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Basis set superposition error free self-consistent field method for molecular interaction in multi-component systems: Projection operator formalism

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The self-consistent field method for molecular interaction (SCF MI) by Gianinetti, Raimondi, and Tornaghi is extended to multi-component systems. A set of equations are written with projection operators, and the accurate approximate equations are derived. The method is applied to water clusters and to a fluoride anion complex with a water dimer. The calculated interaction energies are compared with those estimated with the counterpoise method, and they converge to smaller values for extensive basis sets. The underestimation of the binding energy results from the omission of the most part of charge transfer contribution in the wave function. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1388039]

I. INTRODUCTION

Recently, extensive experimental and theoretical studies on the weak molecular interactions have been reported. The molecular recognition in a biomolecular system is acted by these weak interactions.[1] The molecular clusters bonded by van der Waals interaction and hydrogen bonds have been known as the intermediates of microscopic to mesoscopic systems. In these fields, it is important to estimate the accurate interaction energies. In the molecular orbital theory, the energy is evaluated by the supermolecular approach, in which the interaction energy is calculated as a difference between the energy of the cluster and a sum of the energies of constituent molecules. It has, however, been known that the basis set superposition error (BSSE) due to the basis set incompleteness makes it difficult to accurately estimate the interaction energy. The counterpoise (CP) scheme introduced by Boys and Bernardi[2–4] has extensively been applied in the studies of molecular interactions to eliminate the BSSE. However, it requires $n+1$ computations for a cluster consisting of n molecules. Furthermore, in large or strong interaction systems Xantheas emphasized the importance of BSSE in the structural optimization.[5] There are a few other methods proposed to eliminate the BSSE; one of them is the chemical Hamiltonian approach (CHA) by Mayer,[6,7] and another is the self-consistent field for molecular interaction (SCF MI) for a two-component system by Gianinetti *et al.*[8] Later they extended the SCF MI to a multi-component system.[9] Local correlation methods developed Pulay and co-workers[10,11] were extensively examined by Schütz, Rauhut and Werner[12] to estimate the incremental BSSE at the correlated level.

In this work, using the projection operators, we reformulate the SCF MI for a two-component system by Gianinetti *et al.*[8] The meaning of the equations to be solved becomes more transparent than the original equations, and besides, by generalizing the projection operators, the equations are extended to multi-component systems straightforwardly. It is proved that the equations can be simplified to a form which requires less computational costs. The set of equations indicates that the locally projected SCF method (LP SCF MI) is a more appropriate name than the SCF MI.

To demonstrate the applicability of the present methods, we calculate the interaction energies of the clusters of water molecules (dimer to pentamer) and of fluoride anion (F^-) complexes with a water dimer. Water clusters are the subject of intense research because of their importance in understanding hydrogen bonds and in interpreting various unique features of the structure, dynamics and energetics of condensed phase of water, and because the hydrogen bonds of water molecules are ubiquitous in biological, chemical, and physical systems.[13]

II. FORMULATION WITH PROJECTION OPERATORS

The set of equations for SCF MI derived by Gianinetti *et al.*[8] is simple, but the meaning of the equations is not clear. The equations can be written more transparently by using the projection operators. The projection operator $\hat{P}_{Aoc}$ on to the occupied orbitals of unit A $\{|a_j\rangle,\ j=1,\ M^A\}$ is defined as

$$\hat{P}_{Aoc} \equiv \sum_{i,j=1}^{M_A} |a_j\rangle [(\mathbf{S}_{AA})^{-1}]_{j,i} \langle a_i|, \tag{1}$$

where the matrix $\mathbf{S}_{AA}$ is the overlap matrix in terms of the occupied molecular orbitals $\{|a_j\rangle\}$. Since $\{|a_j\rangle\}$ are expanded within the basis sets centered on the atoms of unit A as

$$|a_j\rangle = \sum_{p=1}^{N^A} |\chi_p^A\rangle t_{pj}, \tag{2}$$

the overlap matrix $\mathbf{S}_{AA}$ is

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$$\mathbf{S}_{AA} \equiv \tilde{\mathbf{T}}_{Aoc}\mathbf{S}^{AA}\mathbf{T}_{Aoc}, \tag{3}$$

where $\mathbf{S}^{AA}$ is the overlap matrix in terms of the basis set $\{|\chi_p^A\rangle, p=1,N^A\}$. Hereafter, the subscripts imply that the matrix is in terms of molecular orbitals (MO), and the superscripts are in terms of basis sets. The rectangular matrix $\mathbf{T}_{Aoc}$ is defined by the molecular orbital vector $\mathbf{t}_j$ as $(\mathbf{t}_1, \mathbf{t}_2, \cdots, \mathbf{t}_{M_A})$. Similarly, the projection operator $\hat{P}_{Boc}$ on to the occupied orbitals of unit B is defined

$$\hat{P}_{Boc} \equiv \sum_{i,j=M_A+1}^{M_A+M_B} |b_j\rangle[(\mathbf{S}_{BB})^{-1}]_{j,i}\langle b_i|, \tag{4}$$

with

$$|b_j\rangle = \sum_{p=N^A+1}^{N^A+N^B} |\chi_p^B\rangle t_{pj}, \tag{5}$$

$$\mathbf{S}_{BB} \equiv \tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BB}\mathbf{T}_{Boc}. \tag{6}$$

Our basis sets are $\{|\chi_p^A\rangle\} \oplus \{|\chi_p^B\rangle\}$, and the number of basis sets is N^A+N^B. Because of the definition Eqs. (2) and (5), the MO coefficient matrices $\mathbf{T}_{Aoc}$ and $\mathbf{T}_{Boc}$ are rectangular matrices of $N^A \times M_A$ and $N^B \times M_B$, respectively.

