. 3 Electronic and spin structures of magnetic transition-metal complexes**

We have described fundamental concepts and methods for our theoretical understanding of electronic and spin structures of SCES in preceding sections SI. 1 and SI. 2. Figure S2 illustrates our computational scheme for SCES such as transition metal complexes, iron-sulfur (Fe-S) clusters, etc. The BS UHF method was applied to elucidate the effective exchange integrals for the 2Fe(III)-2S cluster; L2FeS2FeL2, as shown in Table 2 in the text. Spin vector models based on the CHB approximation were applied to elucidate possible collinear (1D) and non-collinear (2D or 3D) spin structures of multi-nuclear Fe-S clusters, which were characterized with the magnetic group consisted of the time-reversal (T) and spin rotation (S) symmetry [37, 66] as shown in Fig. 7. Spin correlation diagrams for radical reactions can be depicted at this level of theory [37]. Theoretically possible BS solutions for SCES such as Fe-S clusters are constructed using the magnetic double group (*T* × *S* × *P*n) methods [26, 66] as shown in Figs. S1 and S2. Our group-theoretical approaches were applicable for other independent particle (IP) models such as Kohn-Sham (KS) DFT solutions, hybrid HF and DFT (HDFT) models such as B3LYP models [84]. Full geometry optimizations of key intermediates and transition structures (TS) with different spin structures by the corresponding unrestricted BS (UBS) solutions are performed to elucidate structure and reactivity of SCES such as Fe-S clusters illustrated in Fig. 1. To this end, UBS hybrid DFT (HDFT) methods are successfully applicable for full geometry optimizations of large Fe-S clusters with the low-spin (LS), intermediate spin (IS) or high-spin (HS) configurations [29-33] as shown in Fig. 1.

As the next step for beyond IP models, we perform the natural orbital (NO) analysis of the BS HDFT solutions to elucidate UNO and their occupation numbers (*n*). Natural orbitals indeed reflect the symmetry of molecule, which is a key issue for symmetry-adapted (SA) complete active space (CAS) CI(SCF) [34-41] and density matrix renormalized group (DMRG) CI methods [82] in Fig. 9. The CASSCF calculations followed by full geometry optimizations are desirable but are not so easy for large molecules. Therefore, natural orbitals given by diagonalization of the first-order density matrix by BS UHF or hybrid UDFT are useful as an alternative to CAS-CI (SCF) orbitals to elucidate bonding natures on the basis of the symmetry-adapted UNO orbitals [34-41] as shown in Fig. S2.

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| Figure S2 | A quantum mechanical computational scheme for strongly correlated electron systems (SCES) |

**SI.3 Natural orbitals and chemical indices for SCES**

As shown in our series of papers [29-33], chemical indices derived from the occupation numbers of natural orbitals enable us to perform quantitative analysis of chemical bonds. These indices are useful conceptual bridges between BS HDFT and SA CI methods as shown in Fig. S2. The BS orbitals are transformed into the symmetry adapted (SA) natural orbitals (UNO) [29-33, 66]. The first-order reduced density matrix *ρ* from the BS state is diagonalized as shown in Eq. (1). The eigenvectors of the density *ρ* are the natural orbitals *φ*i and each eigenvalue corresponds to the occupation number *n*i. The UNOs are classified into five groups according to the size of the occupation as shown in Fig. 8.

The spin-polarized (1D) orbitals of BS solution have the following relationship with natural orbitals (UNO) and its occupations as,

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|  | (s1a) |
|  | (s1b) |

where is the bonding (antibonding) natural orbital and is its occupation number. *T* (not the T term of the magnetic group) in is the orbital overlaps between  and spin-polarized orbitals in Eq. (10) in the text. These occupation numbers are projected to by the AP procedure,

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|  | (s2) |

The effective bond order *b* and the projected effective bond order *B* (not the B term in Eq. (25)) are defined by the difference between the occupation numbers of the bonding and antibonding natural orbitals as

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|  | (s3a) |

where *b* is 1.0 for the closed-shell (T=1.0) and 0.0 for the complete diradical. The *b* is equal to the orbital overlap *T* between spin-polarized orbitals. The effective bond order *B* after spin projection is defined by

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|  | (s3b) |

The B-value is always larger than the *b*-value because *T* ≤ 1.0.

