

# Extraction of local spin-coupled states by second quantized operators

Cite as: J. Chem. Phys. 157, 014112 (2022); doi: 10.1063/5.0092834

Submitted: 24 March 2022 • Accepted: 10 June 2022 •

Published Online: 7 July 2022



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Kaho Nakatani,<sup>1</sup> Masahiro Higashi,<sup>1,2</sup> and Hirofumi Sato<sup>1,2,3,a)</sup>

## AFFILIATIONS

<sup>1</sup>Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan

<sup>2</sup>Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615-8520, Japan

<sup>3</sup>Fukui Institute for Fundamental Chemistry, Kyoto University, Kyoto 606-8103, Japan

**Note:** This paper is part of the JCP Special Topic on Nature of the Chemical Bond.

**a) Author to whom correspondence should be addressed:** [hirofumi@moleng.kyoto-u.ac.jp](mailto:hirofumi@moleng.kyoto-u.ac.jp)

## ABSTRACT

We present a methodology for analyzing chemical bonds embedded in the electronic wave function of molecules, especially in terms of spin correlations or so-called “local spin.” In this paper, based on biorthogonal second quantization, the spin correlation functions of molecules are naturally introduced, which enables us to extract *local singlet* and *local triplet* elements from the wave function. We also clarify the relationship between these spin correlations and traditional chemical concepts, i.e., resonance structures. Several chemical reactions, including the intramolecular radical cyclization and the formation of preoxetane, are demonstrated to verify the analysis method numerically.

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## I. INTRODUCTION

In the field of chemistry, the correlations of localized spins have special significance in connection with the valence bond concept.<sup>1</sup> Chemical bonding and chemical reactions are understood as coupling electron spins and their recombination. However, such information on the local electronic structure is embedded in the complicated wave function obtained by quantum chemical calculations, making it challenging to utilize the information for our chemical understanding. This paper aims to present a general framework and a new practical method for analyzing local electronic states, especially the correlation of spins.

Historically, a bond order based on the coupling of spins proposed by Penney,<sup>2</sup> so-called Penney–Dirac bond order, is conceptually vital for our understanding of chemical bonding. The Penney–Dirac bond order was used to formulate nuclear spin–spin coupling in the theory of nuclear magnetic resonance.<sup>3,4</sup> Okada and Fueno<sup>5,6</sup> introduced atomic and diatomic components of the “spin coupling matrix,” the integration value of the second-order density matrix multiplied by the spin operator. As a generalization

of the Penney–Dirac bond order, their analysis was applied to molecular wave functions analogously to the Mulliken population analysis.<sup>7</sup>

In today’s computational quantum chemistry, the analysis of the correlation of localized spins in molecular systems is known as “local spin” analysis.<sup>8</sup> The local spin analysis can be considered as a decomposition of the expectation value of the total  $S^2$  operator into atomic components. With the notation of Mayer,<sup>9</sup>

$$\langle S^2 \rangle = \sum_A \langle S^2 \rangle_A + \sum_{\substack{A,B \\ A \neq B}} \langle S^2 \rangle_{AB}, \quad (1)$$

where  $\langle S^2 \rangle_A$  and  $\langle S^2 \rangle_{AB}$  are one- and two-center components, respectively. These components are often called “local spin” themselves. Intuitive understanding or conceptualization of electronic structures of molecules obtained with complicated quantum chemical calculations is not always an easy task, so the local spin analysis attracts attention, especially for the application to organic polyradical molecules<sup>10,11</sup> and transition metal complexes,<sup>12,13</sup> which can be considered as molecular magnets, including a noncollinear spin

case.<sup>14</sup> Clark and Davidson have presented a framework for the decomposition of  $\langle S^2 \rangle$  into one- and two-center components using projection operators in a series of papers.<sup>8,15–17</sup> They estimated the components for correlated wave functions and discussed the electronic structures of benzyne molecules.<sup>16</sup> Various definitions of local spin were then examined<sup>18</sup> because there are infinite ways to decompose  $\langle S^2 \rangle$  similarly to population analyses. For example, Mayer proposed introducing the constraint conditions for the decomposition to satisfy the condition that one-center component becomes zero for the restricted Hartree–Fock case.<sup>19</sup> After that, it became a significant issue to improve the way of decomposition based on the constraint conditions, including correlated wave function cases.<sup>9,20–25</sup> Discussions on this line seem to be settled by the work of Ramos-Cordoba *et al.*<sup>25</sup> Pendás and Francisco recently presented a framework to interpret local spins, by decomposing them into contributions from different numbers of electrons in fragments.<sup>26</sup>

In our view, despite the accumulated contributions on the local spin analysis, it is still unclear from formal aspects what we can say about the molecule's electronic structure through the quantities in Eq. (1). In particular, we would like to point out that the relationship between the local spin correlations and the resonance structures embedded in the wave functions obtained from standard quantum chemical calculations is not fully understood. Although they have often been discussed together, very few works have been devoted to their direct relationship to the best of our knowledge. We intend to clarify the local spin correlation's background and provide the logically clear link between the local spin and the chemical bonding or molecule's electronic structure.

The present study employs the second quantization formalism for a nonorthogonal basis,<sup>27,28</sup> while many previous works derive the local spin based on reduced density matrices and projection operators. Notably, the present representation is closely related to the standard “Mulliken-type” partitioning,<sup>8</sup> utilized for the Mulliken population,<sup>29</sup> Mayer bond order,<sup>28,30</sup> and the recently reported quantity referred to as the “weight of resonance structure.”<sup>31</sup> All of them can be formulated in the same second quantized formalism, and the correspondence between these quantities can be discussed on equal footing.

The paper is organized as follows. We present a method based on second quantized operators related to specific local electronic states, including the coupling of electron spins in Sec. II. The connection with the spin correlation and resonance theory, which allows an intuitive understanding of the electronic structure of molecules, is addressed after a natural derivation of the spin correlation operator in Sec. III. While the connection<sup>32,33</sup> was partially discussed so far, the complete formalism is given in this paper. To quantify the local electronic character, the expectation values for the introduced second quantized operators are evaluated for molecular orbital-based wave functions in Sec. IV. The numerical results are demonstrated in Sec. V, where at first the spin correlation functions obtained from quantum chemical calculations and the Heisenberg spin Hamiltonian model are compared. The numerical behavior of spin correlation functions and coupling of localized spins along the chemical reactions are shown with insights into molecular electronic structures.

## II. LOCAL ELECTRONIC STATES

This section aims to formulate local electronic states and introduce the operators corresponding to the states in a given wave function. We start from the fact that any wave function  $\Psi$  in the linear combination of atomic orbitals (LCAOs) approximation can be represented as a linear combination of atomic spin orbital (ASO)-based determinants  $\{\Phi_i^{\text{ASO}}\}$  as

$$\Psi = \sum_i K_i \Phi_i^{\text{ASO}}, \quad (2)$$

where  $K_i$  is the expansion coefficient of the  $i$ th ASO-based determinant  $\Phi_i^{\text{ASO}}$ . Each ASO-based determinant, representing the local electronic structure, is related to the concept of “resonance structure” in chemistry.<sup>34–36</sup> Focusing on the occupancy of the two atomic orbitals  $\chi_\mu$  and  $\chi_\nu$  ( $\mu \neq \nu$ ), we can group the ASO-based determinants in  $\Psi$ . All the possible occupation patterns are schematically shown in Fig. 1. Expressions of some of these configurations with ASO-determinants are shown later. We first construct the operators corresponding to each configuration schematically shown in the figure. In the mixed second quantized formalism<sup>27,28</sup> for nonorthogonal ASO  $\{\chi_\mu^\sigma\}$  and its biorthogonal spin orbital  $\{\varphi_\mu^\sigma\}$  (labels of spin and spatial functions are given by  $\sigma$  and  $\mu$ , respectively), the number operator for  $\chi_\mu^\sigma$  is given as

$$\hat{N}_\mu^\sigma = \chi_\mu^{\sigma+} \varphi_\mu^{\sigma-}. \quad (3)$$

By using the identity

$$1 = \hat{N}_\mu^\sigma + (1 - \hat{N}_\mu^\sigma), \quad (4)$$

we obtain the following resolution of the identity about the occupancies of the atomic spin orbitals  $\chi_\mu^\alpha$ ,  $\chi_\mu^\beta$ ,  $\chi_\nu^\alpha$  and  $\chi_\nu^\beta$ :