Now, equipped with the projection operators thus defined, the equation for the molecular orbitals of unit A under a restriction of Eq. (2), derived by Gianinetti *et al.*, becomes

$$(1-\hat{P}_{Boc})\hat{F}(1-\hat{P}_{Boc})|a_j\rangle = (1-\hat{P}_{Boc})|a_j\rangle\varepsilon_j, \tag{7}$$

which can be written in terms of the basis sets $\{|\chi_p^A\rangle, p=1,N^A\}$ and the molecular orbital vector as

$$\begin{aligned}&(\mathbf{1}^A, \quad -\mathbf{S}^{AB}\mathbf{T}_{Boc}(\tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BB}\mathbf{T}_{Boc})^{-1}\tilde{\mathbf{T}}_{Boc})\begin{pmatrix}\mathbf{F}^{AA}, & \mathbf{F}^{AB}\\ \mathbf{F}^{BA}, & \mathbf{F}^{BB}\end{pmatrix}\\ &\times\begin{pmatrix}\mathbf{1}^A\\ -\mathbf{T}_{Boc}(\tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BB}\mathbf{T}_{Boc})^{-1}\tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BA}\end{pmatrix}\mathbf{T}_A\\ &=(\mathbf{S}^A-\mathbf{S}^{AB}\mathbf{T}_{Boc}(\tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BB}\mathbf{T}_{Boc})^{-1}\tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BA})\mathbf{T}_A\mathbf{L}_A,\end{aligned} \tag{8}$$

where $\mathbf{1}^A$ is a unit matrix of N^A, $\mathbf{L}_A$ is a diagonal matrix of orbital energy ε_j, and $\mathbf{S}^{AB}$ is the overlap matrix between the basis sets $\{|\chi_p^A\rangle\}$ and $\{|\chi_p^B\rangle\}$. Now it becomes clear that Eq. (8) is equivalent to Eqs. (26) and (27) of Gianinetti *et al.*[8] with the definition of $\mathbf{T}_{Boc}(\tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BB}\mathbf{T}_{Boc})^{-1}\tilde{\mathbf{T}}_{Boc} \equiv \mathbf{D}^{BB}$.

The meaning of Eq. (7) is obvious; the occupied orbitals $\{|a_j\rangle\}$ of unit A are determined outside the space spanned by the occupied orbitals $\{|b_j\rangle\}$ of unit B. The set of equations for units A and B has to be solved iteratively. By multiplying $\langle b_l|$ from the left in Eq. (7), we obtain the relation

$$\langle b_l|(1-\hat{P}_{Boc})\hat{F}(1-\hat{P}_{Boc})|a_j\rangle = \langle b_l|(1-\hat{P}_{Boc})|a_j\rangle\varepsilon_j = 0. \tag{9}$$

With the formulation of Eq. (7), generalization to the spin unrestricted Hartree–Fock (HF) method as well as the open shell restricted HF method becomes trivial. Similarly, the equation can easily be extended to a multi-component system. We introduce the projection operator $\hat{P}_{\ominus Aoc}$ which projects the space spanned by the occupied molecular orbitals except on unit A as

$$\hat{P}_{\ominus Aoc} = \sum_{B,C\neq A}\sum_{j\subset B}\sum_{k\subset C} |b_j\rangle[(\mathbf{S}_{\ominus A})^{-1}]_{j,k}\langle c_k|, \tag{10}$$

where $\mathbf{S}_{\ominus A}$ is the overlap matrix in terms of the occupied orbitals $\{|b_j\rangle\}, \{|c_j\rangle\}, \ldots, \{|f_j\rangle\}$ except on unit A $\{|a_j\rangle\}$. For multi-component systems, Eq. (7) is simply replaced with

$$(1-\hat{P}_{\ominus Aoc})\hat{F}(1-\hat{P}_{\ominus Aoc})|a_j\rangle = (1-\hat{P}_{\ominus Aoc})|a_j\rangle\varepsilon_j, \tag{11}$$

and the corresponding matrix representation can easily be derived. The size of MO overlap matrix $\mathbf{S}_{\ominus A}$ is a sum of the numbers of occupied orbitals

$$\sum_{B\neq A} M_B, \tag{12}$$

and the matrix $\mathbf{S}_{\ominus A}$ is symbolically written as

$$\begin{aligned}\mathbf{S}_{\ominus A} &= (\tilde{\mathbf{T}}_{Boc}, \tilde{\mathbf{T}}_{Coc}, \ldots, \tilde{\mathbf{T}}_{Foc})\\ &\quad\times\sum_{D\neq A}\sum_{E\neq A}\mathbf{S}^{DE}(\mathbf{T}_{Boc}, \mathbf{T}_{Coc}, \ldots, \mathbf{T}_{Foc}),\end{aligned} \tag{13}$$

and it is blocked as $\mathbf{S}_{BB} \equiv \tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BB}\mathbf{T}_{Boc}$, $\mathbf{S}_{BC} \equiv \tilde{\mathbf{T}}_{Boc}\mathbf{S}^{BC}\mathbf{T}_{Coc}, \ldots, \mathbf{S}_{FF} \equiv \tilde{\mathbf{T}}_{Foc}\mathbf{S}^{FF}\mathbf{T}_{Foc}$. The diagonal blocks such as $\mathbf{S}_{BB}$ are close to a unit matrix, and, on the other hand, the matrix elements of the off-diagonal blocks are expected to be much smaller than 1. Therefore, the corresponding blocks of the inverse matrix $(\mathbf{S}_{\ominus A})^{-1}$ can be expanded in terms of the block matrices $\{\mathbf{S}_{BC}\}$. To make it clear, we introduce a matrix $\mathbf{R}_{\ominus A}$,

$$\mathbf{R}_{\ominus A} \equiv (\mathbf{S}_{\ominus A})^{-1}, \tag{14}$$

and its block matrices $\{\mathbf{R}_{BC}\}$. Each block is expanded in terms of the inverse of the diagonal blocks $\{(\mathbf{S}_{BB})^{-1}\}$ and of the off-diagonal blocks $\{\mathbf{S}_{BC}\}$. The diagonal block is

$$\begin{aligned}\mathbf{R}_{BB} &= (\mathbf{S}_{BB})^{-1} - \sum_{D\neq A,B}(\mathbf{S}_{BB})^{-1}\mathbf{S}_{BD}(\mathbf{S}_{DD})^{-1}\mathbf{S}_{DB}(\mathbf{S}_{BB})^{-1}\\ &\quad+\sum_{D\neq A,B}\sum_{E\neq A,B,D\neq E}(\mathbf{S}_{BB})^{-1}\mathbf{S}_{BD}(\mathbf{S}_{DD})^{-1}\\ &\quad\times\mathbf{S}_{DE}(\mathbf{S}_{EE})^{-1}\mathbf{S}_{EB}(\mathbf{S}_{BB})^{-1} - \cdots,\end{aligned} \tag{15}$$

and the off-diagonal block is

$$\begin{aligned}\mathbf{R}_{BC} &= +(\mathbf{S}_{BB})^{-1}\mathbf{S}_{BC}(\mathbf{S}_{CC})^{-1}\\ &\quad-\sum_{D\neq A,B}(\mathbf{S}_{BB})^{-1}\mathbf{S}_{BD}(\mathbf{S}_{DD})^{-1}\mathbf{S}_{DC}(\mathbf{S}_{CC})^{-1} + \cdots.\end{aligned} \tag{16}$$

