

# Electronic Supplementary Information for “Maximum Bonding Fragment Orbitals for Deciphering Complex Chemical Interactions”

Yang Wang<sup>\*,†,‡,¶</sup>

<sup>†</sup>*Departamento de Química, Módulo 13, Universidad Autónoma de Madrid, 28049 Madrid,  
Spain*

<sup>‡</sup>*Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma  
de Madrid, 28049 Madrid, Spain*

<sup>¶</sup>*School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu  
225002, China*

E-mail: yang.wang@uam.es

# Contents

<b>1</b>	<b>Proof that bond order matrices in orthonormal basis are positive semidefinite Hermitian</b>	<b>S3</b>
<b>2</b>	<b>Derivation of density matrix in the MBFO basis</b>	<b>S4</b>
2.1	Proof that the intrafragmental blocks of density matrix in the MBFO basis are diagonal . . . . .	S4
2.2	Separation of the density submatrices associated with the bonding and the nonbonding MBFOs . . . . .	S6
2.3	Density matrix $\bar{\mathbf{D}}$ in the nonbonding MBFO basis . . . . .	S8
2.4	Density matrix $\tilde{\mathbf{D}}$ in the bonding MBFO basis . . . . .	S9
2.4.1	Separation of nondegenerate and degenerate groups . . . . .	S9
2.4.2	Diagonalization of $\tilde{\mathbf{D}}_{AB}^{g_k}$ and $\tilde{\mathbf{D}}_{BA}^{g_k}$ . . . . .	S12
2.4.3	Final form of $\tilde{\mathbf{D}}$ . . . . .	S13
<b>3</b>	<b>Determination of MBO coefficients</b>	<b>S15</b>
<b>4</b>	<b>Derivation of the expressions of MBO bond energy</b>	<b>S17</b>
<b>5</b>	<b>MBFO analysis for H-bond complexes at the M06/def2-TZVPP level</b>	<b>S19</b>
<b>6</b>	<b>Orbital interaction diagrams for MgCp<sub>2</sub> and BaCp<sub>2</sub></b>	<b>S20</b>
<b>7</b>	<b>Orbital deformation for Cp<sup>-</sup> rings in MCp<sub>2</sub> complex with respect to the isolated Cp<sup>-</sup> rings</b>	<b>S21</b>
	<b>References</b>	<b>S22</b>

# 1 Proof that bond order matrices in orthonormal basis are positive semidefinite Hermitian

Firstly, it is easy to demonstrate that bond order matrices are Hermitian. Since the density matrix  $\mathbf{D}$  is Hermitian,<sup>1</sup> its interfragmental blocks have the following relationships:  $\mathbf{D}_{\mathcal{A}\mathcal{B}}^\dagger = \mathbf{D}_{\mathcal{B}\mathcal{A}}$  and  $\mathbf{D}_{\mathcal{B}\mathcal{A}}^\dagger = \mathbf{D}_{\mathcal{A}\mathcal{B}}$ . Then, from the definition of bond matrix  $\mathbf{B}_{\mathcal{A}\mathcal{B}}$  given in the manuscript, we know that  $\mathbf{B}_{\mathcal{A}\mathcal{B}}^\dagger = \mathbf{D}_{\mathcal{B}\mathcal{A}}^\dagger \mathbf{D}_{\mathcal{A}\mathcal{B}}^\dagger = \mathbf{D}_{\mathcal{A}\mathcal{B}} \mathbf{D}_{\mathcal{B}\mathcal{A}} = \mathbf{B}_{\mathcal{A}\mathcal{B}}$ , and thus  $\mathbf{B}_{\mathcal{A}\mathcal{B}}$  is Hermitian.

Now, we prove that  $\mathbf{B}_{\mathcal{A}\mathcal{B}}$  and  $\mathbf{B}_{\mathcal{B}\mathcal{A}}$  are positive semidefinite matrices. Suppose  $\mathbf{B}_{\mathcal{A}\mathcal{B}}$  is an  $N_{\mathcal{A}} \times N_{\mathcal{A}}$  matrix. Then, for any given nonzero column vector  $\vec{v}$  in  $\mathbb{C}^{N_{\mathcal{A}}}$ , we have

$$\vec{v}^\dagger \mathbf{B}_{\mathcal{A}\mathcal{B}} \vec{v} = \vec{v}^\dagger (\mathbf{D}_{\mathcal{A}\mathcal{B}} \mathbf{D}_{\mathcal{B}\mathcal{A}}) \vec{v} = \vec{v}^\dagger (\mathbf{D}_{\mathcal{A}\mathcal{B}} \mathbf{D}_{\mathcal{A}\mathcal{B}}^\dagger) \vec{v} = (\mathbf{D}_{\mathcal{A}\mathcal{B}}^\dagger \vec{v})^\dagger (\mathbf{D}_{\mathcal{A}\mathcal{B}}^\dagger \vec{v}).$$

By defining a new vector  $\vec{w} \equiv \mathbf{D}_{\mathcal{A}\mathcal{B}}^\dagger \vec{v}$ , we obtain  $\vec{v}^\dagger \mathbf{B}_{\mathcal{A}\mathcal{B}} \vec{v} = \vec{w}^\dagger \vec{w} = \|\vec{w}\|^2 \geq 0$ . Therefore,  $\mathbf{B}_{\mathcal{A}\mathcal{B}}$  is positive semidefinite by definition. In the similar way, we can prove that  $\mathbf{B}_{\mathcal{B}\mathcal{A}}$  is also positive semidefinite Hermitian.

We should bear in mind that so far all discussions are based on orthonormal basis functions. In a non-orthonormal basis, however, the Mayer bond order<sup>2-4</sup> between two fragments should be defined in terms of *population matrix*  $\mathbf{P}$ , instead of density matrix  $\mathbf{D}$ :

$$B_{\mathcal{A}\mathcal{B}}^{\text{non-orth}} = \sum_{\mu \in \mathcal{A}} \sum_{\nu \in \mathcal{B}} P_{\mu\nu} P_{\nu\mu}, \quad (\text{S1})$$

where the population matrix is defined as the product of the density matrix and the overlap matrix, i.e.,  $\mathbf{P} \equiv \mathbf{D}\mathbf{S}$ .<sup>2-4</sup> As  $\mathbf{S}$  is not the identity in a non-orthonormal basis,  $\mathbf{P}$  is not Hermitian. Similarly, we can define the bond order matrix between two fragments in a non-orthonormal basis, as

$$\mathbf{B}_{\mathcal{A}\mathcal{B}}^{\text{non-orth}} \equiv \mathbf{P}_{\mathcal{A}\mathcal{B}} \mathbf{P}_{\mathcal{B}\mathcal{A}}, \quad (\text{S2})$$

$$\mathbf{B}_{\mathcal{B}\mathcal{A}}^{\text{non-orth}} \equiv \mathbf{P}_{\mathcal{B}\mathcal{A}} \mathbf{P}_{\mathcal{A}\mathcal{B}}, \quad (\text{S3})$$

where the interfragmental blocks  $\mathbf{P}_{\mathcal{A}\mathcal{B}}$  and  $\mathbf{P}_{\mathcal{B}\mathcal{A}}$  are extracted from the population matrix  $\mathbf{P}$ . Since  $\mathbf{P}$  is not Hermitian, it is easy to show that  $\mathbf{B}_{\mathcal{A}\mathcal{B}}^{\text{non-orth}}$  and  $\mathbf{B}_{\mathcal{B}\mathcal{A}}^{\text{non-orth}}$  are not Hermitian either, and thus not necessarily diagonalizable.

## 2 Derivation of density matrix in the MBFO basis

Here, we will derive the final form of the density matrix in the MBFO basis, as denoted by  $\mathbf{D}'$ . The derivation is outlined in the following. We first prove that the intrafragmental blocks,  $\mathbf{D}'_{AA}$  and  $\mathbf{D}'_{BB}$ , are both diagonal. Then, we prove that  $\mathbf{D}'$  can be separated into two submatrices associated with the bonding and the nonbonding MBFOs,  $\tilde{\mathbf{D}}$  and  $\bar{\mathbf{D}}$ . Finally, we show that the nonbonding submatrix  $\bar{\mathbf{D}}$  is a diagonal matrix with entries being either 2 or 0, while the bonding submatrix  $\tilde{\mathbf{D}}$  has a characteristic form as given by eqns (8)–(10) in the manuscript.