The concept of information entropy is also introduced to express the labile nature of chemical bond. The Jaynes information entropy is defined to express the characteristic of chemical bonds with fractional occupation numbers *n*i by

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|  | (s4a) |

The information entropy plays an important role in the quantum information theory and quantum computing. The normalized Jaynes information entropy is defined by setting the maximum binding state for the closed-shell MO as the reference, as

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|  | (s4b) |

The diradical character *Y* is defined by the weight of doubly excited configuration (*WD*) in the configuration interaction (CI) as

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|  | (s5) |

where *Y* is equal to 1-*B* [29-33].

**SI.3 Spin density and unpaired electron density**

If spin-polarized orbitals exist near to strong bonding region, both effective bond order and information entropy are almost equal to 1. Therefore, the delocalized MO picture provides a good starting point for theoretical description of the Fe-sulfur bonds. On the other hand, spin-polarized orbitals near to dissociation limit are almost localized on Fe ions, and the *b* and *I*n values are almost zero. Spin densities appear in this region, and spin-dependent picture is useful for understanding of the nature of chemical bonds. The spin density *Q* is described by the occupation number ni under the BS approximation as

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|  | (s6) |

Since the spin density should be zero in the singlet state, the unpaired electron density *U* is alternately defined as the deviation of total spin angular momentum from the exact singlet value [66] as

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|  | (s7) |

The spin density is also related to the on top pair density in the case of the BS approximation as follows.

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|  | (s8) |

where denotes the first-order density [66]. The on-top pair density is useful for CAS-CI-DFT approach as a seamless extension of the BS DFT approach, DFT functional for dynamical correlation correction is expressed by the one-top pair density [66]. Figure S3 illustrates important roles of the chemical indices as conceptual bridges between BS and SA methods. The chemical indices are acceptable for characterization of chemical bonds in Fe-S complexes in the text.

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| Figure S3 | Roles of chemical indices for understanding of chemical bonds of SCES |

**SII Variations of occupation numbers of natural orbitals of Fe-S clusters**

**SII.1 Full geometry optimizations of FeMoco**

All HDFT calculations were performed by NWChem6.6 program package and Gaussian 09 program package. Initial structure of FeMoco cluster was taken from PDB crystal structure (PDB ID: 3U7Q) reported by Spatzal et al. [14]. Taking into account the electronic structure of FeMoco cluster, the quantum mechanically optimized region was including as follow: [Fe(II)3Fe(III)4Mo(III)S9C]-1 core, homocitric acid (HCA), Val70, Arg96, Gln191, His195, Tyr229, Cys275, Ser278, Arg359, Glu380, Phe381, Lys426, Glu427, His442, Arg105(B unit) and several water molecules. The optimizations were performed by UB3LYP\*\* functional (10% Hartree-Fock (HF) weight) with D2 dispersion correction for *S*=3/2 (low spin; LS), *S*=25/2(intermediate spin; IS) and *S*=33/2 (high spin; HS) states. Other UB3LYP (20% HF), UB3LYP\* (15% HF) and UB3LYP\*\*\* (5% HF) calculations were performed, assuming the optimized structure for the LS (S=3/2) state by UB3LYP\*\* (10% HF) (see Fig. S4B). The basis sets used for all HDFT calculations were as follows. The Def2-TZVP basis was used for Fe7S9Mo cluster, HCA, Arg96, His195, Cys275, Arg359 and His442 except for Mo atom in Fe7S9Mo cluster, for which applied Jorge's TZP basis. For the remaining amino acid residues and water molecules, Def2-SVP basis was applied. The environmental effect was treated by conductor-like screening model (COSMO) with permittivity 10.0. The cartesian coordinates of alpha carbon atom of amino acids were fixed during the optimization. The optimization took about 3 weeks for each structure optimization with the 30 nodes of NEC LX 406Rh-2 machine (1200 core) in Reserch Center for Computational Science at Okazaki, Japan.

