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LOCALLY PROJECTED MOLECULAR ORBITAL THEORY FOR MOLECULAR INTERACTION WITH A HIGH-SPIN OPEN SHELL MOLECULE

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Locally projected molecular orbital method for molecular interaction is extended to a cluster consisting of a high-spin open shell molecule and many closed shell molecules. While deriving the equations, Hartee-Fock-Roothaan equation without the orthonormal condition is obtained. The stationary conditions for molecular orbitals are expressed in a form of a generalized Brillouin condition. To obtain the molecular orbital coefficient matrix, which satisfies the stationary condition, a single Fock operator form is presented. For the locally projected molecular orbitals for the open shell cluster, the working matrix representaion is given.

Introduction

The theoretical studies of molecular interaction have extensively been reported in recent years. A series of special issues in Chemical Reviews are published[1,2], and there are also review articles in Handbook[3,4] and in Encyclopedia[5]. Atomic and molecular clusters are in most cases formed by weak molecular interaction such as van der Waals forces and hydrogen bond. Now, the theoretical and computational studies of molecular clusters become indispensable. Most of the experimental papers on the molecular clusters refer to the theoretical counter parts or include some computational results carried out along with their experiments. In these practical computational studies of the weak molecular interaction with modest basis sets, the basis set superposition error (BSSE) has to be avoided. The most straightforward way is to increase the size of the basis set, but it is known that the convergence is slow in particular with the correlated methods. Another way is to use the counterpoise (CP) correction method[6,7], which requires $(2N + 1)$ calculations for the clusters of N relaxed molecules.

To avoid the BSSE, Gianinetti et al proposed the self-consistent field for molecular interaction (SCF MI) for the closed shell dimer [8] and then extended it to multi-component systems and to open shell systems.[9] Using the projection operators, we also derived the equations to obtain the molecular orbitals locally defined in a molecule in the cluster of many molecules, and proposed to rename it locally projected molecular orbital for molecular interaction (LP MO MI)[10], because SCFMO MI is too general in meaning and does not suggest the characteristics of the method. In the paper, we pointed out that the interaction energy with LP MO MI (SCFMO MI) is systematically underestimated; the cause of this deficiency is identified as the lack of the charge-transfer, or the delocalization of electrons. In the second of our papers[11], the binding energy corrected by adding the charge-transfer type excitations with the second order perturbation expansion becomes close to the couterpoise corrected SCF binding energy. In the third of the series[12], the perturbation expansion is extended to include the intra-molecular pair excitations and the simultaneous singlet-singlet as well as triplet-triplet excitations. It is numerically shown that the triplet-triplet excitation, which may be called dispersion-exchange term, makes the calculated binding energy close to the counterpoise corrected MP2 energy.

In the present paper, our projection operator formalism is applied to the high-spin open shell cluster. The formalism is different from that used in Gianinetti et al[9], and the equivalency is not proved. Because the locally projected molecular orbitals (LP MO) are non-orthogonal among the occupied orbitals, first the stationary condition is derived for the occupied orbitals of a single Slater determinant of spin-unrestricted wave function without the orthonormal condition. The equation suggests an alternative way to directly obtain the localized molecular orbitals, to bypass the canonical set of Hartree-Fock orbitals. Then, a set of equations is derived for a case when the molecular orbitals are split to two groups. The equation turns out to be equivalent to the stationary condition for the LP MO of a molecule in the closed shell cluster, derived in our previous paper.[11] The equations are applied to the high-spin restricted case, in which the occupied orbitals are grouped to the doubly occupied (DOMO) and singly occupied (SOMO) molecular orbitals. Finaly, the method is extended to the LP MO for a cluster having a high-spin open shell molecule and many closed shell molecules. The matrix form of the Fock operator for the LP MO is presented.

1. Non-orthogonal stationary condition

1.1. *Unrestricted open shell cases*

Before developing the locally projected molecular orbital (LP MO) theory for high-spin molecular clusters, we first derive the stationary condition for unrestricted molecular orbitals without the orthonormal restriction. The one-electron density matrix for α electrons is defined as

$$\boldsymbol{D}^\alpha = \boldsymbol{T}^\alpha (\widetilde{\boldsymbol{T}}^\alpha \boldsymbol{S} \boldsymbol{T}^\alpha)^{-1} \widetilde{\boldsymbol{T}}^\alpha \ , \tag{1}$$

where $\boldsymbol{T}^\alpha$ is a $(N_{basis}, M^\alpha_{occ})$ rectangular MO coefficient matrix, and $\boldsymbol{S}$ is a overlap matrix in terms of the basis set. Similarly the density matrix $\boldsymbol{D}^\beta$ is defined. In this definition, it is assumed that the electronic wave fuction is described by a single Slater determinant with a proper normalization. Also we assume the real MO coefficients. The total electron energy in terms of the one-electron density matrix is

$$E = \sum_{ab}^{N_{basis}} h_{ba} \left(D^{\alpha}_{ab} + D^{\beta}_{ab} \right) \tag{2}$$

$$+ \frac{1}{2} \sum_{abcd}^{N_{basis}} [\mathbf{\Gamma}]_{ab.cd} \left(D^{\alpha}_{ba} D^{\alpha}_{dc} - D^{\alpha}_{da} D^{\alpha}_{bc} + D^{\beta}_{ba} D^{\beta}_{dc} - D^{\beta}_{da} D^{\beta}_{bc} + 2 D^{\alpha}_{ba} D^{\beta}_{dc} \right) ,$$

where the molecular integrals are

$$h_{ba} = \langle \chi_b | \, h_{one-elec} \, | \chi_a \rangle \tag{3}$$

$$[\mathbf{\Gamma}]_{ab.cd} \equiv \langle \chi_a(1) \chi_c(2) | \, \frac{1}{r_{12}} \, | \chi_b(1) \chi_d(2) \rangle \ . \tag{4}$$

By taking the derivatives on the density matrix elements D^{α}_{ab}, the Fock operator matrix elements are defined as

$$\begin{aligned} \frac{\partial E}{\partial D^{\alpha}_{ab}} &= h_{ba} + \sum_{cd}^{M_{basis}} \left[[\mathbf{\Gamma}]_{ab.cd} \left(D^{\alpha}_{dc} + D^{\beta}_{dc} \right) - [\mathbf{\Gamma}]_{ad.cb} \, D^{\alpha}_{dc} \right] \\ &\equiv F^{\alpha}_{ba} \equiv \langle \chi_b | \, \widehat{F}^{\alpha} \, | \chi_a \rangle \end{aligned} \tag{5}$$

With this definition, the total electron energy is

$$E = \frac{1}{2} Tr \left[\boldsymbol{h} \left(\boldsymbol{D}^{\alpha} + \boldsymbol{D}^{\beta} \right) \right] + \frac{1}{2} Tr \left[\boldsymbol{F}^{\alpha} \boldsymbol{D}^{\alpha} + \boldsymbol{F}^{\beta} \boldsymbol{D}^{\beta} \right] \tag{6}$$

The derivative of the energy (5) on the density matrix can be written as

$$\delta E = Tr \left[\boldsymbol{F}^{\alpha} (\boldsymbol{D}^{\alpha}, \boldsymbol{D}^{\beta}) \delta \boldsymbol{D}^{\alpha} + \boldsymbol{F}^{\beta} (\boldsymbol{D}^{\alpha}, \boldsymbol{D}^{\beta}) \delta \boldsymbol{D}^{\beta} \right] \tag{7}$$

where the variation of the density matrix in terms of MO coefficients is

$$\delta \boldsymbol{D}^{\alpha} = \left[1 - \boldsymbol{T}^{\alpha} \left(\widetilde{\boldsymbol{T}}^{\alpha} \boldsymbol{S} \boldsymbol{T}^{\alpha} \right)^{-1} \widetilde{\boldsymbol{T}}^{\alpha} \boldsymbol{S} \right] \delta \boldsymbol{T}^{\alpha} \left(\widetilde{\boldsymbol{T}}^{\alpha} \boldsymbol{S} \boldsymbol{T}^{\alpha} \right)^{-1} \widetilde{\boldsymbol{T}}^{\alpha} + \text{transpose of the first term} \tag{8}$$

$$= \left(1 - \boldsymbol{D}^{\alpha} \boldsymbol{S} \right) \delta \boldsymbol{T}^{\alpha} \mathcal{R}^{\alpha} \widetilde{\boldsymbol{T}}^{\alpha} + \text{transpose of the first term} \tag{9}$$