Note that the second term in Eq. (15) is the third order of the inverse matrix of the MO overlap matrix $(\mathbf{S}_{BB})^{-1}$ and the first term of Eq. (16) is the second order. Inserting the expansion Eqs. (15) and (16) into Eq. (10), and taking only the first order of $(\mathbf{S}_{BB})^{-1}$, we can approximate the set of Eqs. (11) to be solved as

$$\left(1-\sum_{B\neq A}\hat{P}_{Boc}\right)\hat{F}\left(1-\sum_{B\neq A}\hat{P}_{Boc}\right)|a_j\rangle$$
$$=\left(1-\sum_{B\neq A}\hat{P}_{Boc}\right)|a_j\rangle\varepsilon_j\,. \tag{17}$$

The advantage of using the approximate equations is that the dimension of the inverse matrix to be evaluated is M_B, the number of occupied orbitals of each unit, but if we use the exact Eq. (11), we have to invert the full $\Sigma_{B\neq A}M_B$ size of matrix every iteration in solving the equation for each unit. So in the present study, we have mostly used the approximate Eqs. (17). In practice, this approximation is accurate, because the ratios such as $(\mathbf{S}_{BB})^{-1}\mathbf{S}_{BD}$ are small, and because only higher than the third order in the diagonal blocks and the second order in the off-diagonal blocks are discarded. Alternatively, we can use Eq. (17) until the convergency is nearly reached, and then for the last few iterations, the exact Eq. (7) is solved to ensure the equality similar to Eq. (9).

Recently Gianinetti *et al.* extended the SCF MI to a multi-component system.[9] Their equations are more complicated than our Eq. (11). We have not proved the equivalency of our equations for the multi-component system with those of Gianinetti *et al.* We have numerically confirmed that our calculated binding energy of a water trimer is equal to theirs.

As Gianinetti *et al.* have proved, the energy is variationally optimized, and the first derivative of the energy can be evaluated, using the ordinal equations by properly replacing the density matrix with that of the nonorthogonal molecular orbitals. To evaluate the second derivative, the derivatives of the MO coefficients have to be calculated by solving the coupled perturbed Hartree–Fock (CPHF) equation. A little more algebra is required to obtain the equations for the nonorthogonal molecular orbitals under the projection operators.

III. COMPUTATIONAL DETAILS

The computer program is coded as a part of the MOLYX package[14,15] which uses GAMESS-US's integral routines.[16] In the present test calculations, we use a series of Dunning's correlation-consistent polarized valence basis sets.[17] The series forms a hierarchy of increasing basis set quality (cc-pVXZ, X=D, T, Q, and 5 for double, triple, quadruple, and quintuple zeta). Recently, using this series of basis sets, Rappé and Bernstein systematically examined the basis set dependence on the nonbonding interaction and BSSE.[18] In addition, we examine the contribution of diffuse functions with aug-cc-pVXZ.[19] The BSSE is evaluated by following the equation given by Xantheas.[5]

IV. RESULTS AND DISCUSSION

To examine the present locally projected (LP) SCF method for molecular interaction (MI), the size dependence of the binding energies of water clusters is calculated. The structures of the most stable water clusters are known to be cyclic up to a pentamer.[13,20,21] The structures are reoptimized with the SCF/cc-pVDZ and /aug-cc-pVTZ levels of approximation, and are shown in Fig. 1. For the pentamer, we intentionally calculated a less stable isomer which has a central water molecule with four hydrogen bonds and contains two strained rings. It is expected to have a larger BSSE than the cyclic pentamer.

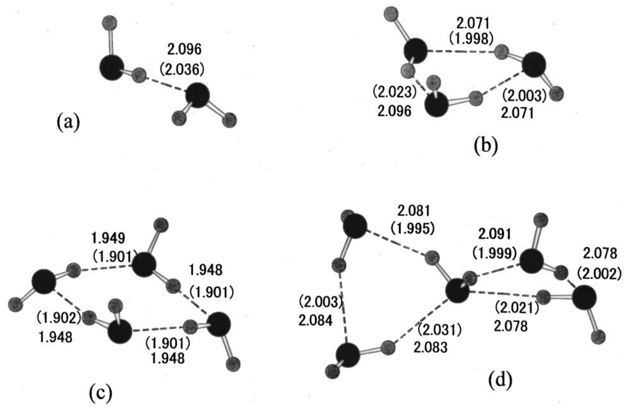

FIG. 1. The geometries of water clusters used in the calculations in Tables I, II, and III. They are optimized with the SCF/aug-cc-pVTZ (SCF/cc-pVDZ) level of approximation.

First we examine the accuracy of the approximate Eqs. (17) for trimer to pentamer of water clusters and for $F^-(H_2O)_2$. Table I shows the difference of the interaction energies evaluated by Eqs. (11) and (17). When the basis set does not contain any diffuse functions, the errors are less than 0.002 kcal/mol. Even for the basis sets augmented with diffuse functions, the maximum error is 0.012 kcal/mol. This accuracy is much better than we expected. As shown in Fig. 1, the hydrogen bonds determined with the cc-VDZ basis set are shorter than those with the aug-cc-VTZ basis set. Therefore, the approximation Eq. (17) for the same basis set is slightly worse for geometries (a) than for geometries (b). As expected, the pentamer has the largest error for both geometries. The interaction between F^- and water molecules is very strong, and therefore, the error is large particularly for geometry (a). Table 1 clearly demonstrates that the approximate Eq. (17) can be used even for these strong interaction cases in place of the exact Eqs. (11). Thus, hereafter, all results shown are the energies based on Eq. (17).

The calculated binding energies for water clusters are given in Tables II and III. In Figs. 2 and 3 the size and basis set dependencies of the total binding energies are shown. The energies of Table II and Figs. 2 and 3 are calculated at the geometries optimized with the SCF/cc-pVDZ level of ap-

TABLE I. Energy difference (kcal/mol) between the exact Eq. (11) and approximate Eq. (17) LP SCF MI equations. (a) Geometry optimized with the cc-pVDZ, (b) with the aug-cc-pVTZ.