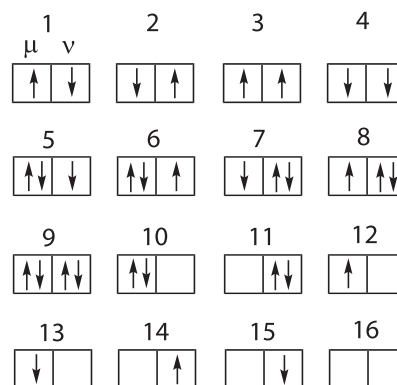


FIG. 1. Schematic representations for the patterns of the occupancies of the atomic orbitals  $\chi_\mu$  and  $\chi_\nu$  constructing the wave function and numbering of the configurations.

$$\begin{aligned}
 1 &= \{ \hat{N}_\mu^\alpha + (1 - \hat{N}_\mu^\alpha) \} \{ \hat{N}_\mu^\beta + (1 - \hat{N}_\mu^\beta) \} \{ \hat{N}_v^\alpha + (1 - \hat{N}_v^\alpha) \} \{ \hat{N}_v^\beta + (1 - \hat{N}_v^\beta) \} \quad (5) \\
 &= \underbrace{\hat{N}_\mu^\alpha (1 - \hat{N}_\mu^\beta)}_1 (1 - \hat{N}_v^\alpha) \hat{N}_v^\beta + (1 - \hat{N}_\mu^\alpha) \underbrace{\hat{N}_\mu^\beta \hat{N}_v^\alpha}_2 (1 - \hat{N}_v^\beta) + \hat{N}_\mu^\alpha (1 - \hat{N}_\mu^\beta) \hat{N}_v^\alpha (1 - \hat{N}_v^\beta) + (1 - \hat{N}_\mu^\alpha) \underbrace{\hat{N}_\mu^\beta (1 - \hat{N}_v^\alpha)}_4 \hat{N}_v^\beta \\
 &\quad + \underbrace{\hat{N}_\mu^\alpha \hat{N}_\mu^\beta (1 - \hat{N}_v^\alpha)}_5 \hat{N}_v^\beta + \underbrace{\hat{N}_\mu^\alpha \hat{N}_\mu^\beta \hat{N}_v^\alpha (1 - \hat{N}_v^\beta)}_6 + (1 - \hat{N}_\mu^\alpha) \underbrace{\hat{N}_\mu^\beta \hat{N}_v^\alpha \hat{N}_v^\beta}_7 + \hat{N}_\mu^\alpha (1 - \hat{N}_\mu^\beta) \underbrace{\hat{N}_v^\alpha \hat{N}_v^\beta}_8 + \hat{N}_\mu^\alpha \hat{N}_\mu^\beta \hat{N}_v^\alpha \hat{N}_v^\beta \\
 &\quad + \underbrace{\hat{N}_\mu^\alpha \hat{N}_\mu^\beta (1 - \hat{N}_v^\alpha)}_{10} (1 - \hat{N}_v^\beta) + (1 - \hat{N}_\mu^\alpha) (1 - \hat{N}_\mu^\beta) \underbrace{\hat{N}_v^\alpha \hat{N}_v^\beta}_{11} + \hat{N}_\mu^\alpha (1 - \hat{N}_\mu^\beta) (1 - \hat{N}_v^\alpha) (1 - \hat{N}_v^\beta) \\
 &\quad + (1 - \hat{N}_\mu^\alpha) \underbrace{\hat{N}_\mu^\beta (1 - \hat{N}_v^\alpha)}_{13} (1 - \hat{N}_v^\beta) + (1 - \hat{N}_\mu^\alpha) (1 - \hat{N}_\mu^\beta) \underbrace{\hat{N}_v^\alpha (1 - \hat{N}_v^\beta)}_{14} + (1 - \hat{N}_\mu^\alpha) (1 - \hat{N}_\mu^\beta) (1 - \hat{N}_v^\alpha) \hat{N}_v^\beta \\
 &\quad + (1 - \hat{N}_\mu^\alpha) (1 - \hat{N}_\mu^\beta) (1 - \hat{N}_v^\alpha) (1 - \hat{N}_v^\beta) \quad (6) \\
 &\quad \underbrace{\hspace{10em}}_{16}
 \end{aligned}$$

where the number (label) of the corresponding configuration represented in Fig. 1 is shown under each term in Eq. (6). This identity shows that the total wave function  $\Psi$  is represented as the superposition of the configurations labeled 1–16. It should be mentioned that the works by Karafiloglou and his co-workers contribute to a systematic construction of projection operators for local electronic states.<sup>37,38</sup> For the spin correlation, we consider the situation in which two electrons, respectively, occupy each orbital. The operators corresponding to the configurations 1–4 are written as

$$\hat{\Theta}_{\mu\nu}^{\alpha\beta} = \hat{N}_\mu^\alpha (1 - \hat{N}_\mu^\beta) (1 - \hat{N}_v^\alpha) \hat{N}_v^\beta, \quad (7)$$

$$\hat{\Theta}_{\mu\nu}^{\beta\alpha} = (1 - \hat{N}_\mu^\alpha) \hat{N}_\mu^\beta \hat{N}_v^\alpha (1 - \hat{N}_v^\beta), \quad (8)$$

$$\hat{\Theta}_{\mu\nu}^{\alpha\alpha} = \hat{N}_\mu^\alpha (1 - \hat{N}_\mu^\beta) \hat{N}_v^\alpha (1 - \hat{N}_v^\beta), \quad (9)$$

$$\hat{\Theta}_{\mu\nu}^{\beta\beta} = (1 - \hat{N}_\mu^\alpha) \hat{N}_\mu^\beta (1 - \hat{N}_v^\alpha) \hat{N}_v^\beta. \quad (10)$$

The actions of these operators are

$$\hat{\Theta}_{\mu\nu}^{\alpha\beta} \Psi = \Psi_{\mu\nu}^{\alpha\beta}, \quad \hat{\Theta}_{\mu\nu}^{\beta\alpha} \Psi = \Psi_{\mu\nu}^{\beta\alpha}, \quad \hat{\Theta}_{\mu\nu}^{\alpha\alpha} \Psi = \Psi_{\mu\nu}^{\alpha\alpha}, \quad \hat{\Theta}_{\mu\nu}^{\beta\beta} \Psi = \Psi_{\mu\nu}^{\beta\beta}, \quad (11)$$

where  $\Psi_{\mu\nu}^{\alpha\beta}$ ,  $\Psi_{\mu\nu}^{\beta\alpha}$ ,  $\Psi_{\mu\nu}^{\alpha\alpha}$ ,  $\Psi_{\mu\nu}^{\beta\beta}$  are represented using ASO-based determinants as

$$\Psi_{\mu\nu}^{\alpha\beta} = \sum_i K_i^{\alpha\beta} \Phi_i^{\alpha\beta} (\chi_\mu^\alpha, \chi_\nu^\beta \in \Phi_i^{\alpha\beta}, \chi_\mu^\beta, \chi_\nu^\alpha \notin \Phi_i^{\alpha\beta}), \quad (12)$$

$$\Psi_{\mu\nu}^{\beta\alpha} = \sum_i K_i^{\beta\alpha} \Phi_i^{\beta\alpha} (\chi_\mu^\beta, \chi_\nu^\alpha \in \Phi_i^{\beta\alpha}, \chi_\mu^\alpha, \chi_\nu^\beta \notin \Phi_i^{\beta\alpha}), \quad (13)$$

$$\Psi_{\mu\nu}^{\alpha\alpha} = \sum_i K_i^{\alpha\alpha} \Phi_i^{\alpha\alpha} (\chi_\mu^\alpha, \chi_\nu^\alpha \in \Phi_i^{\alpha\alpha}, \chi_\mu^\beta, \chi_\nu^\beta \notin \Phi_i^{\alpha\alpha}), \quad (14)$$

$$\Psi_{\mu\nu}^{\beta\beta} = \sum_i K_i^{\beta\beta} \Phi_i^{\beta\beta} (\chi_\mu^\beta, \chi_\nu^\beta \in \Phi_i^{\beta\beta}, \chi_\mu^\alpha, \chi_\nu^\alpha \notin \Phi_i^{\beta\beta}). \quad (15)$$

In Eqs. (12)–(15),  $K_i^{\alpha\beta}$ ,  $K_i^{\beta\alpha}$ ,  $K_i^{\alpha\alpha}$  and  $K_i^{\beta\beta}$  are the expansion coefficients appearing in Eq. (2). For ease of notations, labels of atomic orbitals,  $\mu$  and  $\nu$ , are omitted in  $K_i^{\alpha\beta}$ ,  $K_i^{\beta\alpha}$ ,  $K_i^{\alpha\alpha}$ ,  $K_i^{\beta\beta}$  and in  $\Phi_i^{\alpha\beta}$ ,  $\Phi_i^{\beta\alpha}$ ,  $\Phi_i^{\alpha\alpha}$ ,  $\Phi_i^{\beta\beta}$ .