Here $\mathcal{R}^{\alpha}$, the inverse matrix of MO overlap $\mathcal{S}^{\alpha}$, is defined as

$$\mathcal{R}^{\alpha} \equiv \left[\widetilde{\boldsymbol{T}}^{\alpha} S \boldsymbol{T}^{\alpha} \right]^{-1} = [\mathcal{S}^{\alpha}]^{-1} \tag{10}$$

By inserting (8) in (7), the energy change in terms of MO coefficients are

$$\begin{aligned} \delta E &= 2Tr \left\{ \boldsymbol{F}^{\alpha} (\boldsymbol{D}^{\alpha}, \boldsymbol{D}^{\beta}) \left(1 - \boldsymbol{D}^{\alpha} \boldsymbol{S} \right) \delta \boldsymbol{T}^{\alpha} \mathcal{R}^{\alpha} \widetilde{\boldsymbol{T}}^{\alpha} \right\} \\ &\quad + 2Tr \left\{ \boldsymbol{F}^{\beta} (\boldsymbol{D}^{\alpha}, \boldsymbol{D}^{\beta}) \left(1 - \boldsymbol{D}^{\beta} \boldsymbol{S} \right) \delta \boldsymbol{T}^{\beta} \mathcal{R}^{\beta} \widetilde{\boldsymbol{T}}^{\beta} \right\} \\ &= 2Tr \left\{ \mathcal{R}^{\alpha} \widetilde{\boldsymbol{T}}^{\alpha} \boldsymbol{F}^{\alpha} \left(1 - \boldsymbol{D}^{\alpha} \boldsymbol{S} \right) \delta \boldsymbol{T}^{\alpha} \right\} + 2Tr \left\{ \mathcal{R}^{\beta} \widetilde{\boldsymbol{T}}^{\beta} \boldsymbol{F}^{\beta} \left(1 - \boldsymbol{D}^{\beta} \boldsymbol{S} \right) \delta \boldsymbol{T}^{\beta} \right\} \\ &\equiv 2Tr \widetilde{\boldsymbol{Z}}^{\alpha} \delta \boldsymbol{T}^{\alpha} + 2Tr \widetilde{\boldsymbol{Z}}^{\beta} \delta \boldsymbol{T}^{\beta} \end{aligned} \tag{11}$$

where in the second equality, the character of the trace of matrix is used. Thus, the stationary condition becomes

$$\begin{aligned} \boldsymbol{Z}^{\alpha} &= 0 \\ &= \left[1 - \boldsymbol{S}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1}\widetilde{\boldsymbol{T}}^{\alpha}\right]\boldsymbol{F}^{\alpha}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1} \end{aligned} \tag{12}$$

The matrix $\boldsymbol{Z}^{\alpha}$ is the rectangular matrix of (N_{basis}, M_{occ}). The number of variables (MO coefficients) are $N_{basis}{*}M_{occ}$, and the number of equations is thus $N_{basis}{*}M_{occ}$; because any restriction is not imposed, they are equal to each other. Equation (12) is rewritten as

$$\begin{aligned} \boldsymbol{F}^{\alpha}\boldsymbol{T}^{\alpha} &= \boldsymbol{S}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1}\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{F}^{\alpha}\boldsymbol{T}^{\alpha} \\ &\equiv \boldsymbol{S}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1}\boldsymbol{\Lambda}^{\alpha} \end{aligned} \tag{13}$$

for α orbitals. The second line defines a diagonal matrix $\boldsymbol{\Lambda}^{\alpha} = \widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{F}^{\alpha}\boldsymbol{T}^{\alpha}$. Obviously if the orthonormal condition, $\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha} = 1$, is assumed, eq.(13) becomes the Roothaan-Hartree-Fock equation[13] , and it is a general matrix eigenvalue problem. If the orthonormal condition is not enforced, eq.(13) cannot be solved with matrix algebra even if $\boldsymbol{F}^{\alpha}$ is assumed to be known.

Now we introduce the projection operators $\widehat{P}^{\alpha}$, which projects any function on to the space spanned by the α occupied orbitals,

$$\begin{aligned} \widehat{P}^{\alpha} &\equiv \sum_{i,j}^{\alpha} \left|\phi_i\right\rangle \left\langle\phi_i \right|\left.\phi_j\right\rangle^{-1} \left\langle\phi_j\right| \\ &= \boldsymbol{\chi}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1}\widetilde{\boldsymbol{T}}^{\alpha}\widetilde{\boldsymbol{\chi}} = \boldsymbol{\chi}\boldsymbol{D}^{\alpha}\widetilde{\boldsymbol{\chi}} \end{aligned} \tag{14}$$

With $\widehat{P}^{\alpha}$, eq.(13) can be written in an operator form,

$$\left(\boldsymbol{1}{-}\widehat{P}^{\alpha}\right)\widehat{F}^{\alpha}\boldsymbol{\chi}\boldsymbol{T}^{\alpha} = 0 \tag{15}$$

By introducing the complemental projection operator $\widehat{P}^{um_{-}\alpha}$ for the unoccupied molecular orbitals as[14]

$$\boldsymbol{1} \equiv \widehat{P}^{um_{-}\alpha} + \widehat{P}^{\alpha} \tag{16}$$

the equation (15) can be written as

$$\widehat{P}^{um_{-}\alpha}\widehat{F}^{\alpha}\boldsymbol{\chi}\boldsymbol{T}^{\alpha} = 0 \tag{17}$$

By inserting the equality (16)

$$\widehat{P}^{um_{-}\alpha}\widehat{F}^{\alpha}\left(\widehat{P}^{\alpha} + \widehat{P}^{ext\alpha}\right)\boldsymbol{\chi}\boldsymbol{T}^{\alpha} = 0 \tag{18}$$

Since $\widehat{P}^{um_{-}\alpha}\boldsymbol{\chi}\boldsymbol{T}^{\alpha} = 0$ by definition, the stationary condition for the occupied molecular orbitals becomes

$$\widehat{P}^{um_{-}\alpha}\widehat{F}^{\alpha}\widehat{P}^{\alpha} = 0 \tag{19}$$

which is a general form of the well-known Brillouin condition, and can be used in solving the equation iteratively.

As is often used in solving the Hartree-Fock equation for the restricted open shell case[14], a single Fock operator is defined as

$$\begin{aligned}\widehat{G}^{\alpha} &= \widehat{P}^{\alpha}\left(\widehat{F}^{\alpha}+\widehat{\Omega}_{om}\right)\widehat{P}^{\alpha}+\left(\mathbf{1}-\widehat{P}^{\alpha}\right)\left(\widehat{F}^{\alpha}+\widehat{\Omega}_{um}\right)\left(\mathbf{1}-\widehat{P}^{\alpha}\right)\\ &+\eta_{dm-um}\left[\left(\mathbf{1}-\widehat{P}^{\alpha}\right)\widehat{F}^{\alpha}\widehat{P}^{\alpha}+\widehat{P}^{\alpha}\widehat{F}^{\alpha}\left(\mathbf{1}-\widehat{P}^{\alpha}\right)\right]\end{aligned} \tag{20}$$

where the second line is the stationary condition, and the parameter η_{dm-um} is a dampinng factor selected to a fast convergency. The first line defines the molecular orbitals and their orbital energies. The eigen function of $\widehat{G}^{\alpha}$ satisfies the stationary condition. For the orbitals of β electrons the similar Fock operator is defined. The shift operators (or orbital energy shifters), $\widehat{\Omega}_{om}$ and $\widehat{\Omega}_{um}$, are the arbitrary Hermite operators, and can be used to control the convergency or to determine the proper orbital sets for the further calculations as was done in the electron-hole potential method by Morokuma and Iwata[15]. To solve eq. (20), a good initial non-orthogonal orbital set is expected to be required. Then, using the MO representation of the Fock operator $\widehat{G}^{\alpha}$, the equation is solved to keep the orbitals non-orthogonal.