**SII.2 FeMoCo cluster by DMRG calculations**

The occupation numbers (*n*) of UNOs are very important for selection of complete active space (CAS) for SCES such as Fe-S clusters.Figure S4A illustrates variations of the occupation numbers of the natural orbitals against the orbital numbers obtained by the DMRG calculations of FeMoco [113e, 76o] (**16a**) [48] and FeMoco [54e, 54o] (**14a**). The variations of the occupation numbers of UNO of **10a** are also shown for comparison. Characteristic differences among the computational models are discussed in the text. Figure S4B illustrates variations of the occupation numbers of the natural orbitals (UNO) against the orbital numbers obtained by the natural orbital analysis of the BS HDFT solutions for (**15a**).

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| Figure S4A | Variations of the occupation numbers of natural orbitals against the orbital number (i) for the low-spin (*S*=0) antiferromagnetic spin configuration of the synthetic model cluster [Fe(III)2Fe(II)6 cluster] (**10a**) by the broken-symmetry (BS) calculations. Variations of the occupation numbers of the natural orbitals by DMRG [54e, 54o] calculations for Fe(III)3Fe(II)4Mo(III)S9C (**14a**) [46] and DMRG [113e, 76o] for Fe(III)3Fe(II)4 Mo(IV)S9C (**16a**) [48] were also depicted for comparison. |
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| Figure S4B | Variations of the occupation numbers of natural orbitals (UNO) against the orbital number by BS HDFT solutions (see also Table S4 later). |

**SII.3 GSO DFT calculations of the mixed-valence 2Fe-2S cluster**

Figure S5 illustrates the natural orbitals and occupation numbers for the Fe(III)S2Fe(II) cluster (**4a**) obtained by the natural orbital (NO) analysis of GSO DFT solutions.

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| Figure S5 | Natural orbitals for Fe(III)S2Fe(II) (**4a**) obtained by the NO analysis of the GSO DFT calculations |

**SII.4 GSO DFT calculations of the mixed-valence 3Fe-4S cluster**

Figure S6 illustrates variations of the occupation numbers of the natural orbitals for the [Fe(III)3S4(SH)4] cluster (**5a**) at the highest spin (*S*=15/2), antiferromagnetic spin (S=5/2) and spin-frustrated noncollinear (*S*=1/2) states.

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| Figure S6 | Variations of the occupation numbers of natural orbitals (UNO) against the orbital number (i) for the highest spin (*S*=15/2), antiferromagnetic spin (*S*=5/2) and spin-frustrated noncollinear (*S*=1/2) configurations of the [Fe(III)3S4(SH)4] cluster (**5a**) by the broken-symmetry (BS) calculations. The GSO orbitals, namely two component spinors, are necessary for the last configuration (see text) |

**SII.5 Natural orbitals and their occupation numbers for Fe4S4 cluster**

Table S2 illustrates the group theoretical classification of the BS solutions for 4Fe-4S cluster [26]. The magnetic double group (*T* × *S* × *P*n) in in section SI was used for derivations of possible solutions. The 1D (collinear) spin structure consisted of antiferromagnetic coupling (up-up coupled with down-down spins) between high-spin 2Fe-2S (up-up spins) and high-spin 2Fe-2S (down-down spins) have been used for 4Fe-4S clusters. However, as shown in Table 2, non-collinear (2D) solutions are also conceivable for these clusters [26].

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| Table S2 |  |
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Figure S7 illustrates variations of the occupation numbers of the natural orbitals for

4Fe-4S cluster by the NO analysis of the 1D BS UB3LYP solution.

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|  | | (A) |  | (B) |  |
| Figure S7 | Natural orbitals and their occupation numbers of the Fe(II)Fe(III)3 (SCH3)4. Structures A and B are depicted in Fig. 16. | | | | |

**SII.6 Computational results for P-cluster**

Figure S8 illustrates the collinear (A) and non-collinear (B) spin structures for the P-cluster model **10a** by BS UB3LYP calculation and Monte Calro simulation. Table S3 summarizes the occupation numbers of UNO for **10a** by UB3LYP.