### 2.1 Proof that the intrafragmental blocks of density matrix in the MBFO basis are diagonal

We first derive eqn (4) in the manuscript. Taking the total density matrix  $\mathbf{D}$  of a closed-shell system, we expand the idempotency equation,  $\mathbf{D}^2 = 2\mathbf{D}$ ,<sup>5</sup> in terms of the intra- and inter-fragmental subblocks:

$$\begin{pmatrix} \mathbf{D}_{AA} & \mathbf{D}_{AB} \\ \mathbf{D}_{BA} & \mathbf{D}_{BB} \end{pmatrix}^2 = 2 \begin{pmatrix} \mathbf{D}_{AA} & \mathbf{D}_{AB} \\ \mathbf{D}_{BA} & \mathbf{D}_{BB} \end{pmatrix},$$

which leads to

$$\begin{pmatrix} \mathbf{D}_{AA}^2 + \mathbf{D}_{AB}\mathbf{D}_{BA} & \mathbf{D}_{AA}\mathbf{D}_{AB} + \mathbf{D}_{AB}\mathbf{D}_{BB} \\ \mathbf{D}_{BA}\mathbf{D}_{AA} + \mathbf{D}_{BB}\mathbf{D}_{BA} & \mathbf{D}_{BB}^2 + \mathbf{D}_{BA}\mathbf{D}_{AB} \end{pmatrix} = \begin{pmatrix} 2\mathbf{D}_{AA} & 2\mathbf{D}_{AB} \\ 2\mathbf{D}_{BA} & 2\mathbf{D}_{BB} \end{pmatrix}.$$

By comparing the diagonal blocks on both sides, we know that

$$\begin{aligned} \mathbf{D}_{AA}^2 + \mathbf{D}_{AB}\mathbf{D}_{BA} &= 2\mathbf{D}_{AA}, \\ \mathbf{D}_{BB}^2 + \mathbf{D}_{BA}\mathbf{D}_{AB} &= 2\mathbf{D}_{BB}. \end{aligned}$$

Since  $\mathbf{B}_{AB} = \mathbf{D}_{AB}\mathbf{D}_{BA}$  and  $\mathbf{B}_{BA} = \mathbf{D}_{BA}\mathbf{D}_{AB}$ , we thus obtain eqn (4) in the manuscript:

$$\begin{aligned} \mathbf{B}_{AB} &= 2\mathbf{D}_{AA} - \mathbf{D}_{AA}^2, \\ \mathbf{B}_{BA} &= 2\mathbf{D}_{BB} - \mathbf{D}_{BB}^2. \end{aligned} \tag{S4}$$

As discussed in section 2.2.1 of the manuscript, the bond matrix in the MBFO basis,  $\mathbf{B}'_{AB}$ , is obtained by diagonalizing  $\mathbf{B}_{AB}$  in the original NAO basis with a unitary matrix  $\mathbf{Q}_A$ :

$$\mathbf{B}'_{AB} = \mathbf{Q}_A^\dagger \mathbf{B}_{AB} \mathbf{Q}_A. \tag{S5}$$

To emphasize the fact that  $\mathbf{B}'_{AB}$  is already diagonal, we also denote it by  $\mathbf{\Lambda}_{AB}$ . Using eqn (S4), eqn (S5) becomes

$$\mathbf{\Lambda}_{AB} = \mathbf{Q}_A^\dagger (2\mathbf{D}_{AA} - \mathbf{D}_{AA}^2) \mathbf{Q}_A. \tag{S6}$$

Since  $\mathbf{D}_{AA}$  is Hermitian, there must exist a unitary matrix  $\mathbf{U}_A$  that diagonalizes  $\mathbf{D}_{AA}$ , as:

$$\mathbf{U}_A^\dagger \mathbf{D}_{AA} \mathbf{U}_A = \mathbf{\Lambda}_{AA}. \quad (\text{S7})$$

Thus,

$$\mathbf{D}_{AA} = \mathbf{U}_A \mathbf{\Lambda}_{AA} \mathbf{U}_A^\dagger. \quad (\text{S8})$$

Hence, the intrafragmental block of the density matrix in the MBFO basis is

$$\mathbf{D}'_{AA} = \mathbf{Q}_A^\dagger \mathbf{D}_{AA} \mathbf{Q}_A = \mathbf{V}_A^\dagger \mathbf{\Lambda}_{AA} \mathbf{V}_A, \quad (\text{S9})$$

where  $\mathbf{V}_A \equiv \mathbf{U}_A^\dagger \mathbf{Q}_A$  is a unitary matrix, for both  $\mathbf{U}_A$  and  $\mathbf{Q}_A$  are unitary.

On the other hand, by plugging eqn (S8) into eqn (S6), we get

$$\mathbf{\Lambda}_{AB} = \mathbf{V}_A^\dagger (2\mathbf{\Lambda}_{AA} - \mathbf{\Lambda}_{AA}^2) \mathbf{V}_A. \quad (\text{S10})$$

This equation indicates that  $\mathbf{\Lambda}_{AB}$  and  $(2\mathbf{\Lambda}_{AA} - \mathbf{\Lambda}_{AA}^2)$  are similar to each other and thus have the same spectrum. Since both  $\mathbf{\Lambda}_{AB}$  and  $(2\mathbf{\Lambda}_{AA} - \mathbf{\Lambda}_{AA}^2)$  are diagonal, they must have the same diagonal entries but possibly in different order. In the following, we will divide our discussion into two cases.

First, we consider the nondegenerate case, where the eigenvalues of  $\mathbf{B}_{AB}$  are all distinct, and so are the diagonal entries of  $\mathbf{\Lambda}_{AB}$  and those of  $(2\mathbf{\Lambda}_{AA} - \mathbf{\Lambda}_{AA}^2)$ . As we have seen that  $\mathbf{\Lambda}_{AB}$  and  $(2\mathbf{\Lambda}_{AA} - \mathbf{\Lambda}_{AA}^2)$  only differ in the ordering of diagonal entries which are all distinct, eqn (S10) indicates that  $\mathbf{V}_A$  is just a row-column switching matrix. As a result, from eqn (S9) we know that  $\mathbf{D}'_{AA}$  is a diagonal matrix, which is obtained by swapping certain diagonal entries of  $\mathbf{\Lambda}_{AA}$ . Therefore, we conclude that in nondegenerate cases  $\mathbf{Q}_A$  is the eigenvector matrix that diagonalizes both  $\mathbf{D}_{AA}$  and  $\mathbf{B}_{AB}$ . The intrafragmental block of the density matrix,  $\mathbf{D}_{AA}$ , is simultaneously diagonal in the MBFO basis.

Second, in the degenerate case, some eigenvalues of  $\mathbf{B}_{AB}$  are identical, and so are some of the diagonal entries of  $\mathbf{\Lambda}_{AB}$  and of  $(2\mathbf{\Lambda}_{AA} - \mathbf{\Lambda}_{AA}^2)$ . This means that not all the eigenvectors in matrix  $\mathbf{V}_A$  are unique; we can obtain different matrices  $\mathbf{V}_A$  by making arbitrary combinations of the eigenvectors associated with the same eigenvalues of  $\mathbf{B}_{AB}$ . Consequently,  $\mathbf{V}_A$  is not necessarily a row-column switching matrix, and thus not all choices of  $\mathbf{V}_A$  can make  $\mathbf{D}'_{AA}$  diagonal (see eqn (S9)). Here, we show that, by choosing  $\mathbf{Q}_A = \mathbf{U}_A$  (and thus  $\mathbf{V}_A = \mathbf{I}$ ), both  $\mathbf{D}'_{AA}$  and  $\mathbf{B}'_{AB}$  are simultaneously diagonal. According to eqns (S7) and (S9), by using the unitary transformation with  $\mathbf{U}_A$ , we diagonalize  $\mathbf{D}_{AA}$  to  $\mathbf{D}'_{AA} = \mathbf{\Lambda}_{AA}$ . Then,  $\mathbf{B}'_{AB} = 2\mathbf{D}'_{AA} - \mathbf{D}'_{AA}{}^2 = 2\mathbf{\Lambda}'_{AA} - \mathbf{\Lambda}'_{AA}{}^2$  is also diagonal. We further show that  $\mathbf{B}_{AB}$  is diagonalized to  $\mathbf{B}'_{AB}$  exactly by  $\mathbf{U}_A$ , because  $\mathbf{B}'_{AB} = 2\mathbf{\Lambda}'_{AA} - \mathbf{\Lambda}'_{AA}{}^2 = 2(\mathbf{U}_A^\dagger \mathbf{D}_{AA} \mathbf{U}_A) - (\mathbf{U}_A^\dagger \mathbf{D}_{AA} \mathbf{U}_A)^2 = \mathbf{U}_A^\dagger (2\mathbf{D}_{AA} - \mathbf{D}_{AA}^2) \mathbf{U}_A = \mathbf{U}_A^\dagger \mathbf{B}_{AB} \mathbf{U}_A$ .

Obviously, the same discussion holds for fragment  $\mathcal{B}$ . To sum up, in all cases (whether degenerate or not), we can always diagonalize first  $\mathbf{D}_{AA}$  (or  $\mathbf{D}_{BB}$ ) with a unitary matrix  $\mathbf{U}_A$  (or  $\mathbf{U}_B$ ), and then the latter must simultaneously diagonalize  $\mathbf{B}_{AB}$  (or  $\mathbf{B}_{BA}$ ).