1.2. *Two groups of molecular orbitals*

Before deriving the equation for the restricted high spin open shell case, we examine a more general case, which we also use in deriving the equations for a clusters consisting of many closed shell molecules and an open shell molecule. We assume that the MO coefficient matrix is split as

$$\boldsymbol{T} = \left(\ \boldsymbol{T}_U, \quad \boldsymbol{T}_V \quad \right)$$

Accordingly the (N_{basis}, M_{occ}) rectangular matrix $\boldsymbol{Z}$ defined in (12) becomes two set of equations

$$\left\{1-\boldsymbol{S}\boldsymbol{T}\left(\widetilde{\boldsymbol{T}}\boldsymbol{S}\boldsymbol{T}\right)^{-1}\widetilde{\boldsymbol{T}}\right\}\left(\boldsymbol{F}\boldsymbol{T}_U\mathcal{R}_{U,U}+\boldsymbol{F}\boldsymbol{T}_V\mathcal{R}_{V,U}\right)=0 \tag{22}$$

$$\left\{1-\boldsymbol{S}\boldsymbol{T}\left(\widetilde{\boldsymbol{T}}\boldsymbol{S}\boldsymbol{T}\right)^{-1}\widetilde{\boldsymbol{T}}\right\}\left(\boldsymbol{F}\boldsymbol{T}_V\mathcal{R}_{V,V}+\boldsymbol{F}\boldsymbol{T}_U\mathcal{R}_{U,V}\right)=0 \tag{23}$$

where the matrix

$$\begin{aligned}\mathcal{R} &\equiv \left(\widetilde{\boldsymbol{T}}\boldsymbol{S}\boldsymbol{T}\right)^{-1} \equiv \mathcal{M}^{-1}\\ &= \begin{bmatrix}\mathcal{R}_{U,U}, & \mathcal{R}_{U,V}\\ \mathcal{R}_{V,U}, & \mathcal{R}_{V,V}\end{bmatrix} = \begin{bmatrix}\mathcal{M}_{U,U}, & \mathcal{M}_{U,V}\\ \mathcal{M}_{V,U}, & \mathcal{M}_{V,V}\end{bmatrix}^{-1}\end{aligned} \tag{24}$$

From the (U,V) and (V,U) elements of the equality $\mathcal{M}\mathcal{R}=1$

$$\begin{aligned}\mathcal{M}_{U,U}\mathcal{R}_{U,V}+\mathcal{M}_{U,V}\mathcal{R}_{V,V}&=0\\ \mathcal{M}_{V,U}\mathcal{R}_{U,U}+\mathcal{M}_{V,V}\mathcal{R}_{V,U}&=0\end{aligned}$$

Eqs.(22) and (23) are

$$\left\{1 - \boldsymbol{S}\boldsymbol{T}\left(\widetilde{\boldsymbol{T}}\boldsymbol{S}\boldsymbol{T}\right)^{-1}\widetilde{\boldsymbol{T}}\right\}\left(\boldsymbol{F}\boldsymbol{T}_U - \boldsymbol{F}\boldsymbol{T}_V\left(\mathcal{M}_{V,V}\right)^{-1}\mathcal{M}_{V,U}\right)\mathcal{R}_{U,U} = 0 \tag{25}$$

$$\left\{1 - \boldsymbol{S}\boldsymbol{T}\left(\widetilde{\boldsymbol{T}}\boldsymbol{S}\boldsymbol{T}\right)^{-1}\widetilde{\boldsymbol{T}}\right\}\left(\boldsymbol{F}\boldsymbol{T}_V - \boldsymbol{F}\boldsymbol{T}_U\left(\mathcal{M}_{U,U}\right)^{-1}\mathcal{M}_{U,V}\right)\mathcal{R}_{V,V} = 0 \tag{26}$$

Two MO coefficient matrices $\boldsymbol{T}_U$ and $\boldsymbol{T}_V$ are coupled in (25) and (26). By defining the projection operators

$$\widehat{P} = \boldsymbol{\chi}\boldsymbol{T}\left(\mathcal{M}\right)^{-1}\widetilde{\boldsymbol{T}}\widetilde{\boldsymbol{\chi}} \tag{27}$$

$$\widehat{P}^U = \boldsymbol{\chi}\boldsymbol{T}_U\left(\mathcal{M}_{U,U}\right)^{-1}\widetilde{\boldsymbol{T}}_U\widetilde{\boldsymbol{\chi}} \tag{28}$$

$$\widehat{P}^V = \boldsymbol{\chi}\boldsymbol{T}_V\left(\mathcal{M}_{V,V}\right)^{-1}\widetilde{\boldsymbol{T}}_V\widetilde{\boldsymbol{\chi}} \tag{29}$$

Equation (25) for the stationary condition of MO coefficient matrix $\boldsymbol{T}_U$ can be written as

$$(1-\widehat{P})\widehat{F}\left(1-\widehat{P}^V\right)\boldsymbol{\chi}\boldsymbol{T}_U = (1-\widehat{P})\widehat{F}\left(1-\widehat{P}^V\right)\widehat{P}^U\boldsymbol{\chi}\boldsymbol{T}_U = 0 \tag{30}$$

Now, equation (30) is apparently only for $\boldsymbol{T}_U$. The coupling with the other MO coefficient $\boldsymbol{T}_V$ is hidden in the projection operator $\widehat{P}^V$. The splitting of the MO coefficient matrix is general. So it can be applied to a cluster consisting of many closed shell molecules, which was studied in our previous paper.[11] When $\boldsymbol{T}_U$ is the occupied MO matrix for a molecule A in the cluster, $\boldsymbol{T}_V$ is the occupied MO matrix of the molecules other than molecule A. In that case eq.(30) becomes equivalent to eq.(25) of our previous paper[11] as

$$\widehat{F}\left(1-\widehat{P}^Y\right)\boldsymbol{\chi}\boldsymbol{T}_A = \widehat{P}\widehat{F}\left(1-\widehat{P}^Y\right)\boldsymbol{\chi}\boldsymbol{T}_A \tag{31}$$

1.3. *High-spin restricted open shell cases*

In the restricted open shell case, the equivalence condition for the spacial part of spin-orbitals is imposed. By assuming the number of α spin electrons is larger than the number of β electrons, the occupied MO coefficient matrix $\boldsymbol{T}^\beta$ is a part of $\boldsymbol{T}^\alpha$;

$$\boldsymbol{T}^\beta \equiv \boldsymbol{T}^d \tag{32}$$

$$\boldsymbol{T}^\alpha = \left(\,\boldsymbol{T}^d,\, \boldsymbol{T}^s\,\right) \equiv \boldsymbol{T}^{ds} \tag{33}$$

The energy change is now

$$\delta E = 2Tr\left\{\widetilde{\boldsymbol{Z}}^\alpha\left(\,\delta\boldsymbol{T}^d,\, \delta\boldsymbol{T}^s\,\right)\right\} + 2Tr\left\{\widetilde{\boldsymbol{Z}}^\beta\delta\boldsymbol{T}^d\right\} \tag{34}$$

$$= 2Tr\left\{\left[\widetilde{\boldsymbol{Z}}^\alpha\right]_d + \widetilde{\boldsymbol{Z}}^\beta\right\}\delta\boldsymbol{T}^d + 2Tr\left[\widetilde{\boldsymbol{Z}}^\alpha\right]_s\delta\boldsymbol{T}^s. \tag{35}$$

where

$$\boldsymbol{Z}^\alpha = \left[1 - \boldsymbol{S}\boldsymbol{T}^{ds}\left(\widetilde{\boldsymbol{T}}^{ds}\boldsymbol{S}\boldsymbol{T}^{ds}\right)^{-1}\widetilde{\boldsymbol{T}}^{ds}\right]\boldsymbol{F}^\alpha\boldsymbol{T}^{ds}\left(\widetilde{\boldsymbol{T}}^{ds}\boldsymbol{S}\boldsymbol{T}^{ds}\right)^{-1} \tag{36}$$