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| (A) | | (B) |
| Figure S8 | (A) Spin structure of the AF BS (collinear) solution of [{N(SiMe3)2}-{SC(NMe2)2}Fe4S3]2(μ6-S){μ-N(SiNMe3)2}2 (**10a**) and (B) Spin structure of the non-collinear spin structure of **10a**. | |

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| Table S3 | Chemical indices for the Fe(III)2Fe(II)6S7 (**10a**) cluster model for P-cluster by UB3LYP method |

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| --- | --- | --- | --- |
| -i | *n*H-i (*n*L+i) | b (B) | In |
| 0 | 1.009(0.991) | 0.009(0.018) | 0.007 |
| 1 | 1.032(0.968) | 0.032(0.064) | 0.023 |
| 2 | 1.046(0.954) | 0.046(0.092) | 0.034 |
| 3 | 1.078(0.922) | 0.078(0.155) | 0.058 |
| 4 | 1.156(0.844) | 0.156(0.305) | 0.121 |
| 5 | 1.185(0.815) | 0.185(0.358) | 0.145 |
| 6 | 1.187(0.813) | 0.187(0.361) | 0.147 |
| 7 | 1.205(0.795) | 0.205(0.393) | 0.162 |
| 8 | 1.218(0.782) | 0.218(0.416) | 0.173 |
| 9 | 1.229(0.771) | 0.229(0.435) | 0.183 |
| 10 | 1.262(0.738) | 0.262(0.490) | 0.212 |
| 11 | 1.325(0.675) | 0.325(0.588) | 0.269 |
| 12 | 1.342(0.658) | 0.342(0.612) | 0.285 |
| 13 | 1.387(0.613) | 0.387(0.673) | 0.327 |
| 14 | 1.405(0.595) | 0.405(0.696) | 0.345 |
| 15 | 1.429(0.571) | 0.429(0.725) | 0.368 |
| 16 | 1.440(0.560) | 0.440(0.737) | 0.379 |

Here, the occupation numbers for **15a** are summarized in Table S4 for comparison with those of Fe(II)8S7 (**12a**) in Table S3.

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| Table S4 | Occupation numbers (information entropy) of fractional natural orbitals (NOs) of Fe(III)4Fe(III)3Mo(III)S9(C) cluster (**15a**) |

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| --- | --- | --- | --- | --- | --- |
| NO | | UB3LYP\*\*\* | UB3LYP\*\* | UB3LYP\* | UB3LYP |
| 267 | (DONO) | 1.993(0.991) | 1.991(0.989) | 1.990(0.988) | 1.989(0.986) |
| 268 | (HONO-15) | 1.959(0.950) | 1.939(0.926) | 1.928(0.914) | 1.923(0.907) |
| 269 | (HONO-14) | 1.953(0.943) | 1.935(0.921) | 1.904(0.885) | 1.870(0.844) |
| 270 | (HONO-13) | 1.941(0.929) | 1.905(0.886) | 1.858(0.831) | 1.807(0.771) |
| 271 | (HONO-12) | 1.860(0.833) | 1.802(0.766) | 1.747(0.703) | 1.697(0.647) |
| 272 | (HONO-11) | 1.850(0.821) | 1.786(0.748) | 1.726(0.679) | 1.682(0.630) |
| 273 | (HONO-10) | 1.845(0.815) | 1.778(0.738) | 1.721(0.674) | 1.665(0.612) |
| 274 | (HONO-9) | 1.776(0.736) | 1.697(0.648) | 1.622(0.566) | 1.555(0.495) |
| 275 | (HONO-8) | 1.631(0.576) | 1.541(0.480) | 1.470(0.408) | 1.414(0.353) |
| 276 | (HONO-7) | 1.584(0.525) | 1.501(0.440) | 1.437(0.375) | 1.386(0.326) |
| 277 | (HONO-6) | 1.547(0.487) | 1.457(0.396) | 1.390(0.330) | 1.341(0.283) |
| 278 | (HONO-5) | 1.521(0.461) | 1.444(0.383) | 1.381(0.322) | 1.329(0.273) |
| 279 | (HONO-4) | 1.452(0.391) | 1.364(0.305) | 1.305(0.250) | 1.262(0.212) |
| 280 | (HONO-3) | 1.427(0.366) | 1.354(0.296) | 1.300(0.246) | 1.258(0.208) |
| 281 | (HONO-2) | 1.374(0.315) | 1.294(0.241) | 1.247(0.198) | 1.213(0.169) |
| 282 | (HONO-1) | 1.349(0.292) | 1.276(0.225) | 1.218(0.174) | 1.178(0.139) |
| 283 | (HONO) | 1.142(0.110) | 1.117(0.089) | 1.100(0.075) | 1.087(0.065) |
| 284 | (SONO) | 1.000(0.000) | 1.000(0.000) | 1.000(0.000) | 1.000(0.000) |
| 285 | (SONO+1) | 1.000(0.000) | 1.000(0.000) | 1.000(0.000) | 1.000(0.000) |
| 286 | (SONO+2) | 1.000(0.000) | 1.000(0.000) | 1.000(0.000) | 1.000(0.000) |