The components of  $\Psi$ ,  $\Psi_{\mu\nu}^{\alpha\alpha}$  and  $\Psi_{\mu\nu}^{\beta\beta}$ , are called *local triplet* states ( $\langle S_z \rangle = \pm 1$  types, respectively), obviously related to the antibonding character for the pair of  $\chi_\mu$  and  $\chi_\nu$ . For the bonding character, we found that the expression cannot be written only with the number operators appearing in Eq. (6). First, note that ASO-based determinants  $\Phi_i^{\alpha\beta}$  and  $\Phi_i^{\beta\alpha}$  are associated so as to satisfy

$$|\Phi_i^{\alpha\beta}\rangle = \chi_\mu^{\alpha+} \varphi_\mu^{\beta-} \chi_\nu^{\beta+} \varphi_\nu^{\alpha-} |\Phi_i^{\beta\alpha}\rangle, \quad (16)$$

where the right-hand side of the equation is the determinant in which  $\chi_\mu^\beta$  and  $\chi_\nu^\alpha$  in  $\Phi_i^{\beta\alpha}$  are replaced with  $\chi_\mu^\alpha$  and  $\chi_\nu^\beta$ , respectively, ( $\chi_\mu^\beta \rightarrow \chi_\mu^\alpha$ ,  $\chi_\nu^\alpha \rightarrow \chi_\nu^\beta$ ). We, then, introduce the determinantal expression of the local electronic states to be called the *local singlet* state,  $\Psi_{\mu\nu}^S$ , and the *local triplet* ( $\langle S_z \rangle = 0$  type) state,  $\Psi_{\mu\nu}^{T_0}$ , at  $\chi_\mu$  and  $\chi_\nu$  as follows:

$$\Psi_{\mu\nu}^S = \sum_i \frac{K_i^{\alpha\beta} - K_i^{\beta\alpha}}{2} \Phi_i^S, \quad (17)$$

$$\Psi_{\mu\nu}^{T_0} = \sum_i \frac{K_i^{\alpha\beta} + K_i^{\beta\alpha}}{2} \Phi_i^{T_0}, \quad (18)$$

where

$$\Phi_i^S \equiv \Phi_i^{\alpha\beta} - \Phi_i^{\beta\alpha} = |(\chi_\mu^\alpha \chi_\nu^\beta - \chi_\mu^\beta \chi_\nu^\alpha) \cdots|, \quad (19)$$

$$\Phi_i^{T_0} \equiv \Phi_i^{\alpha\beta} + \Phi_i^{\beta\alpha} = |(\chi_\mu^\alpha \chi_\nu^\beta + \chi_\mu^\beta \chi_\nu^\alpha) \cdots|. \quad (20)$$

In Eqs. (17) and (18), the expansion coefficients are determined so as to satisfy

$$\Psi_{\mu\nu}^{\alpha\beta} + \Psi_{\mu\nu}^{\beta\alpha} = \Psi_{\mu\nu}^S + \Psi_{\mu\nu}^{T_0}. \quad (21)$$

The operator  $\hat{\Theta}_{\mu\nu}^S$ , which satisfies  $\hat{\Theta}_{\mu\nu}^S \Psi = \Psi_{\mu\nu}^S$ , is

$$\hat{\Theta}_{\mu\nu}^S = \frac{1}{2} \left( \hat{\Theta}_{\mu\nu}^{\alpha\beta} + \hat{\Theta}_{\mu\nu}^{\beta\alpha} - \chi_{\mu}^{\beta+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\alpha-} - \chi_{\mu}^{\alpha+} \chi_{\nu}^{\beta+} \varphi_{\nu}^{\alpha-} \varphi_{\mu}^{\beta-} \right). \quad (22)$$

Similarly, the operator  $\hat{\Theta}_{\mu\nu}^{T_0}$ , which satisfies  $\hat{\Theta}_{\mu\nu}^{T_0} \Psi = \Psi^{T_0}$ , is

$$\hat{\Theta}_{\mu\nu}^{T_0} = \frac{1}{2} \left( \hat{\Theta}_{\mu\nu}^{\alpha\beta} + \hat{\Theta}_{\mu\nu}^{\beta\alpha} + \chi_{\mu}^{\beta+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\alpha-} + \chi_{\mu}^{\alpha+} \chi_{\nu}^{\beta+} \varphi_{\nu}^{\alpha-} \varphi_{\mu}^{\beta-} \right). \quad (23)$$

Now, we know all the operators related to the states about the occupancy of the two atomic orbitals  $\chi_{\mu}$  and  $\chi_{\nu}$ , shown in Fig. 1.

### III. SPIN CORRELATION

Here, we first present a second quantized formalism of spin correlation on a nonorthogonal atomic orbital basis. Then, the formal connection between the spin correlation  $\mathbf{s}_{\mu} \cdot \mathbf{s}_{\nu}$  and local electronic states is provided in terms of second quantized operators. Spin operators can be represented in the mixed second quantized formalism as

$$S_x = \sum_{\mu} \frac{1}{2} \left( \chi_{\mu}^{\beta+} \varphi_{\mu}^{\alpha-} + \chi_{\mu}^{\alpha+} \varphi_{\mu}^{\beta-} \right), \quad (24)$$

$$S_y = \sum_{\mu} \frac{i}{2} \left( \chi_{\mu}^{\beta+} \varphi_{\mu}^{\alpha-} - \chi_{\mu}^{\alpha+} \varphi_{\mu}^{\beta-} \right), \quad (25)$$

$$S_z = \sum_{\mu} \frac{1}{2} \left( \hat{N}_{\mu}^{\alpha} - \hat{N}_{\mu}^{\beta} \right). \quad (26)$$

Utilizing the anticommutation relations

$$[\chi_{\mu}^{\sigma_1+}, \varphi_{\nu}^{\sigma_2-}]_{+} = \delta_{\sigma_1\sigma_2} \delta_{\mu\nu}, \quad (27)$$

the total  $S^2$  spin operator in the mixed second quantized formalism<sup>20</sup> can be written as

$$\begin{aligned} S^2 &= S_x^2 + S_y^2 + S_z^2 \\ &= \frac{3}{4} \sum_{\mu} \left( \hat{N}_{\mu}^{\alpha} + \hat{N}_{\mu}^{\beta} \right) + \frac{1}{2} \sum_{\mu,\nu} \left( \chi_{\mu}^{\beta+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\alpha-} + \chi_{\nu}^{\beta+} \chi_{\mu}^{\alpha+} \varphi_{\mu}^{\beta-} \varphi_{\nu}^{\alpha-} \right) \\ &\quad + \frac{1}{4} \sum_{\mu,\nu} \left( \chi_{\mu}^{\alpha+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\alpha-} \varphi_{\mu}^{\alpha-} - \chi_{\mu}^{\alpha+} \chi_{\nu}^{\beta+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\alpha-} \right. \\ &\quad \left. - \chi_{\mu}^{\beta+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\alpha-} \varphi_{\mu}^{\beta-} + \chi_{\mu}^{\beta+} \chi_{\nu}^{\beta+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\beta-} \right). \end{aligned} \quad (28)$$

Here, we introduce the following *local* spin operators:

$$s_{\mu}^x \equiv \frac{1}{2} \left( \chi_{\mu}^{\beta+} \varphi_{\mu}^{\alpha-} + \chi_{\mu}^{\alpha+} \varphi_{\mu}^{\beta-} \right), \quad (29)$$

$$s_{\mu}^y \equiv \frac{i}{2} \left( \chi_{\mu}^{\beta+} \varphi_{\mu}^{\alpha-} - \chi_{\mu}^{\alpha+} \varphi_{\mu}^{\beta-} \right), \quad (30)$$

$$s_{\mu}^z \equiv \frac{1}{2} \left( \hat{N}_{\mu}^{\alpha} - \hat{N}_{\mu}^{\beta} \right), \quad (31)$$

$$\mathbf{s}_{\mu} \equiv (s_{\mu}^x, s_{\mu}^y, s_{\mu}^z). \quad (32)$$

Based on these definitions, we rewrite the two-electron part of  $\mathbf{s}_i \cdot \mathbf{s}_j$  as

$$\begin{aligned} \mathbf{s}_{\mu} \cdot \mathbf{s}_{\nu} &= \frac{1}{2} \left( \chi_{\nu}^{\beta+} \chi_{\mu}^{\alpha+} \varphi_{\mu}^{\beta-} \varphi_{\nu}^{\alpha-} + \chi_{\mu}^{\beta+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\alpha-} \right) \\ &\quad + \frac{1}{4} \left( \chi_{\mu}^{\alpha+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\alpha-} \varphi_{\mu}^{\alpha-} - \chi_{\mu}^{\alpha+} \chi_{\nu}^{\beta+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\alpha-} \right. \\ &\quad \left. - \chi_{\mu}^{\beta+} \chi_{\nu}^{\alpha+} \varphi_{\nu}^{\alpha-} \varphi_{\mu}^{\beta-} + \chi_{\mu}^{\beta+} \chi_{\nu}^{\beta+} \varphi_{\nu}^{\beta-} \varphi_{\mu}^{\beta-} \right). \end{aligned} \quad (33)$$