and the size of the matrix is $(N_{basis}, M_{domo}+M_{somo})$, M_{domo} and M_{somo} being the number of doubly and singly occupied orbitals. In eq. (34), $\left[\widetilde{\boldsymbol{Z}}^{\alpha}\right]_d$ stands for the first M_{domo} rows of the rectangular matrix $\widetilde{\boldsymbol{Z}}^{\alpha}$,and $\left[\widetilde{\boldsymbol{Z}}^{\alpha}\right]_s$ for the last M_{somo} rows. The rectangular matrix $\boldsymbol{Z}^{\beta}$ is similarly defined, and its size is (N_{basis}, M_{domo}). Note that up to here $\left(\widetilde{\boldsymbol{T}}^{ds}\boldsymbol{S}\boldsymbol{T}^{ds}\right)^{-1}$ in $\boldsymbol{D}^{\alpha}$ differs from $\left(\widetilde{\boldsymbol{T}}^{d}\boldsymbol{S}\boldsymbol{T}^{d}\right)^{-1}$ in $\boldsymbol{D}^{\beta}$. Thus, the stationary condition for the doubly occupied orbitals is

$$[\boldsymbol{Z}^{\alpha}]_d + \boldsymbol{Z}^{\beta} = 0 \tag{37}$$

and for the singly occupied orbitals is

$$[\boldsymbol{Z}^{\alpha}]_s = 0 \tag{38}$$

Because $\boldsymbol{T}^{\alpha} = \left(\, \boldsymbol{T}^{d},\, \boldsymbol{T}^{s}\,\right)$, we can use the similar procedure for $\boldsymbol{Z}^{\alpha}$ by replacing V with d and U with s, and the equations becomes

$$(1-\widehat{P}^{ds})\widehat{F}^{\alpha}\left(1-\widehat{P}^{s}\right)\widehat{P}^{d}\boldsymbol{\chi}\boldsymbol{T}_{d}\mathcal{R}_{d,d} + (1-\widehat{P}^{d})\widehat{F}^{\beta}\boldsymbol{\chi}\boldsymbol{T}^{d}\left(\mathcal{M}_{d,d}\right)^{-1} = 0 \tag{39}$$

$$(1-\widehat{P}^{ds})\widehat{F}^{\alpha}\left(1-\widehat{P}^{d}\right)\widehat{P}^{s}\boldsymbol{\chi}\boldsymbol{T}_{s}\mathcal{R}_{s,s} = 0\ . \tag{40}$$

where the projection operators, $\widehat{P}^{ds}$, $\widehat{P}^{s}$ and $\widehat{P}^{d}$, are defined, similar to eq. (14). Note that the first term of (39) corresponds to (25), and (40) to (26). Thus, for the SOMO, the stationary condition is

$$(1-\widehat{P}^{ds})\widehat{F}^{\alpha}\left(1-\widehat{P}^{d}\right)\widehat{P}^{s} = 0 \tag{41}$$

Up to here, the restricition to the equivalence of the space parts of α and β spin orbitals is imposed. For the orthogonal molecular orbitlas, this restriction ensures that the Slater determinant is the eigen fuction of the square of the total spin $\widehat{S}^2$. For the non-orthogonal orbitals, the expectation value of $\widehat{S}^2$ is given as

$$\begin{aligned} &\langle\Phi|\,\widehat{S}^2\,|\Phi\rangle \\ &= \frac{1}{4}N_s(N_s+2) + N_d - Tr\left[D^{\alpha}SD^{\beta}S\right] \end{aligned} \tag{42}$$

where N_s and N_d are the number of the singly and doubly occupied orbitals, repectively. Because the correct expectation value $\langle\Phi|\,\widehat{S}^2\,|\Phi\rangle$ for the high-spin Slater determinant of N_s SOMOs is $\frac{1}{4}N_s(N_s+2)$, the equality

$$Tr\left[D^{\alpha}SD^{\beta}S\right] = N_d \tag{43}$$

has to be hold. The definition of D^{α} and D^{β} is

$$D^{\alpha} = \begin{pmatrix} T^{d} & T^{s} \end{pmatrix}\begin{pmatrix} \mathcal{M}_{d,d}, & \mathcal{M}_{d,s} \\ \mathcal{M}_{s,d}, & \mathcal{M}_{s,s} \end{pmatrix}^{-1}\begin{pmatrix} \widetilde{T}^{d} \\ \widetilde{T}^{s} \end{pmatrix} \tag{44}$$

$$D^{\beta} = T^{d}\mathcal{M}_{d,d}^{-1}\widetilde{T}^{d} \tag{45}$$

if $\mathcal{M}_{s,d} = \widetilde{\mathcal{M}}_{d,s}$ is zero, the equality (43) holds; that is, *the SOMOs have to be orthogonal to all of the DOMO*. Note that $Tr\left(D^{\beta}SD^{\beta}S\right) = Tr\left(D^{\beta}S\right) = N_d$.

The orthogonality condition between the DOMOs and SOMOs is a part of the condition for the restricted high-spin open shell wave function, in addition to the equivalence condition of the space part of the spin-orbitals. This requirement symplifies the stationary conditions. The projection operator $\widehat{P}^{ds}$becomes a sum

$$\widehat{P}^{ds} = \widehat{P}^{d} + \widehat{P}^{s} \tag{46}$$

and in (39) $\mathcal{R}_{d,d} = (\mathcal{M}_{d,d})^{-1}$, and thus the stationary condition for the DOMO becomes

$$\left[(1-\widehat{P}^{d}-\widehat{P}^{s})\widehat{F}^{\alpha}\left(1-\widehat{P}^{s}\right)+(1-\widehat{P}^{d})\widehat{F}^{\beta}\right]\widehat{P}^{d} = \mathbf{0} \tag{47}$$

Interestingly, eq.(47) does hold without the orthogonality condition (43), although the proof requires a page of lines. Using the orthogonality $\widehat{P}^{s}\widehat{P}^{d} = 0$, eq.(47) becomes simply

$$\left[(1-\widehat{P}^{d}-\widehat{P}^{s})\widehat{F}^{\alpha}+(1-\widehat{P}^{d})\widehat{F}^{\beta}\right]\widehat{P}^{d} = \mathbf{0} \tag{48}$$

The conditions (47) and (41) are the generalized Brillouin condition.

Now, a single Fock operator can be defined as

$$\begin{aligned}
\widehat{G} &= \frac{1}{2}\widehat{P}^{d}\left(\widehat{F}^{\alpha}+\widehat{F}^{\beta}+\widehat{\Omega}_{d}\right)\widehat{P}^{d}+(1-\widehat{P}^{d})\widehat{P}^{s}\left(\widehat{F}^{\alpha}+\widehat{\Omega}_{s}\right)\widehat{P}^{s}(1-\widehat{P}^{d})\\
&+(1-\widehat{P}^{d}-\widehat{P}^{s})\left(\frac{1}{2}\left(\widehat{F}^{\alpha}+\widehat{F}^{\beta}\right)+\widehat{\Omega}_{um}\right)(1-\widehat{P}^{d}-\widehat{P}^{s})\\
&+\eta_{d-u}\left[(1-\widehat{P}^{d}-\widehat{P}^{s})\widehat{F}^{\alpha}\widehat{P}^{d}+(1-\widehat{P}^{d})\widehat{F}^{\beta}\widehat{P}^{d}+comp.conj\right]\\
&+\eta_{s-u}\left[(1-\widehat{P}^{d}-\widehat{P}^{s})\widehat{F}^{\alpha}\widehat{P}^{s}+comp.conj\right]
\end{aligned} \tag{49}$$

Here the second term ensures the orthogonality condition.