Figures S9A and S9B illustrate the natural orbitals for the CAS bonding orbitals

of **12a** UB3LYP calculation.

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| Figure S9A | HOMOs for Fe(II)8S7 (**12a**) |

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| Figure S9B | LUMO of Fe(II)8S7 (**12a**) |

**SIII Developments of quantum information science and quantum computing**

**SIII.1 Macroscopic quantum tunneling, coherence and computing**

Iron-sulfur clusters and clusters of the clusters play important roles for electron transports in biological systems. We have employed several model Hamiltonians for theoretical investigation of structure and function of iron-sulfur systems as shown in Fig. S10. Broken-symmetry (BS) and resonating BS (RBS) computations are performed to determine effective interactions parameters such as the effective exchange integral () for Ising model, *J*-values () for Heisenberg model, *t(B)-J* parameters for the t-J model and *t, * and *U* parameters for Hubbard model [66].

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| Figure S10 | Model Hamiltonians for strongly correlated electron systems (SCES) |

These model Hamiltonians can be applicable for quantum simulations of bio-molecular systems such as nitrogenase and bio-inspired artificial systems. For example, iron-sulfur complexes have been accepted as building blocks of molecular functional materials such as molecular wires, spintronics devices, molecular memories [30-33, 65, 66]. The interaction parameters (*t, J,* etc) obtained in the text are applicable for quantum simulations of molecular materials consisted of Fe-S clusters in Table 1. Recently, developments of effective algorithms for quantum simulations by these model Hamiltonians on quantum computers are current topics as illustrated in Fig. S10 [102]. In fact, the exact diagonalization of the Heisenberg models and Hubbard models for P-cluster and FeMoco are hardly possible on a classical computer but it will be feasible on a quantum computer [102].

Molecular design of building blocks for molecular devices is an interesting problem. The concept of macroscopic quantum coherence (MQC) and tunneling (MCT) by Leggett [s7] was the guiding principle for our quantum mechanical investigation of quantum spin systems for construction of molecular memories and qubits for quantum computer [s8-s10]. For example, molecular spin cluster on the linear Crn cluster was considered as a candidate for investigation of the MQT phenomena [s8]. Path integral formulation of the MQT was also presented for quantum dynamics of MnxOy and iron-sulfur (Fe-S) clusters [s9, s10]. We also considered the quantum dynamics of the single molecule magnets such as Mn12O12 and proposed quantum computing based on the MQC of the molecular electronic spin system [s11]. However, de-coherence of the electron spin system was too fast for the purpose. On the other hand, Vandersypen et al. [s12] succeeded the quantum computing using the nuclear spin system of an interesting molecule, CF2=CF-CX=CF2 (X=Fe(CO2)(C5H5), namely seven–qubit system consisted of the C- and F-nuclear spins. The NMR quantum computer was realized because of suppression of the decoherence [s12] in sharp contrast to the molecular spin system [s8-s12]. The NMR computer was effectively used for demonstration of early basic ideas for quantum computing [49-56].