Then, Eq. (28) can simply be represented as follows:

$$S^2 = \frac{3}{4} \sum_{\mu} \left( \hat{N}_{\mu}^{\alpha} + \hat{N}_{\mu}^{\beta} \right) + \sum_{\mu,\nu} \mathbf{s}_{\mu} \cdot \mathbf{s}_{\nu}. \quad (34)$$

The present formulation of the spin correlation is equivalent to that by Clark and Davidson.<sup>8</sup> As we will see later, the formulation gives the same result for the two-center component  $\langle S^2 \rangle_{AB}$  in Eq. (1) as the one by the ‘‘Mulliken-type’’ partitioning of them. [In their scheme, the contribution from the first term on the right-hand side of Eq. (34) is distributed into the one-center component  $\langle S^2 \rangle_A$ . For consistency of notation, this part is represented differently in this paper.] Nevertheless, it is notable that the physical background becomes clear due to the introduction through the second quantized operator. For example, Eq. (33), in the case of  $\mu \neq \nu$ , can be rewritten with the operators introduced in Sec. II as

$$\mathbf{s}_{\mu} \cdot \mathbf{s}_{\nu} = -\frac{3}{4} \hat{\Theta}_{\mu\nu}^S + \frac{1}{4} \hat{\Theta}_{\mu\nu}^{T_0} + \frac{1}{4} \hat{\Theta}_{\mu\nu}^{\alpha\alpha} + \frac{1}{4} \hat{\Theta}_{\mu\nu}^{\beta\beta}. \quad (35)$$

This representation clearly shows that the spin correlation between two orbitals is a sum of contributions from the *local singlet* state weighted with  $-3/4$  and *local triplet* states weighted with  $1/4$ . Especially in the case of  $\mu = \nu$ ,

$$\mathbf{s}_{\mu} \cdot \mathbf{s}_{\mu} = -\frac{3}{2} \hat{N}_{\mu}^{\alpha} \hat{N}_{\mu}^{\beta}. \quad (36)$$

The operator  $\hat{N}_{\mu}^{\alpha} \hat{N}_{\mu}^{\beta}$  projects out the local state in which  $\chi_{\mu}$  is occupied by  $\alpha$ - and  $\beta$ -electrons.

It is worth mentioning the relationship to Penney’s picture of bonding.<sup>2</sup> The Penney–Dirac bond order between orbitals labeled  $i$  and  $j$  is defined as

$$p_{ij} = -\frac{4}{3} \overline{\mathbf{s}_i \cdot \mathbf{s}_j}, \quad (37)$$

where  $\overline{\mathbf{s}_i \cdot \mathbf{s}_j}$  denotes the expectation value of  $\mathbf{s}_i \cdot \mathbf{s}_j$ . This bond order takes following values for the limiting cases of two electrons:

$$p_{ij} = \begin{cases} 1 & \text{(singlet),} \\ -\frac{1}{3} & \text{(triplet),} \\ 0 & \text{(random),} \end{cases} \quad (38)$$

where ‘‘random’’ means the state in which singlet and triplet ( $\langle S_z \rangle = \pm 1, 0$ ) are equally mixed. The Penney–Dirac bond order is considered as the inter-/extrapolation for these two limited values of the singlet and random states. On looking at Eq. (35), the *local singlet* and *local triplet* terms are found to cancel out each other when there is no spin correlation, i.e., random coupling,

$$-\frac{4}{3} \mathbf{s}_{\mu} \cdot \mathbf{s}_{\nu} = \hat{\Theta}_{\mu\nu}^S - \frac{1}{3} \left\{ \hat{\Theta}_{\mu\nu}^{T_0} + \hat{\Theta}_{\mu\nu}^{\alpha\alpha} + \hat{\Theta}_{\mu\nu}^{\beta\beta} \right\}.$$

For the simplest H<sub>2</sub> of the minimal basis set, a *purely* covalent bond is represented by the normalized Heitler–London-type wave function,

$$\Psi^{\text{HL}} = \left| \chi_1^\alpha \chi_2^\beta \right| - \left| \chi_1^\beta \chi_2^\alpha \right|, \quad (39)$$

$$-\frac{4}{3} \langle \Psi^{\text{HL}} | \mathbf{s}_1 \cdot \mathbf{s}_2 | \Psi^{\text{HL}} \rangle = 1. \quad (40)$$

Similarly, the quantity for the triplet state is minus one-third. A bond is generally characterized by a mixing of covalent and ionic characters; hence, the quantity of singlet-coupling, in reality, should be smaller than one. For the Hartree–Fock wave function,  $\Psi^{\text{HF}}$ , the quantity in the left-hand side of Eq. (40) takes the value of 1/2, and the expectation value of the operator  $\langle \Psi^{\text{HF}} | \mathbf{s}_1 \cdot \mathbf{s}_2 | \Psi^{\text{HF}} \rangle$  becomes  $-3/8$ .

We note that the operator for spin correlation  $\mathbf{s}_\mu \cdot \mathbf{s}_\nu$  represented in Eq. (33) is a proper extension of the spin operator appearing in the Heisenberg spin Hamiltonian,

$$\mathcal{H} = J \sum_{\mu \sim \nu} \mathbf{s}_\mu \cdot \mathbf{s}_\nu, \quad (41)$$

where  $J$  is the exchange coupling constant,  $\mu$  and  $\nu$  indicate atomic sites, and  $\mu \sim \nu$  means the sum is taken over the labels of adjacent atomic sites. Equation (33) reduces to  $\mathbf{s}_\mu \cdot \mathbf{s}_\nu$  in Eq. (41) when the atomic orbital basis is orthogonal, as assumed in the standard Heisenberg model.

#### IV. WEIGHTS OF LOCAL ELECTRONIC STATES

The weight  $w_i$  for the ASO-based determinant  $\Phi_i^{\text{ASO}}$  in Eq. (2) can be evaluated based on the definition of Chirgwin and Coulson<sup>39</sup> as

$$w_i = K_i \langle \Psi | \Phi_i^{\text{ASO}} \rangle. \quad (42)$$

These weights sum up to unity for the normalized wave function. Since the ASOs are distributed on atomic sites, the weight of an ASO determinant is identified as the weight of corresponding resonance structure. This weight can be formulated using the number operator represented in Eq. (3).<sup>31</sup> The expectation values of the mixed second quantized operators introduced in the previous sections, which are closely related to the Chirgwin–Coulson weight or the Mulliken-type partitioning, are provided in this section to quantify each contribution of the local electronic states. We assume single-determinant cases (Hartree–Fock wave function or Kohn–Sham determinant) for the present purpose. For a single-determinant wave function,  $\Psi^{\text{HF}}$ , we show that the expectation values of the operators  $\hat{\Theta}_{\mu\nu}^{\alpha\beta}$ ,  $\hat{\Theta}_{\mu\nu}^{\beta\alpha}$ ,  $\hat{\Theta}_{\mu\nu}^{\alpha\alpha}$ ,  $\hat{\Theta}_{\mu\nu}^{\beta\beta}$  and  $\mathbf{s}_\mu \cdot \mathbf{s}_\nu$  can be represented using only the overlap matrix  $\mathbf{S}$  and density matrices  $\mathbf{P}^\sigma$  ( $\sigma = \alpha, \beta$ ), with its element

$$\mathbf{P}_{\mu\nu}^\sigma = \sum_i^{\text{occ.}} c_{i\mu}^\sigma c_{i\nu}^{\sigma*}, \quad (43)$$

where  $c_{i\mu}^\sigma$  is the coefficient of  $\chi_\mu^\sigma$  in the  $i$ th molecular spin orbital  $\phi_i^\sigma$ .