2. Molecular cluster of a high-spin molecule and many closed-shell molecules

Now we develop the equation for the locally projected molecular orbitals, which can be applied to studying the molecular interaction of a cluster, consisting of a high spin molecule and many closed-shell molecules. In the locally projected molecular orbitals (LP MO) for molecular interaction the molecular orbitals of each molecule in the cluster are locally expanded in terms of the basis sets on each molecule. More explicitly the MO coefficient matrix is blocked as

$$\boldsymbol{T}^{\alpha} = (\boldsymbol{T}^{d},\boldsymbol{T}^{s}) = \begin{bmatrix} \boldsymbol{T}_{D} & 0 & \cdots & 0 & 0\\ 0 & \boldsymbol{T}_{C} & 0 & 0 & 0\\ 0 & 0 & \boldsymbol{T}_{B} & 0 & 0\\ 0 & 0 & 0 & \boldsymbol{T}_{A} & \boldsymbol{T}_{As} \end{bmatrix} \equiv \boldsymbol{T}^{ds} \tag{50}$$

$$\boldsymbol{T}^{\beta} = \boldsymbol{T}^{d} = \begin{bmatrix} \boldsymbol{T}_{D} & 0 & \cdots & 0\\ 0 & \boldsymbol{T}_{C} & 0 & 0\\ 0 & 0 & \boldsymbol{T}_{B} & 0\\ 0 & 0 & 0 & \boldsymbol{T}_{A} \end{bmatrix} \tag{51}$$

In this specific example, molecule A is an open-shell molecule and molecules B, C and D are closed-shell molecules. With this constraint, the energy change is a sum

$$\delta E = 2Tr\left\{\widetilde{\boldsymbol{Z}}^{\alpha}_{Ad} + \widetilde{\boldsymbol{Z}}^{\beta}_{A}\right\}\delta\boldsymbol{T}^{d}_{A} + 2Tr\widetilde{\boldsymbol{Z}}^{s}_{As}\delta\boldsymbol{T}^{s}_{A} + 2\sum_{X}^{B,C,D} Tr\left(\widetilde{\boldsymbol{Z}}^{\alpha}_{X} + \widetilde{\boldsymbol{Z}}^{\beta}_{X}\right)\delta\boldsymbol{T}_{X} \quad (52)$$

where the matrices $\boldsymbol{Z}^{\alpha}$ and $\boldsymbol{Z}^{\beta}$ are defined in (36); the size being $(\sum_Y N^{basis}_{Y}, \sum_Y M^{occ}_{Y})$. The rectangular matrices $\boldsymbol{Z}^{\alpha}_{X}$ $(\boldsymbol{Z}^{\beta}_{X})$ is a part of the block $(N^{basis}_{X}, M^{occ}_{X})$ for molecule X in the matrix $\boldsymbol{Z}^{\alpha}$ $(\boldsymbol{Z}^{\beta})$ as

$$\boldsymbol{Z}^{\alpha}_{X} \equiv \left[\left\{1 - \boldsymbol{S}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1}\widetilde{\boldsymbol{T}}^{\alpha}\right\}\boldsymbol{F}^{\alpha}\boldsymbol{T}^{\alpha}\left(\widetilde{\boldsymbol{T}}^{\alpha}\boldsymbol{S}\boldsymbol{T}^{\alpha}\right)^{-1}\right]_{X} \quad (53)$$

Note that even for the closed shell molecules $(X \neq A)$, $\boldsymbol{Z}^{\alpha}_{X} \neq \boldsymbol{Z}^{\beta}_{X}$ because of the SOMO $\boldsymbol{T}_{As}$. The matrix $\boldsymbol{Z}^{\alpha}_{Ad}$ $(\boldsymbol{Z}^{\alpha}_{As})$ for the open-shell molecule is similarly defined for the doubly (singly) occupied orbitals of molecule A.

Now the stationary condition for the SOMO can be obtained by splitting $\boldsymbol{T}^{\alpha}$ to $(\boldsymbol{T}^{d}, \boldsymbol{T}^{s})$ and it is

$$(1 - \widehat{P}^{d} - \widehat{P}^{s}_{As})\widehat{F}^{\alpha}\left(1 - \widehat{P}^{d}\right)\widehat{P}_{A_s} = 0 \quad (54)$$

Besides, the orthogonality to all of the DOMO

$$\widehat{P}_{A_s} = \left(\boldsymbol{1} - \widehat{P}^{d}\right)\widehat{P}_{A_s} \quad (55)$$

has to be enforced.

The stationary condition for the DOMO of a closed shell molecule $X(\neq A)$ is derived by splitting the MO matrix as

$$\boldsymbol{T}^{\alpha} = \begin{bmatrix} \boldsymbol{T}_{X}, & 0 & 0 \\ 0 & \boldsymbol{T}_{Z_X}, & \boldsymbol{T}_{As} \end{bmatrix} \equiv \boldsymbol{T}^{ds} \quad (56)$$

$$\boldsymbol{T}^{\beta} = \begin{bmatrix} \boldsymbol{T}_{X}, & 0 \\ 0, & \boldsymbol{T}_{Z_X} \end{bmatrix} \equiv \boldsymbol{T}^{d} \quad (57)$$

where the set of molecules other than molecule X has a suffix Z_X. The stationary condition for the DOMO for each molecule, including molecule A, is

$$\left\{(1 - \widehat{P}^{d} - \widehat{P}^{s})\widehat{F}^{\alpha}\left(1 - \widehat{P}^{d}_{Z_X} - \widehat{P}^{s}\right) + (1 - \widehat{P}^{d})\widehat{F}^{\beta}\left(1 - \widehat{P}^{d}_{Z_X}\right)\right\}\widehat{P}_{X} = 0 \quad (58)$$

where the projection operator $\widehat{P}^{d}_{Z_X}$ are properly introduced. To derive the equation is not so straight forward as is expected, because $\boldsymbol{T}^{\beta}$ is also split to two groups (in the open shell equation for a single molecule as derived in the previous section, $\boldsymbol{T}^{\beta}$ is not split). But once the orthogaonality condition $\widehat{P}_{X}\widehat{P}^{s} = 0$ which is a part of (55), the procedure used in subsection 1.2 can be used both for $\boldsymbol{Z}^{\alpha}_{X}$ and $\boldsymbol{Z}^{\beta}_{X}$. Then the stationary condition is

$$\left\{(1 - \widehat{P}^{d} - \widehat{P}^{s})\widehat{F}^{\alpha} + (1 - \widehat{P}^{d})\widehat{F}^{\beta}\right\}\left(1 - \widehat{P}^{d}_{Z_X}\right)\widehat{P}_{X} = 0 \quad (59)$$

Note that the similar condition can be derived without eq.(55) after a lengthy lines of equations.

Now the single Fock operator can be defined for a closed shell molecule X $(= D, C, B)$ as

$$\begin{aligned}\widehat{G}_X = {}& \frac{1}{2}\widehat{P}_X\left(\widehat{F}^\alpha + \widehat{F}^\beta + \Omega_X^d\right)\widehat{P}_X + \frac{1}{2}\left(\mathbf{1} - \widehat{P}_X\right)\left(\widehat{F}^\alpha + \widehat{F}^\beta + \Omega_X^u\right)\left(\mathbf{1} - \widehat{P}_X\right) \\ & + \eta_{dm-um}\left[\left\{\left(\mathbf{1} - \widehat{P}^d - \widehat{P}^s_A\right)\widehat{F}^\alpha + \left(\mathbf{1} - \widehat{P}^d\right)\widehat{F}^\beta\right\}\left(\mathbf{1} - \widehat{P}^d_{Z_X}\right)\widehat{P}_X + transpose\right]\end{aligned} \tag{60}$$

For the open shell molecule A, the condition for the SOMO has to be incorporated with the condition for the DOMO, and thus the Fock operator is defined as

$$\begin{aligned}\widehat{G}_A = {}& \frac{1}{2}\widehat{P}^d_A\left(\widehat{F}^\alpha + \widehat{F}^\beta + \Omega_A^\beta\right)\widehat{P}^d_A + \left(\mathbf{1} - \widehat{P}^d\right)\widehat{P}^s_A\left(\widehat{F}^\alpha + \Omega_A^\alpha\right)\widehat{P}^s_A\left(\mathbf{1} - \widehat{P}^d\right) \\ & + \frac{1}{2}\left(\mathbf{1} - \widehat{P}^d_A - \widehat{P}^s_A\right)\left(\widehat{F}^\alpha + \widehat{F}^\beta + \Omega_A^{\alpha um}\right)\left(\mathbf{1} - \widehat{P}^d_A - \widehat{P}^s_A\right) \\ & + \eta_{dm-smum}\left[\left\{(1 - \widehat{P}^d - \widehat{P}^s_A)\widehat{F}^\alpha + (1 - \widehat{P}^d)\widehat{F}^\beta\right\}\left(1 - \widehat{P}^d_{Z_A}\right)\widehat{P}^d_A + transpose\right] \\ & + \eta_{sm-um}\left[(1 - \widehat{P}^d - \widehat{P}^s_A)\widehat{F}^\alpha\widehat{P}^s_A + transpose\right]\end{aligned} \tag{61}$$

These Fock operators are solved within the basis set $\boldsymbol{\chi}_X$ of molecule X, where $\boldsymbol{\chi}_X$ is the row vector of the basis set on molecule X.