## 2.2 Separation of the density submatrices associated with the bonding and the nonbonding MBFOs

Let's divide the whole density matrix in the full MBFO basis,  $\mathbf{D}'$ , into intra- and interfragmental blocks:

$$\mathbf{D}' = \begin{pmatrix} \mathbf{D}'_{\mathcal{A}\mathcal{A}} & \mathbf{D}'_{\mathcal{A}\mathcal{B}} \\ \mathbf{D}'_{\mathcal{B}\mathcal{A}} & \mathbf{D}'_{\mathcal{B}\mathcal{B}} \end{pmatrix}. \quad (\text{S11})$$

For the intrafragmental blocks,  $\mathbf{D}'_{\mathcal{A}\mathcal{A}}$  and  $\mathbf{D}'_{\mathcal{B}\mathcal{B}}$ , which are already diagonal (as proved in section 2.1), we divide each of them into smaller blocks in terms of the bonding and the nonbonding MBFOs:

$$\mathbf{D}'_{\mathcal{A}\mathcal{A}} = \begin{pmatrix} \Lambda_{\mathcal{A}\mathcal{A}}^{\text{bb}} & \mathbf{0} \\ \mathbf{0} & \Lambda_{\mathcal{A}\mathcal{A}}^{\text{nn}} \end{pmatrix}, \quad (\text{S12})$$

$$\mathbf{D}'_{\mathcal{B}\mathcal{B}} = \begin{pmatrix} \Lambda_{\mathcal{B}\mathcal{B}}^{\text{bb}} & \mathbf{0} \\ \mathbf{0} & \Lambda_{\mathcal{B}\mathcal{B}}^{\text{nn}} \end{pmatrix}, \quad (\text{S13})$$

where the superscripts 'b' and 'n' denote, respectively, the bonding and the nonbonding MBFOs; the symbol ' $\Lambda$ ' indicates that the referred matrix is diagonal. Likewise, the interfragmental blocks,  $\mathbf{D}'_{\mathcal{A}\mathcal{B}}$  and  $\mathbf{D}'_{\mathcal{B}\mathcal{A}}$ , can also be divided into subblocks associated with the bonding and the nonbonding MBFOs:

$$\mathbf{D}'_{\mathcal{A}\mathcal{B}} = \begin{pmatrix} \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bb}} & \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bn}} \\ \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nb}} & \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nn}} \end{pmatrix}, \quad (\text{S14})$$

$$\mathbf{D}'_{\mathcal{B}\mathcal{A}} = \begin{pmatrix} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bb}} & \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bn}} \\ \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nb}} & \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nn}} \end{pmatrix}. \quad (\text{S15})$$

Thus, the bond order matrix in the full MBFO basis is:

$$\mathbf{B}'_{\mathcal{A}\mathcal{B}} = \mathbf{D}'_{\mathcal{A}\mathcal{B}} \mathbf{D}'_{\mathcal{B}\mathcal{A}} = \begin{pmatrix} \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bb}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nb}} & \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bn}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nn}} \\ \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bb}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nb}} & \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bn}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nn}} \end{pmatrix}. \quad (\text{S16})$$

Since  $\mathbf{B}'_{\mathcal{A}\mathcal{B}}$  is already diagonal and all bond orders between the nonbonding MBFOs are zero, we have

$$\mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bb}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nb}} = \tilde{\Lambda}, \quad (\text{S17})$$

$$\mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bn}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nn}} = \mathbf{0}, \quad (\text{S18})$$

$$\mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bn}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{bn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nn}} = \mathbf{0}, \quad (\text{S19})$$

$$\mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nb}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{bb}} + \mathbf{D}'_{\mathcal{A}\mathcal{B}}^{\text{nn}} \mathbf{D}'_{\mathcal{B}\mathcal{A}}^{\text{nb}} = \mathbf{0}, \quad (\text{S20})$$

where  $\tilde{\Lambda}$  is a diagonal matrix, whose diagonal entries consist, and consist only all positive eigenvalues of  $\mathbf{B}'_{\mathcal{A}\mathcal{B}}$ .

Before proceeding with the proof, we introduce the following lemma.

**Lemma:** For any matrices  $\mathbf{A}$  and  $\mathbf{B}$  of the same size, if

$$\mathbf{A}^\dagger \mathbf{A} + \mathbf{B}^\dagger \mathbf{B} = \mathbf{0}, \quad (\text{S21})$$

then  $\mathbf{A} = \mathbf{B} = \mathbf{0}$ .

Here is the proof. As demonstrated in section 2.1, the product  $\mathbf{A}^\dagger \mathbf{A}$  is positive semidefinite Hermitian. This means that  $\mathbf{A}^\dagger \mathbf{A}$  can be diagonalized by a unitary matrix  $\mathbf{U}$  to  $\mathbf{\Lambda}_A$ , whose diagonal entries are all nonnegative. Now, we perform a unitary transformation with  $\mathbf{U}$  to both sides of eqn (S21), as follows:  $\mathbf{U}^\dagger \mathbf{A}^\dagger \mathbf{A} \mathbf{U} + \mathbf{U}^\dagger \mathbf{B}^\dagger \mathbf{B} \mathbf{U} = \mathbf{U}^\dagger \mathbf{0} \mathbf{U}$ , which leads to  $(\mathbf{B}\mathbf{U})^\dagger (\mathbf{B}\mathbf{U}) = -\mathbf{\Lambda}_A$ . As we know,  $(\mathbf{B}\mathbf{U})^\dagger (\mathbf{B}\mathbf{U})$  is also positive semidefinite, and thus the left-hand side has all nonnegative diagonal entries. On the other hand, the right-hand side has all nonpositive diagonal entries, for all diagonal entries of  $\mathbf{\Lambda}_A$  are nonnegative. Consequently, the only possibility is that  $(\mathbf{B}\mathbf{U})^\dagger (\mathbf{B}\mathbf{U}) = \mathbf{\Lambda}_A = \mathbf{0}$ . Hence,  $\mathbf{A}^\dagger \mathbf{A} = \mathbf{U} \mathbf{\Lambda}_A \mathbf{U}^\dagger = \mathbf{0}$ . If we suppose  $(\mathbf{A})_{ij} = a_{ij}$ , then  $(\mathbf{A}^\dagger \mathbf{A})_{ij} = \sum_k a_{ik}^* a_{jk} = 0$ . Just by looking at the diagonal entries,  $(\mathbf{A}^\dagger \mathbf{A})_{ii} = \sum_k |a_{ik}|^2 = 0$ , we know that  $a_{ik} = 0$  for all  $(i, k)$ , i.e.,  $\mathbf{A} = \mathbf{0}$ . Following the same procedure, we can prove that  $\mathbf{B} = \mathbf{0}$ . Q.E.D.

By applying this lemma to eqn (S18), and noticing that  $\mathbf{D}'_{AB}{}^{nb} = (\mathbf{D}'_{BA})^{bn\dagger}$  and  $\mathbf{D}'_{AB}{}^{nn} = (\mathbf{D}'_{BA})^{nn\dagger}$ , we obtain

$$\mathbf{D}'_{AB}{}^{nb} = \mathbf{D}'_{BA}{}^{bn} = \mathbf{0}, \quad (\text{S22})$$

$$\mathbf{D}'_{AB}{}^{nn} = \mathbf{D}'_{BA}{}^{nn} = \mathbf{0}. \quad (\text{S23})$$

By expanding  $\mathbf{B}'_{BA}$  in the same manner as we expand  $\mathbf{B}'_{AB}$  in eqn (S16), we can similarly prove that

$$\mathbf{D}'_{AB}{}^{bn} = \mathbf{D}'_{BA}{}^{nb} = \mathbf{0}. \quad (\text{S24})$$

As a result, according to eqns (S14) and (S15), the interfragmental blocks of the density matrix in the full MBFO basis become

$$\mathbf{D}'_{AB} = \begin{pmatrix} \mathbf{D}'_{AB}{}^{bb} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad (\text{S25})$$

$$\mathbf{D}'_{BA} = \begin{pmatrix} \mathbf{D}'_{BA}{}^{bb} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}. \quad (\text{S26})$$

Therefore, the density matrix in the full MBFO basis is

$$\mathbf{D}' = \begin{pmatrix} \mathbf{D}'_{AA} & \mathbf{D}'_{AB} \\ \mathbf{D}'_{BA} & \mathbf{D}'_{BB} \end{pmatrix} = \begin{pmatrix} \mathbf{\Lambda}_{AA}{}^{bb} & \mathbf{0} & \mathbf{D}'_{AB}{}^{bb} & \mathbf{0} \\ \mathbf{0} & \mathbf{\Lambda}_{AA}{}^{nn} & \mathbf{0} & \mathbf{0} \\ \mathbf{D}'_{BA}{}^{bb} & \mathbf{0} & \mathbf{\Lambda}_{BB}{}^{bb} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{\Lambda}_{BB}{}^{nn} \end{pmatrix}. \quad (\text{S27})$$