The general representation of the expectation value for the string of number operators was reported in Ref. 31. The expectation value of the operator appearing in Eqs. (22) and (23) and the first parenthesis in Eq. (33) is calculated as<sup>28,31</sup>

$$\begin{aligned} & \langle \Psi^{\text{HF}} | \chi_\mu^{\alpha+} \phi_\mu^{\beta-} \chi_\nu^{\beta+} \phi_\nu^{\alpha-} | \Psi^{\text{HF}} \rangle \\ & = \sum_{ij} c_{i\nu}^\alpha c_{j\mu}^\beta \langle \Psi^{\text{HF}} | \Psi^{\text{HF}} (\phi_i^\alpha \rightarrow \chi_\nu^\beta, \phi_j^\beta \rightarrow \chi_\mu^\alpha) \rangle \end{aligned} \quad (44)$$

$$= \sum_{ij} c_{i\nu}^\alpha c_{j\mu}^\beta \begin{vmatrix} \langle \phi_i^\alpha | \chi_\nu^\beta \rangle & \langle \phi_i^\alpha | \chi_\mu^\alpha \rangle \\ \langle \phi_j^\beta | \chi_\nu^\beta \rangle & \langle \phi_j^\beta | \chi_\mu^\alpha \rangle \end{vmatrix} \quad (45)$$

$$= \begin{vmatrix} 0 & (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \\ (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} & 0 \end{vmatrix} = -(\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} (\mathbf{P}^\beta \mathbf{S})_{\mu\nu}, \quad (46)$$

where  $\Psi^{\text{HF}}(\phi_i^\alpha \rightarrow \chi_\nu^\beta, \phi_j^\beta \rightarrow \chi_\mu^\alpha)$  in Eq. (44) is the determinant in which molecular orbitals  $\phi_i^\alpha$  and  $\phi_j^\beta$  in  $\Psi^{\text{HF}}$  are replaced by  $\chi_\nu^\beta$  and  $\chi_\mu^\alpha$ , respectively. Similarly,

$$\langle \Psi^{\text{HF}} | \chi_\mu^{\beta+} \phi_\mu^{\alpha-} \chi_\nu^{\alpha+} \phi_\nu^{\beta-} | \Psi^{\text{HF}} \rangle = -(\mathbf{P}^\beta \mathbf{S})_{\nu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu}. \quad (47)$$

These representations are combined and we obtain the following representation for the weights of *local singlet* and *local triplet* ( $\langle S_z \rangle = 0, \pm 1$  types) states. Additionally, we obtain the following representation for the spin correlation function:

$$\begin{aligned} \langle \Psi^{\text{HF}} | \mathbf{s}_\mu \cdot \mathbf{s}_\nu | \Psi^{\text{HF}} \rangle & = -\frac{1}{2} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} - \frac{1}{2} (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \\ & + \frac{1}{4} (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} - \frac{1}{4} (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \\ & + \frac{1}{4} (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} - \frac{1}{4} (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \\ & - \frac{1}{4} (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} - \frac{1}{4} (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} \end{aligned} \quad (48)$$

$$= -\frac{3}{8} \mathbf{D}_{\mu\nu} \mathbf{D}_{\nu\mu} + \frac{1}{8} \mathbf{P}_{\mu\nu}^S \mathbf{P}_{\nu\mu}^S + \frac{1}{4} \mathbf{P}_{\mu\mu}^S \mathbf{P}_{\nu\nu}^S, \quad (49)$$

$$\begin{aligned} w_{\mu\nu}^S & = \langle \Psi^{\text{HF}} | \hat{\Theta}_{\mu\nu}^S | \Psi^{\text{HF}} \rangle \\ & = \frac{1}{2} \left[ \{ (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} - (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} + (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \right. \\ & \quad \times \{ (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} - (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \} \\ & \quad + \{ (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} - (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \} \\ & \quad \times \{ (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} - (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} + (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \\ & \quad \left. + \{ (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \right], \end{aligned} \quad (50)$$

$$\begin{aligned} w_{\mu\nu}^{\text{T}_0} & = \langle \Psi^{\text{HF}} | \hat{\Theta}_{\mu\nu}^{\text{T}_0} | \Psi^{\text{HF}} \rangle \\ & = \frac{1}{2} \left[ \{ (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} - (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} + (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \right. \\ & \quad \times \{ (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} - (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \} \\ & \quad + \{ (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} - (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \} \\ & \quad \times \{ (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} - (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} + (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \\ & \quad \left. - \{ (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \right], \end{aligned} \quad (51)$$



$$\begin{aligned}
 w_{\mu\nu}^{\alpha\alpha} &= \langle \Psi^{\text{HF}} | \hat{O}_{\mu\nu}^{\alpha\alpha} | \Psi^{\text{HF}} \rangle \\
 &= \{ (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} - (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \\
 &\quad \times \left\{ 1 - (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} - (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} + (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} \right. \\
 &\quad \left. - (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \right\}, \quad (52)
 \end{aligned}$$

$$\begin{aligned}
 w_{\mu\nu}^{\beta\beta} &= \langle \Psi^{\text{HF}} | \hat{O}_{\mu\nu}^{\beta\beta} | \Psi^{\text{HF}} \rangle \\
 &= \{ 1 - (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} - (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} + (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\nu} - (\mathbf{P}^\alpha \mathbf{S})_{\mu\nu} (\mathbf{P}^\alpha \mathbf{S})_{\nu\mu} \} \\
 &\quad \times \left\{ (\mathbf{P}^\beta \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\nu\nu} - (\mathbf{P}^\beta \mathbf{S})_{\mu\nu} (\mathbf{P}^\beta \mathbf{S})_{\nu\mu} \right\}. \quad (53)
 \end{aligned}$$

As already mentioned, the treatment is considered to be equivalent to the one by Clark and Davidson. In the bottom line of Eq. (49), the expression is rewritten with  $\mathbf{D} = \mathbf{P}^\alpha + \mathbf{P}^\beta$  (spinless density matrix) and  $\mathbf{P}^S = \mathbf{P}^\alpha - \mathbf{P}^\beta$  (spin density matrix), which might be helpful. To the best of our knowledge, Okada and Fueno reported<sup>6</sup> essentially the same representation as Eq. (48) (different in the factor of  $-4/3$ ), inspired by the Penney–Dirac expression. The present expression resembles the corresponding matrix formulation appearing in Ref. 18. Note that it is straightforward to obtain the Löwdin-type expression by changing the nonorthogonal operator.<sup>40</sup> Equation (48) holds in the case of  $\mu = \nu$ ,

$$\langle \Psi^{\text{HF}} | \mathbf{s}_\mu \cdot \mathbf{s}_\mu | \Psi^{\text{HF}} \rangle = -\frac{3}{2} (\mathbf{P}^\alpha \mathbf{S})_{\mu\mu} (\mathbf{P}^\beta \mathbf{S})_{\mu\mu}. \quad (54)$$

Since the formulation is based on second quantization, the formal extension for multi-configurational wave functions is straightforward. However, the numerical calculation of the weights in Eqs. (50)–(53) requires density matrices of up to the fourth order. In practical analyses of *ab initio* wave functions, the spin correlation operator is redefined as the sum over the basis functions for the pair of atomic centers labeled with *A* and *B*. And its expectation value is evaluated as

$$\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle = \sum_{\mu \in A, \nu \in B} \langle \mathbf{s}_\mu \cdot \mathbf{s}_\nu \rangle. \quad (55)$$

This quantity corresponds to the two-center component  $\langle S^2 \rangle_{AB}$  in Eq. (1). Because each component of the right-hand side can take values between  $-3/4$  and  $1/4$ , the numerical range of  $\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle$  is relatively narrow even after summing up over the basis functions. The numerical results obtained from the equation were confirmed to be consistent with previous works.

By introducing the following quantities,

$$\begin{aligned}
 w_{AB}^S &= \sum_{\mu \in A, \nu \in B} w_{\mu\nu}^S, \quad w_{AB}^{T_0} = \sum_{\mu \in A, \nu \in B} w_{\mu\nu}^{T_0}, \\
 w_{AB}^{\alpha\alpha} &= \sum_{\mu \in A, \nu \in B} w_{\mu\nu}^{\alpha\alpha}, \quad w_{AB}^{\beta\beta} = \sum_{\mu \in A, \nu \in B} w_{\mu\nu}^{\beta\beta}, \quad (56)
 \end{aligned}$$

we can write

$$\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle = -\frac{3}{4} w_{AB}^S + \frac{1}{4} w_{AB}^{T_0} + \frac{1}{4} w_{AB}^{\alpha\alpha} + \frac{1}{4} w_{AB}^{\beta\beta}. \quad (57)$$

The quantities in the left-hand side of Eq. (56),  $w_{AB}^X$ , represent the magnitude of the contribution from the *local singlet* and *local triplet* states in the atomic site *A* and *B* pairs. Unlike the Chirgwin–Coulson weights,  $w_{AB}^X$  are not normalized and can take various values. As it is an accumulated quantity in each spin state, the contribution tends to increase as the size of the basis set becomes larger. Therefore, relative comparisons and changes along a reaction coordinate are more meaningful than absolute values. Note that  $\langle \mathbf{S}_A \cdot \mathbf{S}_B \rangle$  tends to be independent of the basis-set size, as can be seen in Eq. (57).