Up to now, we assume the existance of the SOMO, satisfying eq.(55), which is rewritten as

$$\boldsymbol{\chi}_A\boldsymbol{T}_{A_s} = \left(\mathbf{1} - \widehat{P}^d\right)\boldsymbol{\chi}_A\boldsymbol{T}_{A_s} \tag{62}$$

The equation implies that the SOMOs are expanded only by the basis set $\boldsymbol{\chi}_A$, but that they are orthogonal to all of the occupied orbitals, many of which are expanded by the basis sets on the other molecules. In the previous paper,[11] we demonstrated that there are many such external orbitals unless the basis sets are minimal.

If eq. (62) cannot be satisfied, the SOMO has to be delocalized over the basis sets on the other molecules to keep the SOMO orthogonal to all of the DOMO. To obtain the SOMO, a separate Fock operator is introduced as

$$\begin{aligned}\widehat{G}_{SOMO} = {}& \left(\mathbf{1} - \widehat{P}^d\right)\widehat{P}^s\left(\widehat{F}^\alpha + \Omega_A^\alpha\right)\widehat{P}^s\left(\mathbf{1} - \widehat{P}^d\right) \\ & + \eta_{sm-um}\left[(1 - \widehat{P}^d - \widehat{P}^s)\widehat{F}^\alpha\widehat{P}^s + transpose\right]\end{aligned} \tag{63}$$

and it is solved in terms of the full basis set $\{\boldsymbol{\chi}_D, \boldsymbol{\chi}_C, \boldsymbol{\chi}_B, \boldsymbol{\chi}_A\}$. By replacing $\widehat{P}^s_A$ with $\widehat{P}^s$, eq. (60) (now for $X = A$) is solved together with eq.(63) iteratively. The good localized initial guess for $\boldsymbol{T}_s$ is expected to be important.

3. Procedure to solve the single Fock equation for open-shell LP MO

In the single Fock formalism, the MO representation of the Fock matrix for molecule is often used[14]. When all of occupied and unoccupied molecular orbital coefficient matrix $\boldsymbol{T}_A$ of molecule A is known, the matrix elements of $\widehat{G}_A$ is blocked as

$$\begin{pmatrix} \widetilde{\boldsymbol{T}}_A^{dm} \\ \widetilde{\boldsymbol{T}}_A^{sm} \\ \widetilde{\boldsymbol{T}}_A^{um} \end{pmatrix} \widetilde{\boldsymbol{\chi}}_A \widehat{G}_A \boldsymbol{\chi}_A \begin{pmatrix} \boldsymbol{T}_A^{dm} & \boldsymbol{T}_A^{sm} & \boldsymbol{T}_A^{um} \end{pmatrix}$$

$$= \begin{array}{c|ccc} & dm & sm & um \\ \hline dm & \Lambda_{dm} & \eta_{dm-smum} G_{dm-sm} & \eta_{dm-smum} G_{dm-um} \\ sm & \eta_{dm-smum} \widetilde{G}_{dm-sm} & \Lambda_{sm} & \eta_{sm-um} G_{sm-um} \\ um & \eta_{dm-smum} \widetilde{G}_{dm-um} & \eta_{sm-um} \widetilde{G}_{sm-um} & \Lambda_{um} \end{array} \tag{64}$$

where sub-matrices Λ are diagonal (if the shift operators are all constant). For the closed shell molecule, the MO representation has a similar form except that there are no SOMO blocks. It can be easily proved that mixing terms arising from the stationary conditions do not contribute any to the diagonal blocks of the MO representation. When the convergence reaches, the off-diagonal blocks become zero; the stationary conditions are satisfied. But this procedure requires the MO coefficients even for the unoccupied orbitals. Recent years, even in the moderate level of approximations, a large basis set is required. So a procedure not requiring all of the MO coefficients is preferable. We define the AO (one-particle basis set) representation of the operator

$$\boldsymbol{G}_Y = \widetilde{\boldsymbol{\chi}}_Y \widehat{G}_Y \boldsymbol{\chi}_Y \tag{65}$$

then the general matrix eigenvalue problem

$$\boldsymbol{G}_Y \boldsymbol{T}_Y = \boldsymbol{S}_{YY} \boldsymbol{T}_Y \Lambda_Y \tag{66}$$

is solved, and only the coefficient matrices for the occupied orbitals are calculated. Here, the MOs in a molecule in the cluster become orthonormal. But the MOs between the different molecules are not.

The diagonal blocks are easy to evaluate for instance

$$\widetilde{\boldsymbol{\chi}}_A \widehat{P}_A^d \widehat{F}^\alpha \widehat{P}_A^d \boldsymbol{\chi}_A = \widetilde{\boldsymbol{P}}_A^d \boldsymbol{F}_{AA}^\alpha \boldsymbol{P}_A^d \tag{67}$$

where

$$\boldsymbol{P}_A^d \equiv \boldsymbol{T}_A^{dm} \widetilde{\boldsymbol{T}}_A^{dm} \boldsymbol{S}_{AA} \tag{68}$$

For the mixing term a little care is required. First we calculate the matrix element of the transposed form of the second term of the stationary condition (59) for the DOMO for a closed shell molecule X ;

$$\begin{aligned}
&\widetilde{\boldsymbol{\chi}}_{\boldsymbol{X}}\widehat{P}_{\boldsymbol{X}}\left[\left(\mathbf{1}-\widehat{P}^{d}_{Z_X}\right)\widehat{F}^{\beta}\left(\mathbf{1}-\widehat{P}^{d}\right)\right]\boldsymbol{\chi}_{\boldsymbol{X}}\\
&=\widetilde{\boldsymbol{\chi}}_{\boldsymbol{X}}\widehat{P}_{\boldsymbol{X}}\left[\left(\mathbf{1}-\widehat{P}^{d}_{Z_{\boldsymbol{X}}}\right)\widehat{F}^{\beta}-\left(\mathbf{1}-\widehat{P}^{d}_{Z_{\boldsymbol{X}}}\right)\widehat{F}^{\beta}\widehat{P}^{d}\right]\boldsymbol{\chi}_{\boldsymbol{X}}\\
&=\boldsymbol{S}_{\boldsymbol{X}\boldsymbol{X}}\boldsymbol{D}_{\boldsymbol{X}}\left(\boldsymbol{F}^{\beta}_{\boldsymbol{X}\boldsymbol{X}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\beta}_{Z_{\boldsymbol{X}},\boldsymbol{X}}\right)\\
&-\boldsymbol{S}_{\boldsymbol{X}\boldsymbol{X}}\boldsymbol{D}_{\boldsymbol{X}}\left(\ \boldsymbol{F}^{\beta}_{\boldsymbol{X}Z_{\boldsymbol{X}}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\beta}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}},\quad \boldsymbol{F}^{\beta}_{\boldsymbol{X}\boldsymbol{X}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\beta}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\ \right)\begin{pmatrix}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}}, & \boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\\ \boldsymbol{D}^{d}_{\boldsymbol{X}Z_{\boldsymbol{X}}}, & \boldsymbol{D}^{d}_{\boldsymbol{X}\boldsymbol{X}}\end{pmatrix}\begin{pmatrix}\boldsymbol{S}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\\ \boldsymbol{S}_{\boldsymbol{X}\boldsymbol{X}}\end{pmatrix}\\
&=\widetilde{\boldsymbol{P}}_{\boldsymbol{X}}\left(\boldsymbol{F}^{\beta}_{\boldsymbol{X}\boldsymbol{X}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\beta}_{Z_{\boldsymbol{X}},\boldsymbol{X}}\right)\left(\mathbf{1}-\boldsymbol{P}^{d}_{\boldsymbol{X}\boldsymbol{X}}\right)-\widetilde{\boldsymbol{P}}_{\boldsymbol{X}}\left(\boldsymbol{F}^{\beta}_{\boldsymbol{X}Z_{\boldsymbol{X}}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\beta}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}}\right)\boldsymbol{P}^{d}_{Z_{\boldsymbol{X}}\boldsymbol{X}}
\end{aligned}\tag{69}$$