**SIII.2 Developments of quantum computing**

Here, historical developments of the ideas for quantum computing [49-56] are briefly reviewed. In early 1982 [49], the idea of quantum simulations on quantum computer has been proposed for complex quantum systems. Nakamura et al [s13] first succeeded the coherent control of the superconductor qubit, realizing the MQC of the mesoscopic superconducting circuit. Their finding really demonstrated the MQC by the Leggett proposal [s7] by suppression of decoherence [s13, s14]. Thus, the concept of MQC was experimentally confirmed by developments of the quantum device. Following their success, we performed theoretical formulations of qubits consisted of spin, superconductor, cold atoms, exciton, photon, etc. in spin Hamiltonian models for a systematic understanding of MQC; for example, Anderson pseudo spin Hamiltonian model for superconductivity and Jaynes-Cumming model for quantum qubits [s15]. We have published a monograph summarizing design and synthesis of molecular materials in our specially promoted project for organo-metallic conjugation (OMC) systems [s16]. We further summarized key concepts and theoretical modeling of several quantum phenomena such as MQC and MQT for future developments of molecular quantum systems such as qubits consisted of molecular spins, excitons, photons, etc. [s17]. Lidar and Wang proposed quantum computing of thermal rate constant on a quantum computer [s18]. Aspuru-Guzik et al. [s19] first performed the quantum computing of the molecular Schrödinger equation for small molecules such as water molecule by using a recursive phase estimation algorism (PEA) and mapping procedure of wavefunction into qubits via Kitaev procedure [105]. They have demonstrated that the calculation time for the energy of atoms and molecules scales exponentially with system size on a classical computer but polynomially using quantum algorisms. The coherence time of the superconductive qubits [s13] has been elongated by the improvements [s20-s21], opening possibility of quantum computing for quantum chemistry [46, 48, 95-105, s12, s13].

**SIII.3 Diagonalization of CI matrix by classical and quantum computers**

As mentioned in the text, the hybrid classical and quantum computing methods based on the NISQ (Noisy Intermediate-Scale Quantum) computer [95] have been attracted great interest in quantum chemistry [46, 48, 96-104]. Here, we touch the diagonalization of the large-scale CI matrix by the classical and quantum computers. The UNO CI coefficient in Eqs. (11) (see also Eq. (30)) can be obtained by the diagonalization of the CI matrix, for which the matrix elements are generally given by

|  |  |
| --- | --- |
|  | (s9a) |

where and are the one- and two-electron coupling constants, respectively, and and are one- and two-electron integrals over UNOs. The UNO CI energy Ei, CI for the i state in terms of these coupling constants is therefore given by

|  |  |
| --- | --- |
|  | (s9b) |

The one and two-electron reduced density matrices are often defined for the compact expression of the UNO CI energy as follows.

|  |  |
| --- | --- |
|  | (s10a) |
|  | (s11b) |

The UNO CI energy for any state can be written more compactly as

|  |  |
| --- | --- |
|  | (s12) |

The UNO CI has been feasible for molecules with small CAS on a classical computer by using recently developed CI schemes (see Fig. 9) [42-45]. However, the coupling coefficients in the large-scale UNO CAS CI and MR CI are generally derived using second quantization expression for quantum computation [46, 48]. The Hamiltonian is given by this expression is given by Eq. (30) in the text, where and are the creation and annihilation operators, respectively. The CI computational schemes are transformed into the quantum operators for quantum computing as described below [s22].

**SIII.4 Quantum computing of SCES on the NISQ computer**

The UNO FV CI of SCES [37] was our dream as shown in Fig. 3 and Fig. 21. Nowadays, the diagonalization of the large CI matrix [46, 48] on quantum computer is an interesting topic in quantum chemistry. To this end, Martinis et al. performed the great improvement of the qubits consisted of superconductors [94]. Therefore, they opened the door for quantum computing of complex systems [58]. In fact, the hybrid classical and quantum computing methods based on the NISQ (Noisy Intermediate-Scale Quantum) computer [95] have been attracted great interest in quantum chemistry [46, 48, 96-104] as illustrated in Fig. 21. Therefore, we have also revisited the large-scale UNO CI for strongly correlated electron systems (SCES) [37, 66]. The coupling coefficients in the CAS CI are generally derived using second quantization expression for quantum computation [46, 48, s23, s24]. The Hamiltonian is given by this expression re-cited as (Eq. 30)