Clusters	Geometry	cc-pVDZ	cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ
$(H_2O)_3$	(a)	0.0000	−0.0013	−0.0063	
	(b)			−0.0019	−0.0094
$(H_2O)_4$	(a)	0.0000	0.0000	−0.0044	
	(b)			−0.0031	
$(H_2O)_5$	(a)	0.0000		−0.0119	
	(b)			−0.0050	
$F^-(H_2O)_2$	(a)	0.0000		−0.0082	−0.0094
	(b)			−0.0006	−0.0019

TABLE II. The binding energies (in kcal/mol) of water clusters, optimized with the SCF/cc-pVDZ level of approximation.

Basis set		Dimer	Trimer	Tetramer	Pentamer
cc-pVDZ	SCF	−5.71	−17.32	−29.33	−34.77
	CP BSSE corr.	−4.05	−11.35	−20.74	
	LP SCF MI	−3.42	−8.96	−16.23	−17.80
	Δ(LP-CP)[a]	0.63	2.39	4.51	
	Δ(LP−SCF)[b]	2.29	8.36	13.10	16.97
cc-pVTZ	SCF	−4.35	−12.88	−22.69	
	CP BSSE corr.	−3.61	−10.74	−19.49	
	LP SCF MI	−3.28	−8.91	−15.54	
	Δ(LP-CP)[a]	0.33	1.83	3.95	
	Δ(LP−SCF)[b]	1.07	3.97	7.15	
cc-pVQZ	SCF	−3.89			
	CP BSSE corr.	−3.61			
	LP SCF	−3.05			
	Δ(LP-CP)[a]	0.56			
	Δ(LP−SCF)[b]	0.84			
aug-cc-pVDZ	SCF	−3.80	−11.09	−20.03	−22.50
	CP BSSE corr.	−3.63	−10.49	−19.11	
	LP SCF	−2.91	−7.80	−13.89	−15.36
	Δ(LP-CP)[a]	0.72	2.69	5.22	
	Δ(LP−SCF)[b]	0.89	3.29	6.14	7.14
aug-cc-pVTZ	SCF	−3.66	−10.61	−19.40	
	CP BSSE corr.	−3.60	−10.48	−19.17	
	LP SCF MI	−2.96	−8.07	−14.28	
	Δ(LP-CP)[b]	0.64	2.41	4.89	
	Δ(LP−SCF)[c]	0.70	2.54	5.12	
aug-cc-pVQZ	SCF	−3.66			
	CP BSSE corr.	−3.62			
	LP SCF MI	−3.00			
	Δ(LP-CP)[b]	0.62			
	Δ(LP−SCF)[c]	0.66			

[a] The difference between the LP SCF MI and CP corrected energies.

[b] The difference between the LP SCF MI and SCF energy. In other words, it is the BSSE estimated with the LP SCF MI.

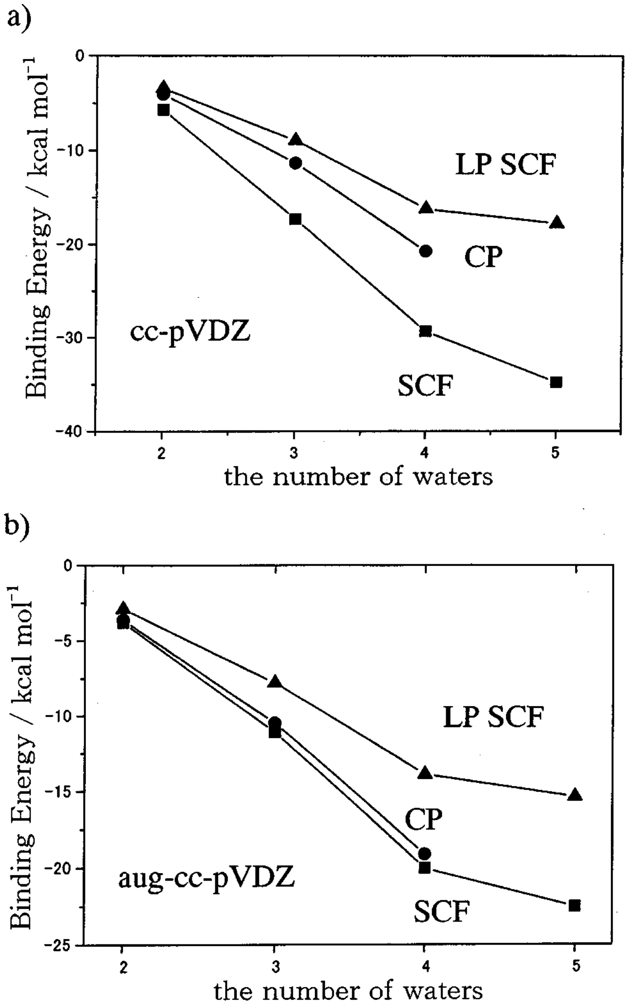

FIG. 2. The size dependence of the total binding energy of water clusters $(H_2O)_n$ for the SCF, CP BSSE corrected SCF, and LP SCF MI methods. The geometries are determined with the SCF/cc-pVDZ level of approximation. (a) The basis set: cc-pVDZ. (b) The basis set: aug-cc-pVDZ.

proximation. As is now well known,[18] Table II and the figures demonstrate that the large BSSE in the SCF/cc-pVXZ calculations is substantially reduced by adding the diffuse functions as in aug-cc-pVXZ; the counterpoise (CP) correction becomes less than 1 kcal mol^{-1} in the augmented basis sets. The difference Δ(LP−SCF) between the SCF and locally projected SCF (LP SCF MI, or SCF MI) is large, which was noticed by Gianinetti *et al.* in their test calculations for the dimer.[8] The larger basis sets in the series of cc-pVXZ and of aug-cc-pVXZ sets yield smaller Δ(LP−SCF) with one exception. Also Δ(LP−SCF) in aug-cc-pVXZ is slightly smaller than in the corresponding cc-pVXZ. Figures 2 and 3 show that the binding energy evaluated with LP SCF MI converges to a higher value than the CP corrected energy. The underestimation for the binding energy in LP SCF MI is inherent to the method, because of the small variational space for the occupied molecular orbitals of each molecular unit. The electron delocalization over the molecular units is almost prohibited by the restricted basis set expansion such as Eqs. (2) and (5). So it is expected that the charge transfer (CT) interaction is substantially underestimated in LP SCF MI. In strong hydrogen bonds such as in the water clusters, the contribution from the CT interaction is large. Very recently Hamza *et al.*[22] systematically examined the difference among their chemical Hamiltonian approach (CHA), CP correction and SCF MI. They noted that the SCF MI underestimated the binding energy, while their CHA agreed with the CP correction for large basis sets. They attributed this difference to the lack of the charge transfer effects in the SCF MI. We will analyze the electron delocalization in the LP SCF MI in details at the last part of this section and in the Appendix. As Fig. 2 and Table II show, the