By rearranging the subblocks in the order of the bonding MBFOs followed by the nonbonding

ones, we finally obtain:

$$\mathbf{D}' = \begin{pmatrix} \tilde{\mathbf{D}} & \mathbf{0} \\ \mathbf{0} & \bar{\mathbf{D}} \end{pmatrix}, \quad (\text{S28})$$

where the submatrix associated with the bonding MBFOs,  $\tilde{\mathbf{D}}$ , is defined as

$$\tilde{\mathbf{D}} \equiv \begin{pmatrix} \Lambda_{AA}^{\text{bb}} & \mathbf{D}_{AB}^{\text{bb}} \\ \mathbf{D}_{BA}^{\text{bb}} & \Lambda_{BB}^{\text{bb}} \end{pmatrix}, \quad (\text{S29})$$

and that associated with the nonbonding MBFOs,  $\bar{\mathbf{D}}$ , is defined as

$$\bar{\mathbf{D}} \equiv \begin{pmatrix} \Lambda_{AA}^{\text{nn}} & \mathbf{0} \\ \mathbf{0} & \Lambda_{BB}^{\text{nn}} \end{pmatrix}. \quad (\text{S30})$$

Furthermore, according to eqns (S16)–(S20), the whole bond order matrix in the full MBFO basis is reduced to

$$\mathbf{B}'_{AB} = \begin{pmatrix} \mathbf{D}_{AB}^{\text{bb}} \mathbf{D}_{BA}^{\text{bb}} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} = \begin{pmatrix} \tilde{\Lambda} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad (\text{S31})$$

indicating that all positive eigenvalues of the bond order matrix of the whole system can be fully derived from the density submatrix in terms of the bonding MBFOs. We can thus define the bond order matrix in terms of only the bonding MBFOs as

$$\tilde{\mathbf{B}}_{AB} \equiv \mathbf{D}_{AB}^{\text{bb}} \mathbf{D}_{BA}^{\text{bb}} = \tilde{\Lambda}, \quad (\text{S32})$$

so that

$$\mathbf{B}'_{AB} = \begin{pmatrix} \tilde{\mathbf{B}}_{AB} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}. \quad (\text{S33})$$

Similar relationship can be obtained for  $\mathbf{B}'_{BA}$  and  $\tilde{\mathbf{B}}_{BA}$ . Moreover, since there is a one-to-one correspondence between all positive eigenvalues of  $\mathbf{B}_{AB}$  and those of  $\mathbf{B}_{BA}$ ,  $\tilde{\mathbf{B}}_{AB}$  and  $\tilde{\mathbf{B}}_{BA}$  must be the same diagonal matrix:

$$\tilde{\mathbf{B}}_{AB} = \tilde{\mathbf{B}}_{BA} = \tilde{\Lambda}. \quad (\text{S34})$$

### 2.3 Density matrix $\bar{\mathbf{D}}$ in the nonbonding MBFO basis

Using eqn (S28), it is easy to verify that the idempotent property also holds for  $\tilde{\mathbf{D}}$  and  $\bar{\mathbf{D}}$ :

$$2\tilde{\mathbf{D}} = \tilde{\mathbf{D}}^2, \quad (\text{S35})$$

$$2\bar{\mathbf{D}} = \bar{\mathbf{D}}^2. \quad (\text{S36})$$

On the other hand, since  $\bar{\mathbf{D}}$  is a diagonal matrix (see eqn (S30)), let  $\{\bar{\lambda}_i\}$  denotes its diagonal entries. Then, from eqn (S36) we get  $\bar{\lambda}_i(\bar{\lambda}_i - 2) = 0$ , which means that either  $\bar{\lambda}_i = 0$  or

$\bar{\lambda}_i = 2$ , and thus proves that the diagonal matrix  $\tilde{\mathbf{D}}$  only have entries of either 2 or 0.

## 2.4 Density matrix $\tilde{\mathbf{D}}$ in the bonding MBFO basis

### 2.4.1 Separation of nondegenerate and degenerate groups

Among all  $2m$  bonding MBFOs, we suppose that there are  $\gamma$  groups of degenerate bonding MBFOs, each of which is associated with  $m_k^g$  identical eigenvalues of  $\mathbf{B}_{A\mathcal{B}}$  ( $m_k^g \geq 2$  and  $k = 1, 2, \dots, \gamma$ ). We put all the rest  $m^h$  nondegenerate bonding MBFOs together, which are associated with  $m^h$  eigenvalues that are all distinct from one another. For convenience, we arrange all bonding MBFO basis functions in the following order: the nondegenerate group and the degenerate groups of bonding MBFOs of  $\mathcal{A}$ , followed by the nondegenerate group and the degenerate groups of bonding MBFOs of  $\mathcal{B}$ . Accordingly, the bond order matrix in this basis, which is diagonalized, takes the following form:

$$\tilde{\mathbf{B}}_{A\mathcal{B}} = \tilde{\mathbf{B}}_{\mathcal{B}A} = \begin{pmatrix} \tilde{\Lambda}_{A\mathcal{B}}^h & & & & \\ & \tilde{\Lambda}_{A\mathcal{B}}^{g_1} & & & \\ & & \tilde{\Lambda}_{A\mathcal{B}}^{g_2} & & \\ & & & \ddots & \\ & & & & \tilde{\Lambda}_{A\mathcal{B}}^{g_\gamma} \end{pmatrix} = \begin{pmatrix} \tilde{\Lambda}_{A\mathcal{B}}^h & & & & \\ & B_1^g \mathbf{I} & & & \\ & & B_2^g \mathbf{I} & & \\ & & & \ddots & \\ & & & & B_\gamma^g \mathbf{I} \end{pmatrix} \quad (\text{S37})$$

where  $B_k^g$  is the eigenvalue (bond order) corresponding to the  $k$ th degenerate group.

As proved in section 2.1, all intrafragmental blocks of the density matrix in the MBFO basis are diagonal, and thus so are the intrafragmental blocks of  $\tilde{\mathbf{D}}$ , which take the following form:

$$\tilde{\mathbf{D}}_{A\mathcal{A}} = \begin{pmatrix} \tilde{\Lambda}_{A\mathcal{A}}^h & & & & \\ & \tilde{\Lambda}_{A\mathcal{A}}^{g_1} & & & \\ & & \tilde{\Lambda}_{A\mathcal{A}}^{g_2} & & \\ & & & \ddots & \\ & & & & \tilde{\Lambda}_{A\mathcal{A}}^{g_\gamma} \end{pmatrix} \quad (\text{S38})$$

and

$$\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{B}} = \begin{pmatrix} \tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^h & & & & \\ & \tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_1} & & & \\ & & \tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_2} & & \\ & & & \ddots & \\ & & & & \tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_\gamma} \end{pmatrix} \quad (\text{S39})$$

where the symbol  $\tilde{\Lambda}$  denotes a diagonal matrix; the superscripts  $h$  and  $g_k$  indicate, respectively, the nondegenerate group and the  $k$ th degenerate group of bonding MBFOs.

For the diagonal blocks corresponding to degenerate groups,  $\tilde{\Lambda}_{A\mathcal{A}}^{g_k}$  and  $\tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_k}$ , they have identical diagonal entries, which can be proved as follows. According to eqns (S4) and (S28),

we know that  $\tilde{\mathbf{B}}_{\mathcal{A}\mathcal{B}} = 2\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{A}} - \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{A}}^2$ . Then, from eqns (S37) and (S38), we get

$$B_k^g \mathbf{I} = 2\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^{g_k} - (\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^{g_k})^2. \quad (\text{S40})$$

This equation infers that all diagonal entries of  $\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^{g_k}$  are the same and we thus have

$$\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^{g_k} = n_{\mathcal{A}}^{g_k} \mathbf{I}, \quad (\text{S41})$$

where  $n_{\mathcal{A}}^{g_k}$  is constant for the same degenerate group  $g_k$ , and has the meaning of the occupancy of an MBFO. Similar results can be obtained for  $\mathcal{B}$ 's degenerate bonding MBFOs:

$$\tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_k} = n_{\mathcal{B}}^{g_k} \mathbf{I}. \quad (\text{S42})$$

Now, let's examine the interfragmental blocks,  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$ . We first demonstrate that both matrices are unitarily diagonalizable. According to eqn (S34),  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}} = \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$ , namely,  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$  commute with each other. Since  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}} = \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^\dagger$ , it is evident that  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^\dagger = \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^\dagger\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$ , meaning that  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$  are normal matrices,<sup>6</sup> and thus are diagonalizable by a unitary matrix.