In Sec. V, we numerically verify these quantities together with the verification of the spin correlation function.

## V. NUMERICAL DEMONSTRATIONS

In this section, we present the results of quantum chemical calculations based on the discussion in the previous sections. First, spin correlation functions obtained from the density functional theory (DFT) and the Heisenberg model are compared. Second, numerical behaviors of spin correlation functions in chemical reaction processes are interpreted from the viewpoint of local coupling of spins or resonance theory. The self-consistent field calculations and geometry optimizations were performed with the Gaussian 16 program.<sup>41</sup> The spin correlation function and contributions of *local singlet* and *local triplet* states were subsequently evaluated with the overlap matrix and molecular orbital coefficients based on Eqs. (48), (50)–(53), (55), and (56).

### A. Comparison with Heisenberg spin Hamiltonian

We analyzed the bonding in *ortho* (*o*-), *para* (*p*-), and *meta* (*m*-)quinodimethanes (QDMs), shown in Fig. 2. The singlet ground states of *o*- and *p*-QDMs and the triplet ground state of *m*-QDM were calculated by B3LYP<sup>42–44</sup> with the 6-31G(d,p) basis set, treating the triplet state with the unrestricted method (UB3LYP). Molecular structures of *o*-, *p*-, and *m*-QDMs were optimized at the same computational levels, imposing  $C_{2v}$ ,  $D_{2h}$ , and  $C_{2v}$  symmetries, respectively. To evaluate the numerical effects from electrons in the space other than the valence space, spin correlation functions were calculated in the whole of the orbital space (which is common in the local spin analysis) and only in the  $\pi$ -type canonical orbital space, concerning construction of the density matrices,  $\mathbf{P}^\sigma$  ( $\sigma = \alpha, \beta$ ). Ground state wave functions of QDMs for the Heisenberg spin Hamiltonian in Eq. (41) were considered in the subspace of  $\langle S_z \rangle = 0$ . The only input for the Heisenberg model is the adjacency matrix corresponding to the carbon skeleton shown in Fig. 2. Assuming the positive value of the exchange coupling constant  $J > 0$ , i.e., antiferromagnetism, the wave function was obtained by diagonalizing the Hamiltonian matrix. Then, the spin correlation functions were calculated based on Eq. (33).

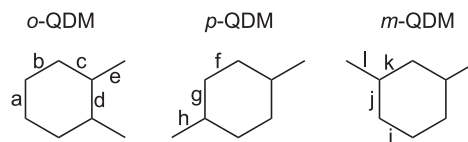
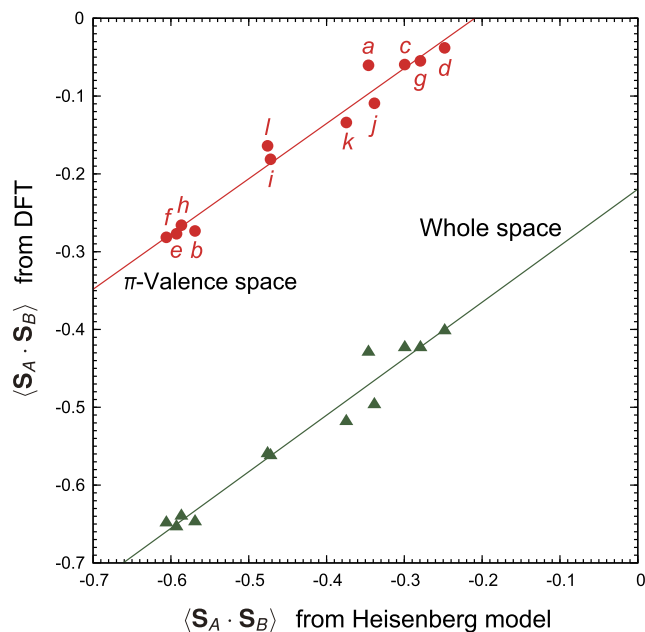


FIG. 2. Carbon skeletons for *o*-, *p*-, and *m*-QDMs and labels of bonds.



**FIG. 3.** Correlation of spin correlation functions for  $\sigma$ -,  $p$ -, and  $m$ -QDMs obtained from the DFT [B3LYP/6-31G(d,p)] and Heisenberg spin Hamiltonian model. Spin correlation functions from the DFT were evaluated in the occupied  $\pi$ -valence orbital space (" $\pi$ -Valence space") and in the whole of the occupied orbital space ("Whole space"). Corresponding labels of bonds shown in Fig. 2 are included.

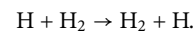
Computational results obtained from the DFT are plotted about the values from the Heisenberg model (horizontal axis) in Fig. 3. In the limit of fully singlet-coupled (purely covalent) bonds, the spin correlation function takes the value of  $-3/4 = -0.75$ . Conversely, in the limit of fully triplet-coupled bonds, it takes the value of  $1/4 = 0.25$ . The spin correlation functions shown are negative, indicating that bonds are surely formed. In addition, the results of the three models correlate very well with each other, suggesting that the bond characteristics of the molecules are very similar in all the models. The absolute values on the  $\pi$ -valence space are about half of the values in the Heisenberg model, which is attributed to the fact that a chemical bond described with a single Slater determinant typically contains ionic bond characters as discussed in Sec. III. By adding the  $\sigma$ -bond contribution, the DFT results for the whole orbital space are shifted by about  $-3/8$ . The resulting values are closer to those of the Heisenberg model.

The electronic structures of QDMs and  $\pi$ -conjugated systems incorporating a QDM moiety are usually understood as resonance hybrids of quinoidal Kekulé and diradical structures.<sup>45,46</sup> The absolute values of computed spin correlation functions are larger for the bonds  $b$ ,  $e$  in  $\sigma$ -QDM and for  $f$ ,  $h$  in  $p$ -QDM, corresponding to a double bond in this position. Thus, the contribution from the quinoidal Kekulé structure is significant. On the other hand, for the triplet  $m$ -QDM, the moderate values in the correlation functions show that the occurrence of bond alternation is unlikely.

## B. Spin correlations in chemical reaction processes

### 1. Hydrogen exchange reaction in $H_3$

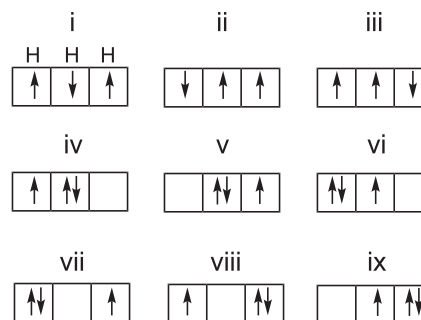
As a simple model, hydrogen exchange reaction is considered.