TABLE III. The binding energies (in kcal/mol) of water clusters, evaluated with the SCF/ aug-cc-pVTZ level of approximation at the geometries optimized at the SCF/aug-cc-pVTZ (SCF/cc-pVDZ) level.

	Dimer	Trimer	Tetramer
SCF	−3.74(−3.66)	−11.13(−10.61)	−19.80(−19.40)
BSSE CP corr.	−3.67(−3.60)	−10.91(−10.48)	−19.48(−19.17)
LP SCF MI	−3.19(−2.96)	−9.27(−8.07)	−15.65(−14.28)
Δ(LP-CP)[a]	0.48(0.64)	1.64(2.41)	3.83(4.89)
Δ(LP−SCF)[b]	0.55(0.70)	1.86(2.54)	4.15(5.12)

[a] The difference between the LP SCF and CP corrected energies.

[b] The energy difference of the LP SCF MI and SCF.

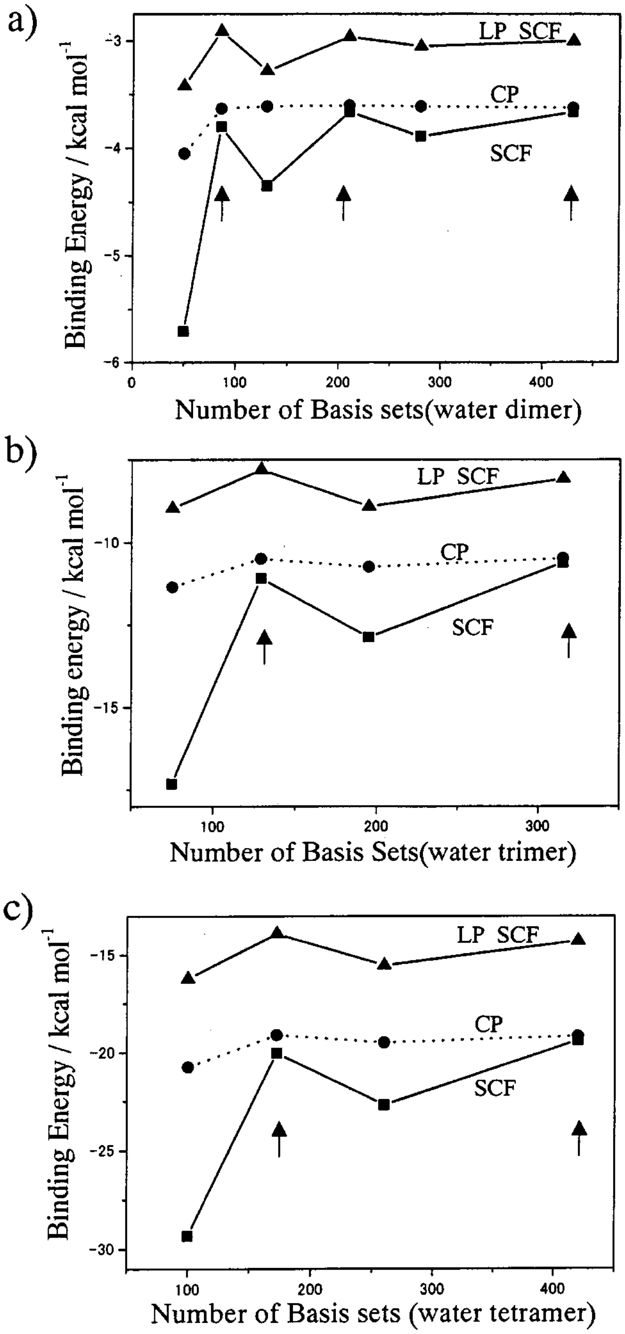

FIG. 3. The basis set dependence of the binding energy of water clusters $(H_2O)_n$ for the SCF, CP BSSE corrected SCF, and LP SCF MI methods. The basis sets pointed by an arrow are those of aug-cc-pVXZ. The geometries are determined with the SCF/cc-pVDZ level of approximation. (a) Dimer, (b) trimer, (c) tetramer.

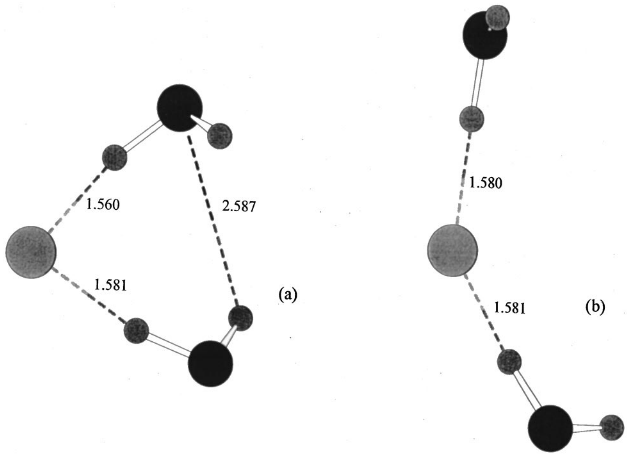

FIG. 4. The geometries of $F^-(H_2O)_2$: (a) optimized with the SCF/cc-pVDZ level; (b) optimized with the SCF/aug-cc-pVTZ level.

difference Δ(LP−SCF) per the hydrogen bonds for each basis set increases with the size of cyclic clusters, which is expected because of the stronger hydrogen bonds in the larger cyclic clusters and thus of the larger CT contribution.