Furthermore, we show that  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$  are both invertible. For the convenience of discussion, we rewrite eqn (S34) as two separate equations:

$$\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}} = \tilde{\Lambda}, \quad (\text{S43})$$

$$\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}} = \tilde{\Lambda}. \quad (\text{S44})$$

Since the diagonal entries of the diagonal matrix  $\tilde{\Lambda}$ ,  $\{\tilde{\lambda}_i\}$ , are all positive eigenvalues associated with the bonding MBFOs, we can define  $\tilde{\Lambda}^{-1}$  and  $\tilde{\Lambda}^{-\frac{1}{2}}$  as the diagonal matrices whose diagonal entries are  $\{\tilde{\lambda}_i^{-1}\}$  and  $\{\tilde{\lambda}_i^{-\frac{1}{2}}\}$ , respectively. By left and right multiplying both sides of eqn (S43) by  $\tilde{\Lambda}^{-\frac{1}{2}}$  and using that  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}} = \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^\dagger$ , we obtain  $(\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\Lambda}^{-\frac{1}{2}})^\dagger(\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\Lambda}^{-\frac{1}{2}}) = \mathbf{I}$ , which means that  $\mathbf{U} \equiv \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\Lambda}^{-\frac{1}{2}}$  is a unitary matrix. Hence,  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}} = \mathbf{U}\tilde{\Lambda}^{\frac{1}{2}}$  is invertible, and its inverse is  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1} = \tilde{\Lambda}^{-\frac{1}{2}}\mathbf{U}^\dagger = \tilde{\Lambda}^{-\frac{1}{2}}(\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\Lambda}^{-\frac{1}{2}})^\dagger = \tilde{\Lambda}^{-1}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$ . Similarly, we can prove that  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  is invertible and its inverse is  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{-1} = \tilde{\Lambda}^{-1}\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$ .

Next, we want to prove that both  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$  commute with the diagonal matrix  $\tilde{\Lambda}$ . By right multiplying both sides of eqn (S43) by  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1}$ , we get  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}} = \tilde{\Lambda}\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1}$ . Meanwhile, we can also left multiply both sides of eqn (S44) by  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1}$  and obtain  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}} = \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1}\tilde{\Lambda}$ . Therefore, we have  $\tilde{\Lambda}\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1} = \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{-1}\tilde{\Lambda}$ . By left and right multiplying both sides by  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$ , we get  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}\tilde{\Lambda} = \tilde{\Lambda}\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}$ . In similar way, we can prove  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}\tilde{\Lambda} = \tilde{\Lambda}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$ .

Supposing that the matrix elements of  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  are denoted by  $(\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}})_{ij} = a_{ij}$ , it is easy to show that  $(\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}\tilde{\Lambda}_{\mathcal{A}\mathcal{B}})_{ij} = \lambda_j a_{ij}$  and  $(\tilde{\Lambda}_{\mathcal{A}\mathcal{B}}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}})_{ij} = \lambda_i a_{ij}$ . As  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}\tilde{\Lambda}_{\mathcal{A}\mathcal{B}} = \tilde{\Lambda}_{\mathcal{A}\mathcal{B}}\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$ , we know that  $\lambda_j a_{ij} = \lambda_i a_{ij}$  for all  $(i, j)$ . Consequently, for all  $(i, j)$  pairs with  $i \neq j$  and  $\lambda_i \neq \lambda_j$ , we must have  $a_{ij} = a_{ji} = 0$ . This indicates that the off-diagonal element of  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  vanishes if it is associated with two bonding MBFOs that correspond to distinct eigenvalues of the bond order matrix. As a result, for  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$ , the off-diagonal subblocks between two different degenerate groups,  $g_k$  and  $g_l$  ( $k \neq l$ ), and those between the nondegenerate group and any degenerate group, are all zeros. Moreover, since all corresponding eigenvalues are distinct

within the nondegenerate group, the entire nondegenerate subblock is diagonal. Therefore,  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}$  takes the following form:

$$\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}} = \begin{pmatrix} \tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^h & & & & \\ & \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_1} & & & \\ & & \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_2} & & \\ & & & \ddots & \\ & & & & \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_\gamma} \end{pmatrix}. \quad (\text{S45})$$

Likewise, it can be demonstrated that

$$\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}} = \begin{pmatrix} \tilde{\Lambda}_{\mathcal{B}\mathcal{A}}^h & & & & \\ & \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_1} & & & \\ & & \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_2} & & \\ & & & \ddots & \\ & & & & \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_\gamma} \end{pmatrix}. \quad (\text{S46})$$

Finally, by placing together the subblocks corresponding to the same degenerate or non-degenerate group in eqns (S38), (S39), (S45) and (S46), we obtain  $\tilde{\mathbf{D}}$  in the following form:

$$\tilde{\mathbf{D}} = \begin{pmatrix} \tilde{\mathbf{D}}^h & & & & \\ & \tilde{\mathbf{D}}^{g_1} & & & \\ & & \tilde{\mathbf{D}}^{g_2} & & \\ & & & \ddots & \\ & & & & \tilde{\mathbf{D}}^{g_\gamma} \end{pmatrix}, \quad (\text{S47})$$

where the subblock associated with the nondegenerate group,  $h$ , is

$$\tilde{\mathbf{D}}^h = \begin{pmatrix} \tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^h & \tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^h \\ \tilde{\Lambda}_{\mathcal{B}\mathcal{A}}^h & \tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^h \end{pmatrix} \quad (\text{S48})$$

and the subblock associated with the  $k$ th degenerate group,  $g_k$ , is

$$\tilde{\mathbf{D}}^{g_k} = \begin{pmatrix} \tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^{g_k} & \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k} \\ \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} & \tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_k} \end{pmatrix} = \begin{pmatrix} n_{\mathcal{A}}^{g_k} \mathbf{I} & \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k} \\ \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} & n_{\mathcal{B}}^{g_k} \mathbf{I} \end{pmatrix}, \quad (\text{S49})$$

where  $n_{\mathcal{A}}^{g_k}$  and  $n_{\mathcal{B}}^{g_k}$  are single numbers, corresponding to the natural occupancy of a bonding MBFO in group  $g_k$ . Note that  $\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^h$ ,  $\tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^h$ ,  $\tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^h$ ,  $\tilde{\Lambda}_{\mathcal{B}\mathcal{A}}^h$ ,  $\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^{g_k}$  and  $\tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^{g_k}$  are all diagonal matrices, while  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k}$  are not necessarily diagonal. The procedure of diagonalizing  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k}$  and  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k}$  is provided in the next subsection. In addition, eqn (S49) also indicates that all bonding MBFOs of  $\mathcal{A}$  (or of  $\mathcal{B}$ ) that are degenerate in bond order have the same occupancy.

### 2.4.2 Diagonalization of $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k}$ and $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k}$

Given a degenerate group  $g_k$  of bonding MBFOs, let's consider a unitary matrix  $\tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k}$  that transforms the  $m_k^g$  degenerate bonding MBFOs of  $\mathcal{A}$ , and a unitary matrix  $\tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k}$  that transforms the  $m_k^g$  degenerate bonding MBFOs of  $\mathcal{B}$ . Thus, the total transformation matrix for all  $2m_k^g$  bonding MBFOs of  $\mathcal{A}$  and  $\mathcal{B}$  is written as

$$\tilde{\mathbf{Q}}^{g_k} = \begin{pmatrix} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k} & \mathbf{0} \\ \mathbf{0} & \tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k} \end{pmatrix}. \quad (\text{S50})$$

Hence, according to eqns (S50) and (S49), the transformed density matrix is

$$\tilde{\mathbf{D}}^{g_{k'}} = \tilde{\mathbf{Q}}^{g_{k'}} \tilde{\mathbf{D}}^{g_k} \tilde{\mathbf{Q}}^{g_k} = \begin{pmatrix} n_{\mathcal{A}}^{g_k} \mathbf{I} & \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k \dagger} \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k} \\ \tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k \dagger} \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k} & n_{\mathcal{B}}^{g_k} \mathbf{I} \end{pmatrix}. \quad (\text{S51})$$

By comparing it with eqn (S49), we can see that the diagonal blocks of  $\tilde{\mathbf{D}}^{g_k}$  remain unaltered after the basis transformation by  $\tilde{\mathbf{Q}}^{g_k}$ .