where the projection operator matrix

$$\boldsymbol{P}^{d}\equiv\begin{pmatrix}\boldsymbol{P}^{d}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}} & \boldsymbol{P}^{d}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\\ \boldsymbol{P}^{d}_{\boldsymbol{X}Z_{\boldsymbol{X}}} & \boldsymbol{P}^{d}_{\boldsymbol{X}\boldsymbol{X}}\end{pmatrix}\equiv\begin{pmatrix}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}} & \boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\\ \boldsymbol{D}^{d}_{\boldsymbol{X}Z_{\boldsymbol{X}}} & \boldsymbol{D}^{d}_{\boldsymbol{X}\boldsymbol{X}}\end{pmatrix}\begin{pmatrix}\boldsymbol{S}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}}, & \boldsymbol{S}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\\ \boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}, & \boldsymbol{S}_{\boldsymbol{X}\boldsymbol{X}}\end{pmatrix}\tag{70}$$

and for the case of the delocalization of the SOMO, the projection operator $\boldsymbol{P}^{s}$ is defined as

$$\boldsymbol{P}^{s}\equiv\begin{pmatrix}\boldsymbol{P}^{s}_{Z_{\boldsymbol{A}}Z_{\boldsymbol{A}}} & \boldsymbol{P}^{s}_{Z_{\boldsymbol{A}}\boldsymbol{A}}\\ \boldsymbol{P}^{s}_{\boldsymbol{A}Z_{\boldsymbol{A}}} & \boldsymbol{P}^{s}_{\boldsymbol{A}\boldsymbol{A}}\end{pmatrix}\equiv\begin{pmatrix}\boldsymbol{D}^{s}_{Z_{\boldsymbol{A}}Z_{\boldsymbol{A}}} & \boldsymbol{D}^{s}_{Z_{\boldsymbol{A}}\boldsymbol{A}}\\ \boldsymbol{D}^{s}_{\boldsymbol{A}Z_{\boldsymbol{A}}} & \boldsymbol{D}^{s}_{\boldsymbol{A}\boldsymbol{A}}\end{pmatrix}\begin{pmatrix}\boldsymbol{S}_{Z_{\boldsymbol{A}}Z_{\boldsymbol{A}}}, & \boldsymbol{S}_{Z_{\boldsymbol{A}}\boldsymbol{A}}\\ \boldsymbol{S}_{\boldsymbol{A}Z_{\boldsymbol{A}}}, & \boldsymbol{S}_{\boldsymbol{A}\boldsymbol{A}}\end{pmatrix}\tag{71}$$

which is simplified as

$$\boldsymbol{P}^{s}_{A}=\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \boldsymbol{P}^{s}_{\boldsymbol{A}\boldsymbol{A}}\end{pmatrix}\tag{72}$$

if the SOMO can be locally obtained.

The density matrix for the co-group Z_X

$$\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\equiv\boldsymbol{T}^{d}_{Z_{\boldsymbol{X}}}\left(\widetilde{\boldsymbol{T}}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{S}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}}\boldsymbol{T}^{d}_{Z_{\boldsymbol{X}}}\right)^{-1}\widetilde{\boldsymbol{T}}^{d}_{Z_{\boldsymbol{X}}}\tag{73}$$

is defined. In the computations, the inverse matrix is required for each molecule at every iteration. For the weak interaction molecules in the cluster, the off-diagonal elements of MO overlap matrix are expected small, and so the approximation used in the coding; in Appendix A, the approximation is described.

The Fock matrix for molecule X becomes

$$\begin{aligned}
\boldsymbol{G}_{\boldsymbol{X}}&=\widetilde{\boldsymbol{\chi}}_{\boldsymbol{X}}\widehat{G}_{\boldsymbol{X}}\boldsymbol{\chi}_{\boldsymbol{X}}\\
&=\frac{1}{2}\widetilde{\boldsymbol{P}}_{\boldsymbol{X}}\boldsymbol{F}^{\alpha\beta}_{\boldsymbol{X}\boldsymbol{X}}\boldsymbol{P}_{\boldsymbol{X}}+\frac{1}{2}\left(\mathbf{1}-\widetilde{\boldsymbol{P}}_{\boldsymbol{X}}\right)\boldsymbol{F}^{\alpha\beta}_{\boldsymbol{X}\boldsymbol{X}}\left(\mathbf{1}-\boldsymbol{P}_{\boldsymbol{X}}\right)\\
&+\eta_{dm-um}\left[\widetilde{\boldsymbol{P}}_{\boldsymbol{X}}\left\{\begin{array}{c}\left(\boldsymbol{F}^{\alpha\beta}_{\boldsymbol{X}\boldsymbol{X}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\alpha\beta}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\right)\left(\mathbf{1}-\boldsymbol{P}^{d}_{\boldsymbol{X}\boldsymbol{X}}\right)\\ -\left(\boldsymbol{F}^{\alpha\beta}_{\boldsymbol{X}Z_{\boldsymbol{X}}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\alpha\beta}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}}\right)\boldsymbol{P}^{d}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\end{array}\right\}+transpose\right]\\
&+\eta_{dm-um}\left[-\widetilde{\boldsymbol{P}}_{\boldsymbol{X}}\left\{\begin{array}{c}\left(\boldsymbol{F}^{\alpha}_{\boldsymbol{X}\boldsymbol{X}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\alpha}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\right)\boldsymbol{P}^{s}_{\boldsymbol{X}\boldsymbol{X}}\\ +\left(\boldsymbol{F}^{\alpha}_{\boldsymbol{X}Z_{\boldsymbol{X}}}-\boldsymbol{S}_{\boldsymbol{X}Z_{\boldsymbol{X}}}\boldsymbol{D}^{d}_{Z_{\boldsymbol{X}}}\boldsymbol{F}^{\alpha}_{Z_{\boldsymbol{X}}Z_{\boldsymbol{X}}}\right)\boldsymbol{P}^{s}_{Z_{\boldsymbol{X}}\boldsymbol{X}}\end{array}\right\}+transpose\right]
\end{aligned}\tag{74}$$

where $\boldsymbol{F}^{\alpha\beta} = \boldsymbol{F}^{\alpha} + \boldsymbol{F}^{\beta}$.

The matrix element of the transposed form of the stationary condition (54) for the SOMO for molecule A is

$$\begin{aligned}
&\boldsymbol{\chi}_A \widehat{P}^s_{As} \left[\widehat{F}^{\alpha} \left(\mathbf{1} - \widehat{P}^d - \widehat{P}^s_{As} \right) \right] \boldsymbol{\chi}_A \\
&= \widetilde{\boldsymbol{\chi}}_A \widehat{P}^s_A \left[\widehat{F}^{\alpha} - \widehat{F}^{\alpha} \widehat{P}^d - \widehat{F}^{\alpha} \widehat{P}^s_{As} \right] \boldsymbol{\chi}_A \\
&= \boldsymbol{S}_{AA} \boldsymbol{D}^s_A \boldsymbol{F}^{\alpha}_{AA} \\
&- \boldsymbol{S}_{\boldsymbol{AA}} \boldsymbol{D}^s_{\boldsymbol{A}} \left(\ \boldsymbol{F}^{\alpha}_{AZ_A}, \quad \boldsymbol{F}^{\alpha}_{\boldsymbol{AA}} \ \right) \begin{pmatrix} \boldsymbol{D}^d_{Z_A Z_A}, & \boldsymbol{D}^d_{Z_A \boldsymbol{A}} \\ \boldsymbol{D}^d_{\boldsymbol{A} Z_A}, & \boldsymbol{D}^d_{\boldsymbol{AA}} \end{pmatrix} \begin{pmatrix} \boldsymbol{S}_{Z_A \boldsymbol{A}} \\ \boldsymbol{S}_{\boldsymbol{AA}} \end{pmatrix} \\
&- \boldsymbol{S}_{\boldsymbol{AA}} \boldsymbol{D}^s_{\boldsymbol{A}} \left(\ \boldsymbol{F}^{\alpha}_{AZ_A}, \quad \boldsymbol{F}^{\alpha}_{\boldsymbol{AA}} \ \right) \begin{pmatrix} \boldsymbol{D}^s_{Z_A Z_A}, & \boldsymbol{D}^s_{Z_A \boldsymbol{A}} \\ \boldsymbol{D}^s_{\boldsymbol{A} Z_A}, & \boldsymbol{D}^s_{\boldsymbol{AA}} \end{pmatrix} \begin{pmatrix} \boldsymbol{S}_{Z_A \boldsymbol{A}} \\ \boldsymbol{S}_{\boldsymbol{AA}} \end{pmatrix} \\
&= \widetilde{\boldsymbol{P}}^s_A \left[\boldsymbol{F}^{\alpha} \left(\mathbf{1} - \boldsymbol{P}^d - \boldsymbol{P}^s \right) \right]_{A,A}
\end{aligned} \tag{75}$$