Table III compares the binding energies evaluated with the aug-cc-pVTZ basis set. Two geometries for each cluster, optimized with SCF/aug-cc-pVTZ (cc-pVDZ), are examined; they differ in the hydrogen bond lengths. As mentioned above, if the hydrogen bonds are optimized with the augmented basis set, the bonds become longer. Therefore, the difference Δ(LP−SCF) is smaller for the structures optimized with the augmented basis set than for those without it. The CP correction for both basis sets is small and nearly equal to each other.

Figure 3 examines the basis set dependence of the binding energy for water dimer, trimer, and tetramer. Because the addition of the diffuse functions reduces the BSSE, each plot behaves in a zigzag manner. The CP plots are smooth in all cases. The amplitude of the zigzag of the LP SCF MI plots are much smaller than that of the SCF plots. The LP SCF MI with aug-cc-pVDZ always yields a nearly converged value. Figure 3 clearly demonstrates that LP SCF MI underestimates the binding energy and gives us a good estimation of the lower bound of the binding energy.

The second example we examined is a fluoride anion (F^-) complex with two water molecules. Recently the complexes of the anion with water clusters were studied both experimentally and theoretically by Lisy and co-workers,[23] and theoretically by Baik *et al.*[24] The optimized geometries with the SCF/cc-pVDZ and SCF/aug-cc-pVTZ levels are shown in Fig. 4, and they differ substantially from each other. Without augmented diffuse functions, the hydrogen bond between water molecules is formed. On the other hand, when the diffuse functions are augmented, the anion-water interaction becomes stronger, and the hydrogen bond is broken. Experimentally the vibrational spectra indicate the existence of the stronger $F^- \cdots HO$ interaction.[23] As Table IV shows, structure (b) optimized with the SCF/aug-cc-pVTZ

TABLE IV. The binding energies (kcal/mol) of halogen anion (F^-) complexes with a water dimer.

Method/Basis set	cc-pVDZ	aug-cc-pVDZ	aug-cc-pVTZ
SCF/cc-pVDZ[a]	−63.94	−41.29	−41.08
LP SCF MI/cc-pVDZ[a]	−41.03	−31.68	−32.76
Δ(LP−SCF)[b]	22.91	9.61	8.32
SCF/aug-cc-pVTZ[c]		−42.83	−42.82
LP SCF MI/aug-cc-pVTZ[c]		−33.87	−34.90
Δ(LP−SCF)[b]		8.96	7.98

[a] The geometry is optimized with the SCF/cc-pVDZ level.
[b] The energy difference of the LP SCF MI and SCF.
[c] The geometry is optimized with the SCF/aug-cc-pVTZ level.

TABLE V. Comparison of the Mulliken (MA) and Löwdin (LA) gross population analysis.

Clusters			Gross population		
$F^-(H_2O)_2$	Basis sets/geometry	Methods	H_2O	H_2O	F^-
	cc-pVDZ	SCF (MA)	−0.109	−0.113	0.222
	/cc-pVDZ	(LA)	−0.136	−0.136	0.272
		LP SCF MI (LA)	−0.068	−0.065	0.132
	cc-pVTZ	SCF (MA)	−0.094	−0.096	0.189
	/cc-pVDZ	(LA)	−0.192	−0.190	0.381
		LP SCF MI (LA)	−0.144	−0.140	0.285
	aug-VDZ	SCF (MA)	−0.014	−0.011	0.025
	/cc-pVDZ	(LA)	−0.174	−0.175	0.350
		LP SCF MI (LA)	−0.152	−0.150	0.303
$(H_2O)_2$			H_2O^a	H_2O	
	VDZ	SCF (MA)	0.035	−0035	
	/aug-VDZ	(LA)	0.036	−0.036	
		LP SCF MI (LA)	0.017	−0.017	
	VTZ	SCF (MA)	0.023	−0.023	
	/aug-VTZ	(LA)	0.047	−0.047	
		LP SCF MI (LA)	0.037	−0.037	
	aug-VDZ	SCF (MA)	−0.024	0.024	
	/aug-VTZ	(LA)	0.054	−0.054	
		LP SCF MI (LA)	0.051	−0.051	

[a] The proton acceptor water molecule.

level has a larger binding energy than structure (a) having a hydrogen bond. As the geometries suggest, the difference $\Delta(\mathrm{LP}-\mathrm{SCF})$ for structure (a) is larger than for structure (b). A large $\Delta(\mathrm{LP}-\mathrm{SCF})$ even for structure (b) may indicate the importance of the electron delocalization in the binding.

As repeatedly mentioned, the binding energy in LP SCF MI is always smaller than the CP corrected SCF binding energy. Hamza *et al.*[22] argued that the SCF MI excludes any delocalization between the molecular units. Because the molecular orbitals in the SCF MI are not orthogonal, care should be taken in analyzing the electron distribution. A few ways of the population analysis in the *ab initio* molecular orbital theories have been used. The most popular one is that of Mulliken,[25] and Löwdin's analysis[26] is also widely used. It is known that the gross population is dependent on the analysis used. In the Appendix, we prove that the Mulliken gross population results in no electron delocalization in the SCF MI as were intuitively argued by Hamza *et al.*[23] But, with the Löwdin gross population, because of the nonorthogonality of the occupied orbitals, the electron transfer between the molecular units is possible. Table V demonstrates the examples for water dimer and $F^-(H_2O)_2$. With the SCF wave function, the charge transfer in the Löwdin gross population is always larger than in the Mulliken gross population, and the difference of the two methods is larger for larger basis sets, in particular with the augmented functions. It should be noted that the direction of the charge transfer in the Mulliken gross population for water dimer becomes unphysical for the aug-cc-pVDZ basis set. It has been known that the Mulliken population analysis with diffuse basis functions often gives us a chemically unacceptable picture of the electron destitution. As analytically shown in the Appendix, the Löwdin gross population with LP SCF MI yields substantial amounts of the charge transfer, which are close to those of the SCF wave function, in particular, for the augmented basis sets. We should recall, as Mayer pointed out correctly,[7] that we cannot make the counterpoise correction to the population analysis. We would like to emphasize that the population analysis is one of the measures of the electron destitution in the molecule and molecular cluster, and that it is not the observable.