Now, we show that the off-diagonal blocks of  $\tilde{\mathbf{D}}^{g_{k'}}$  are diagonalized if the *unitary* matrices  $\tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k}$  and  $\tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k}$  fulfill the following relationship:

$$\tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k} = \frac{1}{\sqrt{B_k^g}} \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k}. \quad (\text{S52})$$

With the transformation matrices given by this equation, the off-diagonal block  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_{k'}}$  is:

$$\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_{k'}} = \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_{k'}} \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{B}}^{g_k} = \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_{k'}} \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_k} \frac{1}{\sqrt{B_k^g}} \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k} = \frac{1}{\sqrt{B_k^g}} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_{k'}} \tilde{\mathbf{B}}_{\mathcal{A}\mathcal{B}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k}. \quad (\text{S53})$$

Notice that the bond order matrix  $\tilde{\mathbf{B}}_{\mathcal{A}\mathcal{B}}^{g_k}$ , which corresponds to the degenerate group  $g_k$ , is already diagonalized with identical diagonal elements (see eqn (S37)):

$$\tilde{\mathbf{B}}_{\mathcal{A}\mathcal{B}}^{g_k} = \tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^{g_k} = B_k^g \mathbf{I}. \quad (\text{S54})$$

Thus, from eqn (S53), we know that  $\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_{k'}}$  is diagonal with identical diagonal elements:

$$\tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_{k'}} = \sqrt{B_k^g} \mathbf{I}. \quad (\text{S55})$$

Likewise, we can show that  $\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_{k'}}$  is also diagonal with identical diagonal elements:

$$\tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_{k'}} = \tilde{\mathbf{Q}}_{\mathcal{B}}^{g_{k'}} \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k} = \left( \frac{1}{\sqrt{B_k^g}} \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k} \right)^\dagger \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_k} \tilde{\mathbf{Q}}_{\mathcal{A}}^{g_k} = \sqrt{B_k^g} \mathbf{I}. \quad (\text{S56})$$

In addition, it is easy to check that the corresponding bond order matrices,  $\tilde{\mathbf{B}}_{\mathcal{A}\mathcal{B}}^{g_{k'}}$  and  $\tilde{\mathbf{B}}_{\mathcal{B}\mathcal{A}}^{g_{k'}}$ , are unaltered after the basis transformation (cf. eqn (S54)):  $\tilde{\mathbf{B}}_{\mathcal{A}\mathcal{B}}^{g_{k'}} = \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_{k'}} \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_{k'}} = B_k^g \mathbf{I}$  and  $\tilde{\mathbf{B}}_{\mathcal{B}\mathcal{A}}^{g_{k'}} = \tilde{\mathbf{D}}_{\mathcal{B}\mathcal{A}}^{g_{k'}} \tilde{\mathbf{D}}_{\mathcal{A}\mathcal{B}}^{g_{k'}} = B_k^g \mathbf{I}$ .



equations:

$$\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}^2 + \tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^2 = 2\tilde{\Lambda}_{\mathcal{A}\mathcal{A}}, \quad (\text{S63})$$

$$\tilde{\Lambda}_{\mathcal{B}\mathcal{B}}^2 + \tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^2 = 2\tilde{\Lambda}_{\mathcal{B}\mathcal{B}}, \quad (\text{S64})$$

$$(\tilde{\Lambda}_{\mathcal{A}\mathcal{A}} + \tilde{\Lambda}_{\mathcal{B}\mathcal{B}} - 2\mathbf{I})\tilde{\Lambda}_{\mathcal{A}\mathcal{B}} = \mathbf{0}. \quad (\text{S65})$$

Since the product of two diagonal matrices is just the multiplication of their diagonal entries, eqn (S65) is thus equivalent to  $(n_i^{\mathcal{A}} + n_i^{\mathcal{B}} - 2)\sqrt{B_i} = 0$ . As  $\sqrt{B_i} > 0$  for all bonding MBFOs, we then arrive at eqn (S60):  $n_i^{\mathcal{A}} + n_i^{\mathcal{B}} = 2$ .

On the other hand, by summing up eqns (S63) and (S64), we obtain  $\tilde{\Lambda}_{\mathcal{A}}^2 + \tilde{\Lambda}_{\mathcal{B}}^2 + 2\tilde{\Lambda}_{\mathcal{A}\mathcal{B}}^2 = 2(\tilde{\Lambda}_{\mathcal{A}} + \tilde{\Lambda}_{\mathcal{B}})$ , and hence  $(n_i^{\mathcal{A}})^2 + (n_i^{\mathcal{B}})^2 + 2B_i = 2(n_i^{\mathcal{A}} + n_i^{\mathcal{B}})$ . Combining it with eqn (S60), we thus obtain eqn (S61):  $B_i = n_i^{\mathcal{A}}n_i^{\mathcal{B}}$ .

### 3 Determination of MBO coefficients

Following the discussion in the manuscript, a pair of MBFOs,  $\tilde{\theta}_i^A$  and  $\tilde{\theta}_i^B$ , form a bonding MBO and an antibonding MBO:

$$\Omega_i = a_i \tilde{\theta}_i^A + b_i \tilde{\theta}_i^B, \quad (\text{S66})$$

$$\Omega_i^* = b_i \tilde{\theta}_i^A - a_i \tilde{\theta}_i^B. \quad (\text{S67})$$

This transformation can be represented by the following matrix:

$$\tilde{\mathbf{T}} = \begin{pmatrix} \Lambda_a & \Lambda_b \\ \Lambda_b & -\Lambda_a \end{pmatrix}, \quad (\text{S68})$$

where  $\Lambda_a$  and  $\Lambda_b$  are  $m \times m$  diagonal matrices with  $(\Lambda_a)_{ii} = a_i$  and  $(\Lambda_b)_{ii} = b_i$  ( $i = 1, 2, \dots, m$ ). Since both MBFOs and MBOs are orthonormal bases, the transformation matrix  $\tilde{\mathbf{T}}$  should be unitary, which requires that  $\Lambda_a^2 + \Lambda_b^2 = \mathbf{I}$ . Accordingly, from eqns (S62) and (S68), the density matrix in the bonding MBO basis becomes

$$\begin{aligned} \mathbf{D}^{\text{MBO}} &= \tilde{\mathbf{T}}^\dagger \tilde{\mathbf{D}} \tilde{\mathbf{T}} \\ &= \begin{pmatrix} \Lambda_a^2 \tilde{\Lambda}_{AA} + \Lambda_b^2 \tilde{\Lambda}_{BB} + 2\Lambda_a \Lambda_b \tilde{\Lambda}_{AB} & \Lambda_a \Lambda_b (\tilde{\Lambda}_{AA} - \tilde{\Lambda}_{BB}) - (\Lambda_a^2 - \Lambda_b^2) \tilde{\Lambda}_{AB} \\ \Lambda_a \Lambda_b (\tilde{\Lambda}_{AA} - \tilde{\Lambda}_{BB}) - (\Lambda_a^2 - \Lambda_b^2) \tilde{\Lambda}_{AB} & \Lambda_b^2 \tilde{\Lambda}_{AA} + \Lambda_a^2 \tilde{\Lambda}_{BB} - 2\Lambda_a \Lambda_b \tilde{\Lambda}_{AB} \end{pmatrix}. \end{aligned} \quad (\text{S69})$$

Following our chemical intuition, in ground state the occupancies should be maximized for the bonding MBOs and minimized for the antibonding ones. This means that we are looking for an optimal set of coefficients  $\{a_i\}$  and  $\{b_i\}$  so that  $\mathbf{D}^{\text{MBO}}$  is diagonalized. Consequently, the required set of  $\{a_i\}$  and  $\{b_i\}$  must fulfill that

$$\Lambda_a \Lambda_b (\tilde{\Lambda}_{AA} - \tilde{\Lambda}_{BB}) - (\Lambda_a^2 - \Lambda_b^2) \tilde{\Lambda}_{AB} = \mathbf{0}, \quad (\text{S70})$$

which leads to

$$a_i b_i (n_i^A - n_i^B) - (a_i^2 - b_i^2) \sqrt{n_i^A n_i^B} = 0. \quad (i = 1, 2, \dots, m) \quad (\text{S71})$$

Using eqns (S60) and (S71) with the normalization condition,  $a_i^2 + b_i^2 = 1$ , and noticing that  $a_i, b_i, n_i^A, n_i^B$  are all positive, we obtain

$$\begin{aligned} a_i &= \sqrt{\frac{n_i^A}{2}}, \\ b_i &= \sqrt{\frac{n_i^B}{2}}. \end{aligned} \quad (\text{S72})$$

With this result, it is easy to verify (using eqn (S69)) that

$$\mathbf{D}^{\text{MBO}} = \begin{pmatrix} 2\mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix}, \quad (\text{S73})$$

where matrices  $\mathbf{I}$  and  $\mathbf{0}$  are both of dimension  $m \times m$ .