|  |  |
| --- | --- |
|  | (s13) |

where and are the creation and annihilation operators, respectively, for an electron in UNO spin orbital, and one- and two-electron integrals are also expressed by using the notation of UNO spin orbitals, respectively [37, 66]. Dimension of the Hamiltonian matrix for UNO CI in eq. (30) increases in the exponential manner with the

number of active electrons and active orbitals [95] for SCES such as Fe-S clusters, indicating that it becomes over any allowed memory size in the classical computers based on the classical bits [46, 48]. On the other hand, the memory size becomes 2N if the N-qubits are used in the quantum computer, for example 253=1016 [46]. To this end, the creation and annihilation operators in eq. (30) (s13) are expressed by the quantum operators based on the Bravyi-Kitaev (BK) [104] and/or Jordan-Wigner (JW) [105] transformation formula. For example, the JW transformation is defined by

|  |  |
| --- | --- |
|  | (s14a) |
|  | (s14b) |
|  | (s14c) |

where (), () and ()are Pauli operators. The Hamiltonian in eq. (s13) is rewritten by the Pauli operators for qubits via the JW transformation in eq. (s14) as follows.

|  |  |
| --- | --- |
|  | (s15a) |

where .

Recently, several procedures [96-104] to perform the exact diagonalization of the transformed quantum Hamiltonian on the NISQ computer have been proposed to obtain the ground and lower-lying states by CI procedures such as a large-scale UNO CAS CI [37]. One of these procedures is the hybrid classical and quantum scheme [46], where the quantum computation is limited for the diagonalization process, and other parts such as calculations of molecular integrals and total energies are performed using the classical computers as illustrated in Fig. 21. From Fig. 21, full geometry optimization for each spin state is also performed using classical computer. The variational quantum eigensolver (VQE) method [96-104] has been proposed to obtain the ground state of UNO CAS CI in the hybrid calculations. The VQE algorithm is an application of the time-independent variational principle. Therefore, very good trial orbitals for VQE are desirable for good convergence toward the exact ground state of quantum systems [46, 48]. The VQE algorithm can be broken down into the following steps in Fig. 21.

(1) State preparation: A parametrized quantum state is prepared on the quantum device. This is achieved by applying a parametrized unitary to an easy-to-prepared initial state : . Therefore, the dimension of is 2n when n-qubits are used for quantum device.

(2) Energy estimation: The expectation value of Hamiltonian is given by

|  |  |
| --- | --- |
|  | (s15b) |

(3) The expectation value of Hamiltonian is given by the quantum eigenvalue problem of the 2n × 2n matrix, for example 253=1016.

(4) Variational calculation: Use a classical non-linear optimizer such as the simplex method to determine new values of *θ* values that decrease .

(5) Iteration calculation: Iterate the procedure until convergence in the value of the energy. The parameter *θ* at convergence define the desired state.

The size of the CI matrix in the step (2) is limited by the size of qubits. For the reduction purpose of active space, we have re-visited scope and applicability of UNO [37, 66] for efficient VQE processes as illustrated in Fig. 21. Very recently, a new argorithm was discovered for MR CI calculations on a quantum computer [s23-s25].

Reiher et al. [46] have already emphasized that the choice of orbitals is crucial for accurate calculations because orbital optimization requires the one- and two-body reduced density matrices, whose calculation will not be efficient on a quantum computer with present-day algorisms. They have therefore pointed out it is decisive to start from suitable molecular orbitals which do not require further optimizations. According to the Reiher’ criterion, UNO is one of such molecular orbitals because of the similarity between the occupation numbers between DMRG and UNO CI as shown in Fig. 11. In fact, UNO is useful enough for large-scale CI of large strongly correlated electron systems such as FeMoco, for which large-scale MCSCF [s24] are not practical.

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