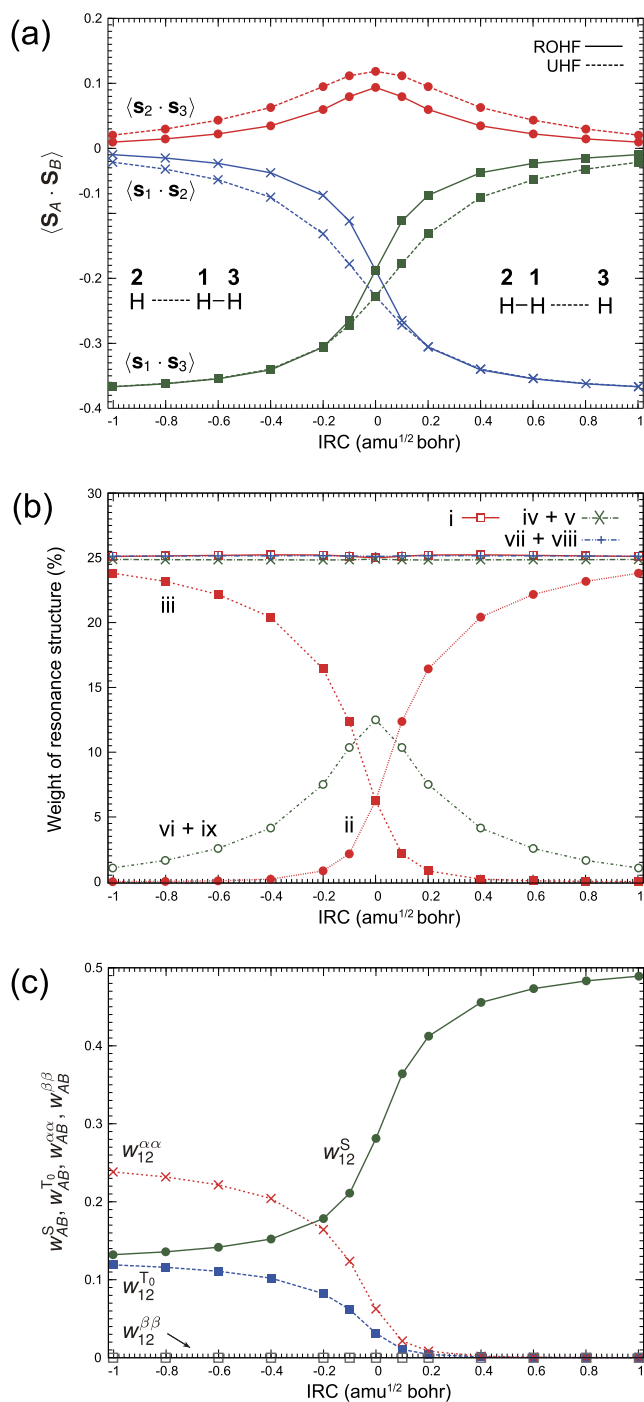
For the electronic structure calculations, we used the minimal STO-3G basis set for simplicity. Geometry optimization was performed using unrestricted Hartree-Fock (UHF) to compute the intrinsic reaction coordinate (IRC). Then, the spin correlation functions were calculated with UHF and with restricted open-shell Hartree-Fock (ROHF) along the IRC. At the same time, weights of resonance structures were calculated with ROHF to eliminate the effects of spin-contamination. All the patterns of occupancies of atomic orbitals that can be identified as resonance structures for this system are shown in Fig. 4. We note that the direct contributions of ionic-type structures (iv–ix) to spin correlation functions are zero.

The results are shown in Fig. 5. The UHF and ROHF results resemble each other, as illustrated in Fig. 5(a), indicating that the spin-contamination does not affect the qualitative discussion here. When the distance between H atoms labeled as 1 and 3 becomes large,  $\langle S_1 \cdot S_3 \rangle$  approaches zero. This result can be explained by the fact that weights of the structures (i) and (ii) are both 25% at the dissociated limit as shown in Fig. 5(b). In other words, the contributions from these two resonance structures cancel each other, and the corresponding spin correlation functions become zero for the non-bonding pair at the dissociation limit. The behavior is consistent with our intuition. On the other hand,  $\langle S_1 \cdot S_2 \rangle$  asymptotically approaches  $-3/8$ , the typical value of a single bond.

We found a maximum of  $\langle S_2 \cdot S_3 \rangle$  at the transition state (TS; IRC = 0). We can see from Fig. 5(b) that the sum of the weights of ionic type structures (vi) and (ix) takes the maximum value at the TS. On the contrary, the sum of the weights of structures (ii) and (iii) significantly reduces at the TS. The configurations corresponding to these two structures contribute negatively, and a reduction in their contribution causes an increase in  $\langle S_2 \cdot S_3 \rangle$ . Note that the weight of the resonance structure (i) is constant at  $\sim 25\%$ . To summarize, the maximum of  $\langle S_2 \cdot S_3 \rangle$  at the TS is not due to an increase in contribution from structure (i), but it is due to a decrease in contribution those from structures (ii) and (iii).



**FIG. 4.** All the patterns of the occupancies of the atomic orbitals constructing the wave function in the  $H_3$  system.



**FIG. 5.** (a) Changes in spin correlation functions calculated by ROHF (solid lines) and by UHF (dashed lines) with STO-3G. (b) Changes in weights of resonance structures represented in Fig. 4 calculated with ROHF/STO-3G. (c) Changes in contributions from *local singlet* and *local triplet* ( $\langle S_2 \rangle = 0, \pm 1$  types) states at atomic sites 1 and 2 [see (a) for the numbering] calculated with ROHF/STO-3G, along the IRC of hydrogen exchange reaction in the H<sub>3</sub> system.

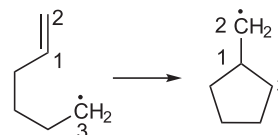
We show the changes in contributions from the *local singlet* and *local triplet* states in Fig. 5(c). Note that, unlike the resonance structure weights shown in Fig. 5(b), their sum is not normalized. Alternatively, the result obtained by summing over them multiplied with the proper constants is  $\langle S_1 \cdot S_2 \rangle$ , as shown in Eq. (57). We find  $w_{12}^S$ , whose relative magnitude can be considered as an index of the bonding character, it increases along with the bond formation. On the other hand,  $w_{12}^{T_0}$  and  $w_{12}^{\alpha\alpha}$ , which are related to the antibonding character, decrease. The interpretation of these behaviors is consistent with and complementary to the above discussion. The weight  $w_{12}^{\beta\beta}$  is constantly zero because there is only a single  $\beta$ -electron in the system.

## 2. Intramolecular radical cyclization of 5-hexenyl radical

As another example, we consider the behavior of spin correlation functions in the process of intramolecular radical cyclization of 5-hexenyl radical<sup>47</sup> shown in Fig. 6. The chemical process of this reaction is similar to the hydrogen exchange reaction. We used UB3LYP/6-31G(d,p) for the electronic structure calculations.

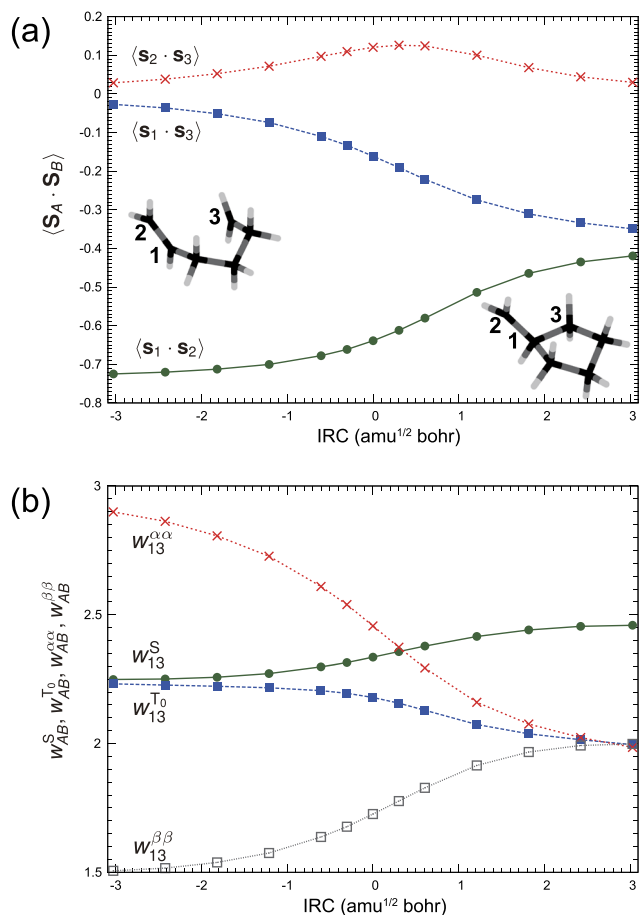
In addition to using the extended basis set, the behavior of spin correlation will be affected by electrons in the space other than the valence orbitals. However, numerical results suggested that the main features discussed in Subsection V B 1 remain almost the same for this case, as shown in Fig. 7(a). The spin correlation function  $\langle S_1 \cdot S_3 \rangle$  takes a value almost equal to 0 for the two dissociated atomic sites and approaches around  $-3/8$  along with the bond formation. At the same time,  $\langle S_1 \cdot S_2 \rangle$  behaves in the opposite manner. A double bond is formed between atomic sites 1 and 2 at the reactant state. The spin coupling is essentially proportional to the bond order and contributes additively. Hence, it takes a value close to  $-3/4$ , which is twice the typical value for the single-bond case. We find the maximum of  $\langle S_2 \cdot S_3 \rangle$  around the TS such as in the case of the hydrogen exchange reaction.