V. CONCLUSIONS

We have reformulated the SCF for molecular interaction (MI) by Gianinetti *et al.*[8] and extended it for a multicomponent system. The set of equations implies that the locally projected SCF method is a more appropriate name than SCF MI. The test calculations for water clusters show that the binding energy is substantially underestimated and that it converges to the lower energy at the basis set limit.[20] The perturbation correction is essential to evaluate the accurate binding energy. Recently Specchio *et al.* have succeeded in including the correlation contribution in terms of valence bond theory using the nonorthogonal molecular orbitals.[27] In their expansion they intentionally excluded the charge transfer interaction. Currently we are developing a perturbation expansion theory, starting from the LP SCF MI. Because of the localized nature of the orbitals, the terms in the perturbation expansion can be restricted and classified, although the orbitals are not orthogonalized.

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APPENDIX: GROSS POPULATION

One particle density is written as

$$\rho(r)=\sum_{p,q}|\chi_p\rangle P_{pq}\langle\chi_q|\equiv\tilde{\boldsymbol{\chi}}\mathbf{P}\boldsymbol{\chi}, \tag{A1}$$

where $\boldsymbol{\chi}$ is a column vector of the basis functions $|\chi_p\rangle$, and the matrix $\mathbf{P}$ is the density matrix in terms of the basis functions. For the nonorthogonal occupied molecular orbitals, the matrix $\mathbf{P}$ is given as

$$\mathbf{P}=\mathbf{2}\sum_{i,j=1}^{N_{\mathrm{occ}}}\mathbf{t}_i(\mathcal{S}^{-1})_{ij}\tilde{\mathbf{t}}_j\,, \tag{A2}$$

$$\mathcal{S}^{-1}\equiv(\tilde{\mathbf{T}}\mathbf{S}\mathbf{T})^{-1},$$

for the closed shell system, where $\mathbf{T}$ is a rectangular MO matrix of the occupied orbitals $\mathbf{t}_i$ and $\mathbf{S}$ is the overlap matrix over the basis set. By integrating the density,

$$\int\rho(r)d\mathbf{r}=\int\tilde{\boldsymbol{\chi}}\mathbf{P}\boldsymbol{\chi}\,d\mathbf{r}=\mathbf{2}\sum_{i,j=1}^{N_{\mathrm{occ}}}(\mathcal{S}^{-1})_{ij}\tilde{\mathbf{t}}_j\mathbf{S}\mathbf{t}_i=2N_{\mathrm{occ}}\,, \tag{A3}$$

we recover the number of electron. If the basis set $\tilde{\boldsymbol{\chi}}$ is divided to $\{\widetilde{\boldsymbol{\chi}_A},\widetilde{\boldsymbol{\chi}_B}\}$, and thus the MO $\tilde{\mathbf{t}}_i=\{\tilde{\mathbf{t}}_{iA},\tilde{\mathbf{t}}_{iB}\}$, the density matrix in terms of MO is split to

$$\begin{aligned}\tilde{\mathbf{t}}_j\mathbf{S}\mathbf{t}_i&=\tilde{\mathbf{t}}_{jA}\mathbf{S}^{AA}\mathbf{t}_{iA}+\tilde{\mathbf{t}}_{jB}\mathbf{S}^{BA}\mathbf{t}_{iA}+\tilde{\mathbf{t}}_{jA}\mathbf{S}^{AB}\mathbf{t}_{iB}+\tilde{\mathbf{t}}_{jB}\mathbf{S}^{BB}\mathbf{t}_{iB}\\&=(S_{AA})_{ji}+(S_{BA})_{ji}+(S_{AB})_{ji}+(S_{BB})_{ji}\,,\end{aligned} \tag{A4}$$

and thus

$$\begin{aligned}2N_{\mathrm{occ}}&=2\sum_{i,j=1}^{N_{\mathrm{occ}}}[(\mathcal{S}^{-1})_{ij}\{(S_{AA})_{ji}+(S_{BA})_{ji}\}]\\&\quad+2\sum_{i,j=1}^{N_{\mathrm{occ}}}[(\mathcal{S}^{-1})_{ij}\{(S_{AB})_{ji}+(S_{BB})_{ji}\}],\\&\equiv N_A^{\text{Mull-elec}}+N_B^{\text{Mull-elec}},\end{aligned} \tag{A5}$$

where $N_A^{\text{Mull-elec}}(N_B^{\text{Mull-elec}})$ is the Mulliken gross population of molecular unit A (B).

Up to here, the equations are general. Now, in LP SCF MI for a two-component system, T is a block matrix,

$$\mathbf{T}\equiv\begin{pmatrix}\mathbf{T}^A&0\\0&\mathbf{T}^B\end{pmatrix},$$

and thus, the gross population is

$$\begin{aligned}N_A^{\text{Mull-elec}}&=2\sum_{i=1}^{N_{\mathrm{occ}}^A}\left[\sum_{j=1}^{N_{\mathrm{occ}}^A}(\mathcal{S}^{-1})_{ij}(S_{AA})_{ji}\right.\\&\quad\left.+\sum_{j=N_{\mathrm{occ}}^A+1}^{N_{\mathrm{occ}}^A+N_{\mathrm{occ}}^B}(\mathcal{S}^{-1})_{ij}(S_{BA})_{ji}\right]\\&=2\,\mathrm{Tr}(\mathbf{R}_{AA}\mathbf{S}_{AA}+\mathbf{R}_{AB}\mathbf{S}_{BA}),\end{aligned} \tag{A6}$$

where the blocks of the inverse matrix are defined as

$$\mathbf{1}_{N_{\mathrm{occ}}}=\mathcal{S}^{-1}\mathcal{S}=\begin{pmatrix}\mathbf{R}_{AA}&\mathbf{R}_{AB}\\\mathbf{R}_{BA}&\mathbf{R}_{BB}\end{pmatrix}\begin{pmatrix}\mathbf{S}_{AA}&\mathbf{S}_{AB}\\\mathbf{S}_{BA}&\mathbf{S}_{BB}\end{pmatrix}. \tag{A7}$$

Now,

$$N_A^{\text{Mull-elec}}=2\;\mathrm{Tr}(\mathbf{1}_{N_{\mathrm{occ}}^A})=2N_{\mathrm{occ}}^A\,, \tag{A8}$$

so that no electron transfer is possible between A and B in the Mulliken population analysis even when the MOs are not orthogonal.