## 4 Derivation of the expressions of MBO bond energy

As defined in the manuscript, the *bond energy* of the  $i$ -th bonding MBO,  $\Omega_i$ , is

$$\Delta E_i \equiv 2(\epsilon_i^A - \epsilon_i^{\text{MBO}}), \quad (\text{S74})$$

where  $\epsilon_i^A$  is the energy of the electron-withdrawing MBFO (i.e., assuming that  $\epsilon_i^A \leq \epsilon_i^B$ ) and  $\epsilon_i^{\text{MBO}}$  is the energy of MBO,  $\Omega_i$ , which is evaluated as

$$\epsilon_i^{\text{MBO}} = \langle \Omega_i | \hat{F} | \Omega_i \rangle = \frac{n_i^A}{2} \epsilon_i^A + \frac{n_i^B}{2} \epsilon_i^B + \sqrt{B_i} F_i. \quad (\text{S75})$$

Plugging eqn (S75) into eqn (S74), we obtain

$$\Delta E_i = (2 - n_i^A) \epsilon_i^A - n_i^B \epsilon_i^B - 2\sqrt{B_i} F_i. \quad (\text{S76})$$

Since we have assumed that  $\epsilon_i^A \leq \epsilon_i^B$ , there are normally more electrons populated in fragment  $\mathcal{A}$  than in fragment  $\mathcal{B}$ , namely,  $n_i^A \geq n_i^B$ . Hence,  $n_i^A = 1 + \delta_i$  and  $n_i^B = 1 - \delta_i$ . As a result, eqn (S76) becomes

$$\begin{aligned} \Delta E_i &= (\delta_i - 1)(\epsilon_i^B - \epsilon_i^A) - 2\sqrt{B_i} F_i \\ &= (\delta_i - 1)\Delta_i - 2\sqrt{B_i} F_i. \end{aligned} \quad (\text{S77})$$

Noticing that  $B_i = 1 - \delta_i^2$ , we see from eqn (S77) that  $\Delta E_i$  is a function of  $\delta_i$ . Thus, there exist an optimal value of  $\delta_i = \delta_i^{\text{opt}}$  that determines the maximum possible value of  $\Delta E_i$ , given that  $\Delta_i$  and  $F_i$  are fixed.

Let  $\delta_i = \cos \theta$ ,  $\sqrt{B_i} = \sin \theta$  ( $0 \leq \theta \leq \pi/2$ ) and  $\Delta_i^{AB}/r = \cos \varphi$ ,  $-2F_i/r = \sin \varphi$  ( $0 \leq \varphi \leq \pi/2$ ), where  $r \equiv \sqrt{\Delta_i^2 + 4F_i^2}$ . Then, eqn (S77) is transformed to

$$\Delta E_i = \sqrt{\Delta_i^2 + 4F_i^2} \cos(\theta - \varphi) - \Delta_i.$$

Evidently,  $\Delta E_i$  takes the maximum value of  $\sqrt{\Delta_i^2 + 4F_i^2} - \Delta_i$  when  $\cos(\theta - \varphi) = 1$ . Since both  $\theta$  and  $\varphi$  lie between 0 and  $\pi/2$ , we know that  $\theta = \varphi$  gives the maximum  $\Delta E_i$ . Therefore, the optimal values of  $\delta_i$  and  $B_i$  are

$$\delta_i^{\text{opt}} = \cos \theta = \cos \varphi = \frac{\Delta_i}{\sqrt{\Delta_i^2 + 4F_i^2}}, \quad (\text{S78})$$

$$B_i^{\text{opt}} = \sin^2 \theta = \sin^2 \varphi = \frac{4F_i^2}{\Delta_i^2 + 4F_i^2}. \quad (\text{S79})$$

Let

$$\alpha \equiv \frac{\Delta_i}{2|F_i|}, \quad (\text{S80})$$

then both  $\delta_i^{\text{opt}}$  and  $B_i^{\text{opt}}$  are exclusively a function of  $\alpha$ :

$$\delta_i^{\text{opt}} = \frac{\alpha}{\sqrt{1 + \alpha^2}}, \quad (\text{S81})$$

$$B_i^{\text{opt}} = \frac{1}{1 + \alpha^2}. \quad (\text{S82})$$

Consequently, the MBO bond energy  $\Delta E_i$ , as variationally determined by  $\delta_i^{\text{opt}}$ , is then

$$\Delta E_i = \sqrt{\Delta_i^2 + 4F_i^2} - \Delta_i. \quad (\text{S83})$$

In the case of MBOs with strong covalent character,  $\delta_i \approx 0$ ,  $B_i \approx 1$  and thus  $\alpha \approx 0$  and  $\Delta_i \ll |F_i|$ . Accordingly, eqn (S83) can be approximated as

$$\begin{aligned} \Delta E_i &= 2|F_i|(\sqrt{1 + \alpha^2} - \alpha) \approx 2|F_i|(1 + \frac{1}{2}\alpha^2 - \alpha) \\ &\approx 2|F_i|(1 - \alpha) = 2\left(|F_i| - \frac{\Delta_i}{2}\right). \end{aligned} \quad (\text{S84})$$

On the other hand, for highly polarized MBOs,  $\delta_i \approx 1$ ,  $B_i \approx 0$  and thus  $1/\alpha \approx 0$  and  $\Delta_i \gg |F_i|$ . Hence, we have the following approximation for eqn (S83):

$$\Delta E_i = \Delta_i(\sqrt{1 + 1/\alpha^2} - 1) \approx \Delta_i(1 + \frac{1}{2\alpha^2} - 1) = \frac{\Delta_i}{2\alpha^2} = 2\frac{F_i^2}{\Delta_i}. \quad (\text{S85})$$

Meanwhile, the charge transfer from the donor MBFO ( $\theta_i^A$ ) to the acceptor MBFO ( $\theta_i^B$ ) can be estimated as (note that  $1/\alpha \approx 0$ ):

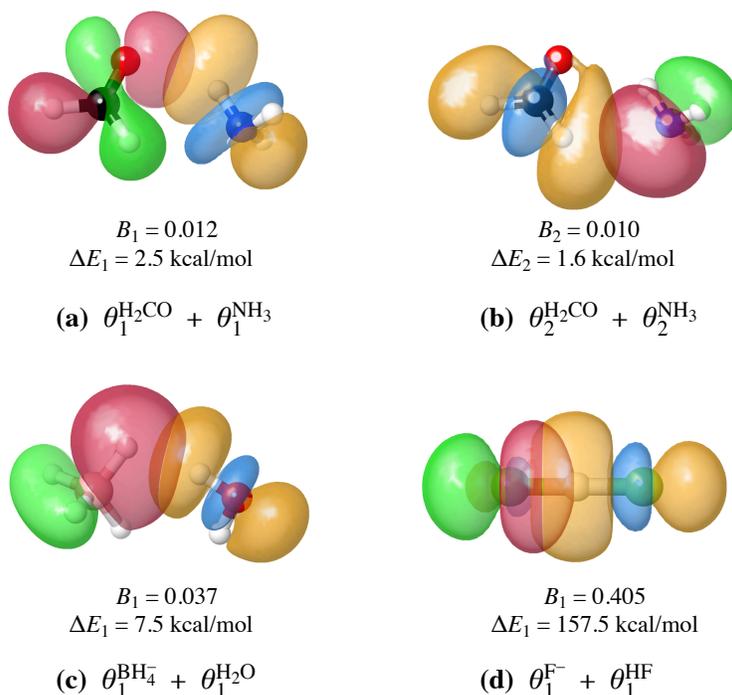
$$\Delta q_i = n_i^B = 1 - \delta_i = 1 - \frac{\alpha}{\sqrt{1 + \alpha^2}} \approx \frac{1}{2\alpha^2} = 2\left(\frac{F_i}{\Delta_i}\right)^2. \quad (\text{S86})$$

Now, by including the second order term in the Taylor expansion of  $\sqrt{1 + 1/\alpha^2}$  in eqn (S85), we have

$$\begin{aligned} \Delta E_i &= \Delta_i(\sqrt{1 + 1/\alpha^2} - 1) \approx \Delta_i(1 + \frac{1}{2\alpha^2} - \frac{1}{8\alpha^4} - 1) = \frac{\Delta_i}{4\alpha^2}(2 - \frac{1}{2\alpha^2}) \\ &= (2 - \Delta q_i)\frac{F_i^2}{\Delta_i} = n_i^A\frac{F_i^2}{\Delta_i}. \end{aligned} \quad (\text{S87})$$