As shown in Fig. 7(b), essentially the same discussion can be applied to the behaviors of  $w_{13}^S$ ,  $w_{13}^{T_0}$ , and  $w_{13}^{\alpha\alpha}$  as the case of the hydrogen exchange reaction though the absolute values are larger. The rise of  $w_{13}^{\beta\beta}$  is due to the formation of the  $\sigma$ -bonds adjacent to the bonds between atomic sites 1 and 3. The larger absolute values in the contributions are because the carbon atoms are focused on, which have more atomic orbitals, described with the extended basis functions. Again, the sum over all of them multiplied with the proper constants is  $\langle S_1 \cdot S_3 \rangle$ . As mentioned earlier, the relative changes as the reaction proceeds are more critical.

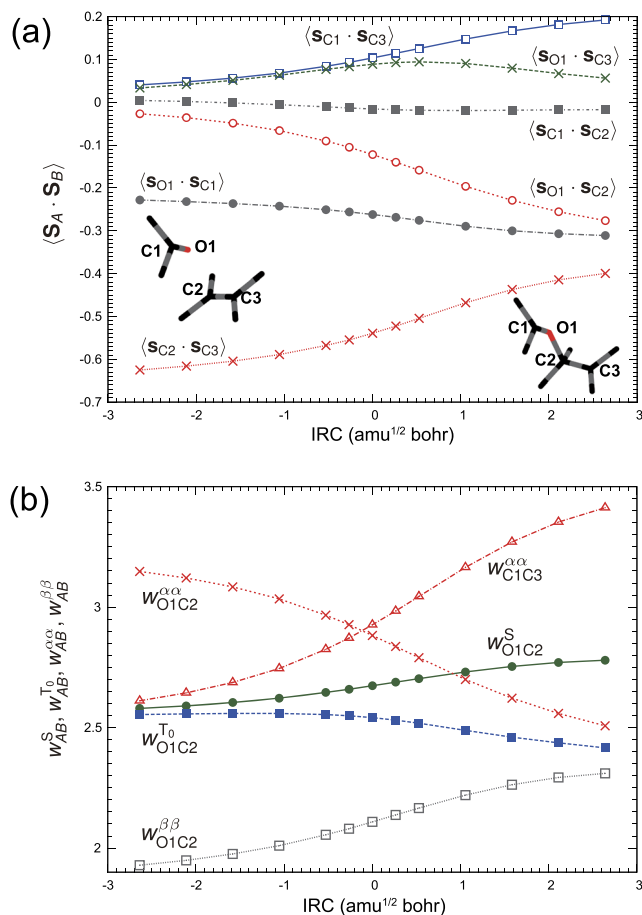


**FIG. 6.** Intramolecular radical cyclization of 5-hexenyl radical and numbering of the atomic sites.





**FIG. 7.** (a) Changes in spin correlation functions (b) Changes in contributions from *local singlet* and *local triplet* ( $\langle S_z \rangle = 0, \pm 1$  types) states at atomic sites 1 and 3 (see Fig. 6 for the numbering). Calculated with UB3LYP/6-31G(d,p) along the IRC of the intramolecular radical cyclization of 5-hexenyl radical.

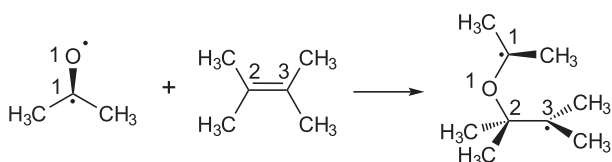


**FIG. 9.** (a) Changes in spin correlation functions. (b) Changes in contributions from *local singlet* and *local triplet* ( $\langle S_z \rangle = 0, \pm 1$  types) states between atomic sites O1 and C2 and between C1 and C3 (see Fig. 8 for the numbering). Calculated with UB3LYP/6-31G(d,p) along the IRC of the formation reaction of preoxetane from dimethyl ketone in the triplet state and tetramethylethylene.

### 3. Formation of preoxetane from dimethyl ketone in the triplet state and tetramethylethylene

The process of formation of preoxetane from triplet dimethyl ketone and tetramethylethylene (Fig. 8) is discussed. This photochemical reaction is known as the initial process of the Paternò-Büch reaction.<sup>48,49</sup>

Spin correlation functions calculated with UB3LYP/6-31G(d,p) for this system are shown in Fig. 9(a). The observed behaviors



**FIG. 8.** The process of formation of preoxetane from triplet dimethyl ketone and tetramethylethylene (the initial process of the Paternò-Büch reaction) and numbering of the atomic sites.

of some spin correlations were also similar to the cases of the hydrogen exchange reaction in the  $\text{H}_3$  system and intramolecular radical cyclization of 5-hexenyl radical; we can see the maximum of  $\langle \mathbf{s}_{O1} \cdot \mathbf{s}_{C3} \rangle$  around the TS,  $\langle \mathbf{s}_{O1} \cdot \mathbf{s}_{C2} \rangle$  decreases and  $\langle \mathbf{s}_{C2} \cdot \mathbf{s}_{C3} \rangle$  increases along with the O1–C2 bond formation and the dissociation of the C2–C3  $\pi$ -bond. As can be expected, the changes of  $\langle \mathbf{s}_{C1} \cdot \mathbf{s}_{C2} \rangle$  and  $\langle \mathbf{s}_{O1} \cdot \mathbf{s}_{C1} \rangle$  were relatively small. In contrast to three-center cases discussed so far, we found the rise of  $\langle \mathbf{s}_{C1} \cdot \mathbf{s}_{C3} \rangle$  along with the reaction between the atomic sites C1 and C3 separated by two atoms. The rise of  $\langle \mathbf{s}_{C1} \cdot \mathbf{s}_{C3} \rangle$  is attributed to the increasing contribution of the *local triplet* ( $\langle S_z \rangle = 1$  type) coupling on C1 and C3 based on the information from Fig. 9(b). This behavior is also confirmed from the spin-density distribution, where the unpaired electrons are primarily distributed around C1 and C3 positions. The behaviors of  $w_{O1C2}^S$ ,  $w_{O1C2}^{T_0}$ ,  $w_{O1C2}^{\alpha\alpha}$ , and  $w_{O1C2}^{\beta\beta}$  were very similar to those of the corresponding weights in the case of the intramolecular radical cyclization.

Finally, we analyzed the open-shell singlet state of the preoxetane product. We used the broken-symmetry (UB3LYP) method at the geometry optimized in the triplet state. The result was  $w_{\text{C1C3}}^{\text{S}} = 2.172$ ,  $w_{\text{C1C3}}^{\text{T}_0} = 2.171$ ,  $w_{\text{C1C3}}^{\alpha\alpha} = 1.721$ , and  $w_{\text{C1C3}}^{\beta\beta} = 1.812$ . Interestingly, this diradical was characterized by equally contributing  $w_{\text{C1C3}}^{\text{S}}$  and  $w_{\text{C1C3}}^{\text{T}_0}$ . To understand the situation, it is worth recalling the behavior of  $\text{H}_2$ . For the equilibrium geometry, the covalent bond is characterized only by the contribution from the *local singlet* state,  $(w_{12}^{\text{S}}, w_{12}^{\text{T}_0}, w_{12}^{\alpha\alpha}, w_{12}^{\beta\beta}) = (0.5, 0, 0, 0)$ . For the dissociated  $\text{H}_2$ , the electronic structure is characterized by the equally mixed singlet- and triplet ( $\langle S_z \rangle = 0$  type)-couplings, namely,  $(0.5, 0.5, 0, 0)$ . The same applies to the preoxetane product, that is, the diradical is characterized by equal mixing.

## VI. CONCLUDING REMARKS

This paper introduced the operators for the correlation of localized spins that enable us to extract the local character of electronic structures such as singlet- and triplet-couplings. Using the second quantized formalism for nonorthogonal orbitals, we can clarify the formal relationship between the correlation of localized spins and the weights of resonance structures. A detailed analysis of several reactions confirms that the spin correlations and the weights of the resonance structures change appropriately as the reaction proceeds, in perfect agreement with our intuition.

## SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the Cartesian coordinates of selected species.

## ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant Nos. JP20J23328, JP17H03009, and JP20H05839. Theoretical computations were partly performed at the Research Center for Computational Science, Okazaki, Japan.

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

## Author Contributions

**Kaho Nakatani:** Conceptualization (equal); Funding acquisition (equal); Investigation (lead); Writing – original draft (equal). **Masahiro Higashi:** Funding acquisition (equal); Investigation (supporting); Supervision (equal). **Hirofumi Sato:** Conceptualization (equal); Funding acquisition (equal); Investigation (supporting); Project administration (equal); Supervision (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#). Other data are available from the corresponding author upon reasonable request.

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