where the suffix A, A implies the A, A block of (N_{basis}, N_{basis}) matrix. The mixing term of the DOMO and UOMO also requires a care;

$$\begin{aligned}
&\widetilde{\boldsymbol{\chi}}_A \widehat{P}^d_A \left(1 - \widehat{P}^d_{Z_A} \right) \widehat{F}^{\beta} (1 - \widehat{P}^d) \boldsymbol{\chi}_A \\
&= \widetilde{\boldsymbol{P}}^d_A \left[\boldsymbol{F}^{\beta}_{AA} - \boldsymbol{S}_{\boldsymbol{A} Z_{\boldsymbol{A}}} \boldsymbol{D}^d_{Z_A} \boldsymbol{F}^{\beta}_{Z_A \boldsymbol{A}} \right] \\
&- \widetilde{\boldsymbol{P}}^d_A \left[\left(\ \boldsymbol{F}^{\beta}_{AZ_A}, \quad \boldsymbol{F}^{\beta}_{\boldsymbol{AA}} \ \right) - \boldsymbol{S}_{\boldsymbol{A} Z_{\boldsymbol{A}}} \boldsymbol{D}^d_{Z_A} \left(\boldsymbol{F}^{\beta}_{Z_A Z_A}, \boldsymbol{F}^{\beta}_{Z_A \boldsymbol{A}} \right) \right] \begin{pmatrix} \boldsymbol{P}^d_{Z_A \boldsymbol{A}} \\ \boldsymbol{P}^d_{\boldsymbol{AA}} \end{pmatrix}
\end{aligned} \tag{76}$$

The Fock matrix for the open shell molecule is

$$\begin{aligned}
\boldsymbol{G}_A &= \widetilde{\boldsymbol{\chi}}_A \widehat{G}_A \boldsymbol{\chi}_A \\
&= \frac{1}{2} \widetilde{\boldsymbol{P}}^d_A \boldsymbol{F}^{\alpha\beta}_{AA} \boldsymbol{P}^d_A + \left(1 - \widetilde{\boldsymbol{P}}^d \right) \widetilde{\boldsymbol{P}}^s_A \boldsymbol{F}^{\alpha}_{AA} \boldsymbol{P}^s_A \left(1 - \boldsymbol{P}^d \right) \\
&+ \frac{1}{2} \left(\mathbf{1} - \widetilde{\boldsymbol{P}}^d_A - \widetilde{\boldsymbol{P}}^s_A \right) \boldsymbol{F}^{\alpha\beta}_{AA} \left(\mathbf{1} - \boldsymbol{P}^d_A - \boldsymbol{P}^s_A \right) \\
&+ \eta_{dm-smum} \begin{bmatrix} \widetilde{\boldsymbol{P}}^d_A \left(\boldsymbol{F}^{\alpha\beta}_{AA} - \boldsymbol{S}_{\boldsymbol{A} Z_{\boldsymbol{A}}} \boldsymbol{D}^d_{Z_A} \boldsymbol{F}^{\alpha\beta}_{Z_A \boldsymbol{A}} \right) \\ -\widetilde{\boldsymbol{P}}^d_A \left[\left(\ \boldsymbol{F}^{\alpha\beta}_{AZ_A}, \quad \boldsymbol{F}^{\alpha\beta}_{\boldsymbol{AA}} \ \right) - \boldsymbol{S}_{\boldsymbol{A} Z_{\boldsymbol{A}}} \boldsymbol{D}^d_{Z_A} \left(\boldsymbol{F}^{\alpha\beta}_{Z_A Z_A}, \boldsymbol{F}^{\alpha\beta}_{Z_A \boldsymbol{A}} \right) \right] \begin{pmatrix} \boldsymbol{P}^d_{Z_A \boldsymbol{A}} \\ \boldsymbol{P}^d_{\boldsymbol{AA}} \end{pmatrix} \\ -\widetilde{\boldsymbol{P}}^d_A \left[\left(\ \boldsymbol{F}^{\alpha}_{AZ_A}, \quad \boldsymbol{F}^{\alpha}_{\boldsymbol{AA}} \ \right) - \boldsymbol{S}_{\boldsymbol{A} Z_{\boldsymbol{A}}} \boldsymbol{D}^d_{Z_A} \left(\boldsymbol{F}^{\alpha}_{Z_A Z_A}, \boldsymbol{F}^{\alpha}_{Z_A \boldsymbol{A}} \right) \right] \begin{pmatrix} \boldsymbol{P}^s_{Z_A \boldsymbol{A}} \\ \boldsymbol{P}^s_{\boldsymbol{AA}} \end{pmatrix} \\ +transpose \end{bmatrix}
\end{aligned} \tag{77}$$

$$+ \eta_{sm-um} \left[\widetilde{\boldsymbol{P}}^s_A \left[\boldsymbol{F}^{\alpha} \left(\mathbf{1} - \boldsymbol{P}^d - \boldsymbol{P}^s \right) \right]_{A,A} + transpose \right] \tag{78}$$

The code was developed in MOLYX package^{16} and some test calculations will be published separately. In the present code, an option is added to solve the non-orthogonal super-molecule Hartree-Fock equation (49), using the LP MO as an initial guess MO. The code works also for the cluster only of closed shell molecules, and the agreement with the previous code[10] was examined.

As we have shown in our previous works[10][11][12], the LP MO is a deficient method without including the partial electron delocalization. It is expected that this deficiency is more profound for the open shell cluster than for the closed shell cluster; the perturbation expansion or the other correlated methods have to be developed.

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Appendix A

The projection operator $\widehat{P}_{Z_A}$ for the co-group Z_A is required in solving the equation for molecule A. The required matrix is

$$\boldsymbol{D}_{Z_A}\boldsymbol{S}_{Z_A A} \equiv \boldsymbol{T}_{Z_A}\left(\widetilde{\boldsymbol{T}}_{Z_A}\boldsymbol{S}_{Z_A Z_A}\boldsymbol{T}_{Z_A}\right)^{-1}\widetilde{\boldsymbol{T}}_{Z_A}\boldsymbol{S}_{Z_A A} \tag{79}$$

in which the inverse MO overlap matrix has to be evaluated. Because the MO matrix $\boldsymbol{T}_{Z_A}$ is blocked, it becomes the sum

$$\boldsymbol{D}_{Z_A}\boldsymbol{S}_{Z_A A} = \sum_{D\neq A}\sum_{F\neq A}\boldsymbol{T}_D\mathcal{R}_{DF}\widetilde{\boldsymbol{T}}_F\boldsymbol{S}_{FA} \tag{80}$$

where $\mathcal{R}_{DF}$ is the block of the MO inverse matrix $\left(\widetilde{\boldsymbol{T}}_{Z_A}\boldsymbol{S}_{Z_A Z_A}\boldsymbol{T}_{Z_A}\right)^{-1}$. Assuming the MO overlap between the different molecules in the cluster is small, the sum is approximated as

$$\begin{aligned}\boldsymbol{D}_{Z_A}\boldsymbol{S}_{Z_A A} \approx &\sum_{D\neq A}\left\{\boldsymbol{T}_D^d\widetilde{\boldsymbol{T}}_D^d\boldsymbol{S}_{DX} + \sum_{G\neq X,D}\boldsymbol{T}_D^d\mathcal{M}_{DG}\mathcal{M}_{GD}\widetilde{\boldsymbol{T}}_D^d\boldsymbol{S}_{DX}\right\} \\ &-\sum_{D\neq A}^{D\neq F}\sum_{F\neq A}\boldsymbol{T}_D^d\mathcal{M}_{DF}\widetilde{\boldsymbol{T}}_F^d\boldsymbol{S}_{FX}\end{aligned} \tag{81}$$

where the MOs in each constituent molecule is assumed to be normalized as $\boldsymbol{T}_D^d\boldsymbol{S}_{DD}\widetilde{\boldsymbol{T}}_D^d = 1$. In the previous paper[10], we examined the accuracy of the approximation. Even when only the first term is retained, the calculated total energy was accurate enough.

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