## 5 MBFO analysis for H-bond complexes at the M06/def2-TZVPP level

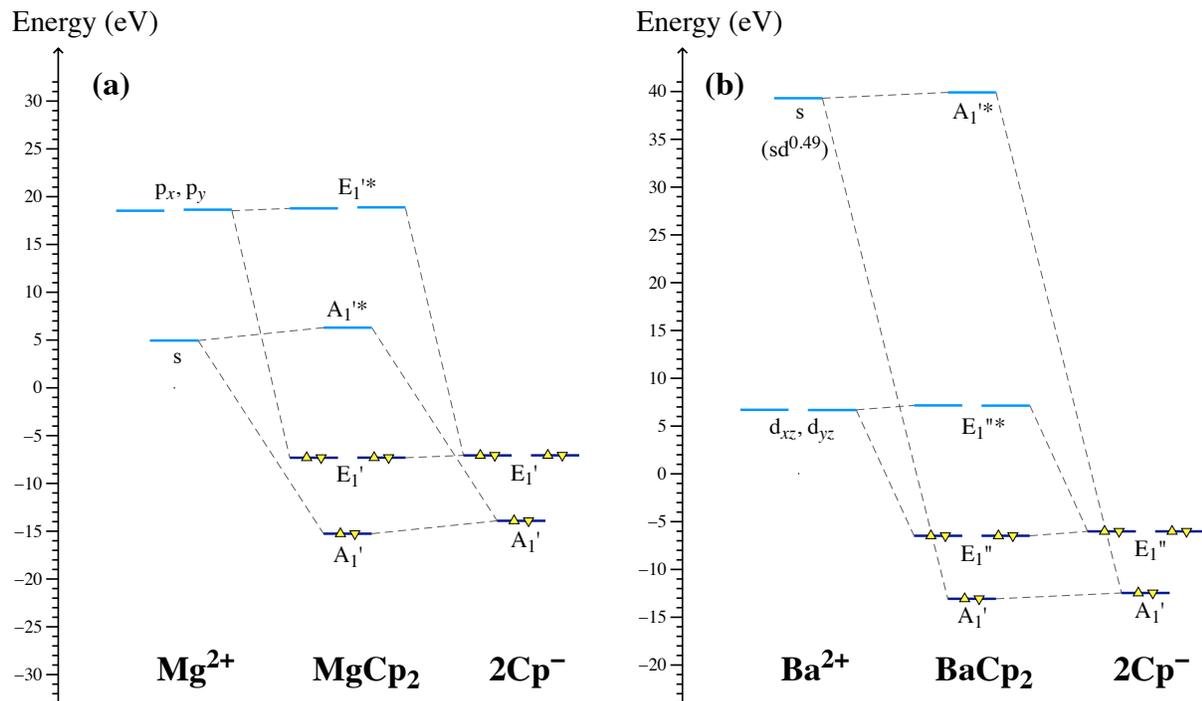
Fig. S1 shows the results of the MBFO analysis for some H-bond complexes at the M06/def2-TZVPP level. Comparing this figure with Fig. 8 in the manuscript, we can see that the results of MBFO analysis at both the M06/def2-TZVPP and B3LYP/aug-cc-pvDZ levels give quite similar MBFO orbital shapes, decomposed bond orders and MBO bond energies.



**Figure S1.** Results of the MBFO analysis at the M06/def2-TZVPP level of theory. Interaction between the principal MBFO pairs ( $\theta_1^A$  and  $\theta_1^B$ ) in H-bond complexes, (a)  $\text{H}_2\text{CO} \cdots \text{HNH}_2$ , (c)  $\text{H}_3\text{BH}^- \cdots \text{HOH}$  and (d)  $\text{F}^- \cdots \text{HF}$ . The interaction between the second principal MBFO pairs ( $\theta_2^A$  and  $\theta_2^B$ ) is also shown for complex  $\text{H}_2\text{CO} \cdots \text{HNH}_2$  (panel b). In each case, the positive and negative phases of donor MBFO are indicated by red and green colors, respectively, while the corresponding color codes for acceptor MBFO are orange and blue, respectively. All orbitals are plotted with an isovalue of 0.03. The corresponding bond order ( $B_i$ ) and bond energy ( $\Delta E_i$ ) are also given.

## 6 Orbital interaction diagrams for $\text{MgCp}_2$ and $\text{BaCp}_2$

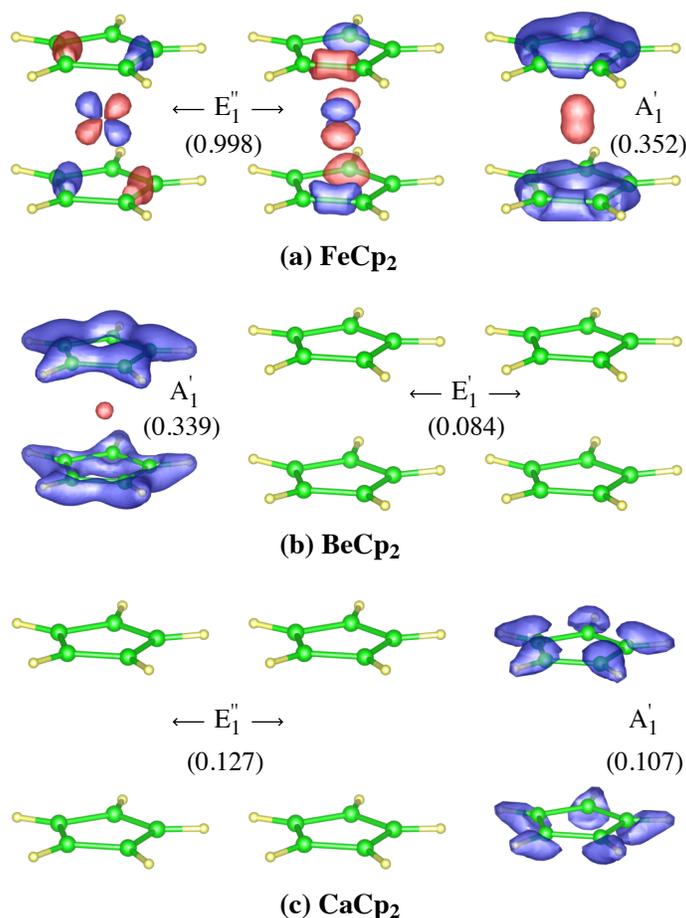
The orbital interaction diagrams for  $\text{MgCp}_2$  and  $\text{BaCp}_2$  are presented in Figure S2. For clarity, we only show the most important MBOs and the corresponding MBFOs with a bond order greater than 0.03.



**Figure S2.** Orbital interaction diagram for (a)  $\text{MgCp}_2$  and (b)  $\text{BaCp}_2$ . For clarity, only MBOs and the corresponding MBFOs with a bond order greater than 0.03 are shown. Filled energy levels are indicated in dark blue with two yellow triangles representing an electron pair, and empty levels are distinguished by light blue color. The MBFOs and MBOs are labeled by their symmetry notation, which, in the case of antibonding MBOs, is followed by an asterisk. The oxidation state +2 of the metal, as denoted by  $\text{Mg}^{2+}$  or  $\text{Ba}^{2+}$ , has been determined by filling electrons into lowest possible energy MBFOs.

## 7 Orbital deformation for $\text{Cp}^-$ rings in $\text{MCp}_2$ complex with respect to the isolated $\text{Cp}^-$ rings

Figure S3 plots the difference in wave function between the MBFO of  $\text{Cp}^-$  rings in  $\text{MCp}_2$  complex and the corresponding MO of the isolated  $\text{Cp}^-$  rings, for the three leading metal–ligand bonding interactions in  $\text{FeCp}_2$ ,  $\text{BeCp}_2$  and  $\text{CaCp}_2$ . As we can see, all three leading MBFOs of  $\text{Cp}^-$  rings in  $\text{FeCp}_2$  have undergone a substantial deformation. For  $\text{BeCp}_2$ , only the leading MBFO ( $A'_1$ ) of  $\text{Cp}^-$  rings shows a considerable deformation. As to  $\text{CaCp}_2$ , the deformation of MBFOs of  $\text{Cp}^-$  rings is much less significant.



**Figure S3.** The difference in wave function between the MBFO of  $\text{Cp}^-$  rings in  $\text{MCp}_2$  and the corresponding MO of the isolated  $\text{Cp}^-$  rings, for (a)  $\text{FeCp}_2$ , (b)  $\text{BeCp}_2$  and (c)  $\text{CaCp}_2$ . Only the MBFOs corresponding to the three leading metal–ligand interactions are shown (with bond orders given in parentheses). All isosurfaces are plotted with an isovalue of 0.05.

## References

- (1) Miller, D. A. B. *Quantum Mechanics for Scientists and Engineers*; Cambridge University Press: New York, 2008; p 339.
- (2) Mayer, I. Charge, bond order and valence in the AB initio SCF theory. *Chem. Phys. Lett.* **1983**, *97*, 270 – 274.
- (3) Mayer, I. Bond order and valence: Relations to Mulliken’s population analysis. *Int. J. Quantum Chem.* **1984**, *26*, 151–154.
- (4) Bridgeman, A. J.; Empson, C. J. Bond Orders between Molecular Fragments. *Chem. Eur. J.* **2006**, *12*, 2252–2262.
- (5) Mayer, I. Bond order and valence indices: A personal account. *J. Comput. Chem.* **2007**, *28*, 204–221.
- (6) Horn, R. A.; Johnson, C. R. *Matrix Analysis*; Cambridge University Press: Cambridge, 1985.