In the Löwdin population analysis, the density matrix is projected on the Löwdin orthogonalized orbitals,

$$\boldsymbol{\chi}_L=\mathbf{S}^{-1/2}\chi, \tag{A9}$$

and thus,

$$\begin{aligned}N_{\mathrm{elec}}&=\int\rho(r)d\mathbf{r}\\&=\int\tilde{\boldsymbol{\chi}}_L\mathbf{S}^{1/2}\mathbf{P}\mathbf{S}^{1/2}\boldsymbol{\chi}_L\;d\mathbf{r}\\&=\mathrm{Tr}(\mathbf{M}^{AA}\mathbf{P}^{AA}\mathbf{M}^{AA}+\mathbf{M}^{AA}\mathbf{P}^{AB}\mathbf{M}^{BA}+\mathbf{M}^{AB}\mathbf{P}^{BA}\mathbf{M}^{AA}\\&\quad+\mathbf{M}^{AB}\mathbf{P}^{BB}\mathbf{M}^{BA})+\mathrm{Tr}(\mathbf{M}^{BB}\mathbf{P}^{BB}\mathbf{M}^{BB}\\&\quad+\mathbf{M}^{BB}\mathbf{P}^{BA}\mathbf{M}^{AB}+\mathbf{M}^{BA}\mathbf{P}^{AB}\mathbf{M}^{BB}+\mathbf{M}^{BA}\mathbf{P}^{AA}\mathbf{M}^{AB})\\&\equiv N_A^{\text{Löwd-elec}}+N_B^{\text{Löwd-elec}},\end{aligned} \tag{A10}$$

where the root square matrix of the overlap matrix in terms of the basis set is defined as

$$\mathbf{M}\equiv\begin{pmatrix}\mathbf{S}^{AA}&\mathbf{S}^{AB}\\\mathbf{S}^{BA}&\mathbf{S}^{BB}\end{pmatrix}^{1/2}\equiv\begin{pmatrix}\mathbf{M}^{AA}&\mathbf{M}^{AB}\\\mathbf{M}^{BA}&\mathbf{M}^{BB}\end{pmatrix}. \tag{A11}$$

After a few manipulation, we obtain the Löwdin gross population,

$$\begin{aligned}N_A^{\text{Löwd-elec}}&=\mathrm{Tr}\{\mathbf{S}^{AA}\mathbf{P}^{AA}-\mathbf{M}^{AB}\mathbf{M}^{BA}\mathbf{P}^{AA}+(\mathbf{M}^{BA}\mathbf{M}^{AB})\mathbf{P}^{BB}\}\\&\quad+\mathrm{Tr}\{\mathbf{S}^{AB}\mathbf{P}^{BA}-\mathbf{M}^{AB}\mathbf{M}^{BB}\mathbf{P}^{BA}+(\mathbf{M}^{BA}\mathbf{M}^{AA})\mathbf{P}^{AB}\}.\end{aligned} \tag{A12}$$

Up to here, the equations are general. Now, in LP SCF MI for a two-component system, the sub-blocks of the density matrix in terms of the basis set are

$$\mathbf{P}^{AA}=2\sum_{i=1}^{N_{\mathrm{occ}}^{A}}\sum_{j=1}^{N_{\mathrm{occ}}^{A}}(\mathcal{S}^{-1})_{ij}\mathbf{t}_{iA}\tilde{\mathbf{t}}_{jA},$$

$$\mathbf{P}^{BA}=2\sum_{j=N_{\mathrm{occ}}^{A}+1}^{N_{\mathrm{occ}}^{A}+N_{\mathrm{occ}}^{B}}\sum_{i=1}^{N_{\mathrm{occ}}^{A}}(\mathcal{S}^{-1})_{ij}\mathbf{t}_{iA}\tilde{\mathbf{t}}_{jB}. \tag{A13}$$

Therefore,

$$\begin{aligned}\mathrm{Tr}(\mathbf{S}^{AA}\mathbf{P}^{AA})&=2\sum_{i=1}^{N_{\mathrm{occ}}^{A}}\sum_{j=1}^{N_{\mathrm{occ}}^{A}}(\mathcal{S}^{-1})_{ij}\sum t_{p,jA}(\mathbf{S}^{AA})_{pr}t_{r,iA}\\&=2\sum_{i=1}^{N_{\mathrm{occ}}^{A}}\sum_{j=1}^{N_{\mathrm{occ}}^{A}}(\mathcal{S}^{-1})_{ij}(\mathbf{S}_{AA})_{ji}\\&=2\ \mathrm{Tr}(\mathbf{R}_{AA}\mathbf{S}_{AA})\\&=2\ \mathrm{Tr}(1-\mathbf{R}_{AB}\mathbf{S}_{BA})\\&=2N_{\mathrm{occ}}^{A}-2\ \mathrm{Tr}(\mathbf{R}_{AB}\mathbf{S}_{BA}).\end{aligned} \tag{A14}$$

Thus,

$$\begin{aligned}N_{A}^{\text{Löwd-elec}}=2N_{\mathrm{occ}}^{A}+\mathrm{Tr}\{&-\mathbf{M}^{AB}\mathbf{M}^{BA}\mathbf{P}^{AA}+\mathbf{M}^{BA}\mathbf{M}^{AB}\mathbf{P}^{BB}\\&-\mathbf{M}^{AB}\mathbf{M}^{BB}\mathbf{P}^{BA}+\mathbf{M}^{BA}\mathbf{M}^{AA}\mathbf{P}^{AB}\}.\end{aligned} \tag{A5}$$

Because $\mathbf{M}^{AB}\mathbf{M}^{BA}$ is a product of blocks of the root square overlap matrix, the terms in the second line cannot be simplified further. For instance,

$$\begin{aligned}&\mathrm{Tr}(\mathbf{M}^{BA}\mathbf{M}^{AB}\mathbf{P}^{BB})\\&=\sum_{p=M^{A}+1}^{M^{A}+M^{B}}\sum_{q=1}^{M_{A}}\sum_{r=M^{A}+1}^{M^{A}+M^{B}}(\mathbf{M}^{BA})_{pq}(\mathbf{M}^{AB})_{qr}(\mathbf{P}^{BB})_{rp}\\&=2\sum_{p=M^{A}+1}^{M^{A}+M^{B}}\sum_{q=1}^{M_{A}}\sum_{r=M^{A}+1}^{M^{A}+M^{B}}(\mathbf{M}^{BA})_{pq}(\mathbf{M}^{AB})_{qr}\\&\quad\times\sum_{i=N_{\mathrm{occ}}^{A}+1}^{N_{\mathrm{occ}}^{A}+N_{\mathrm{occ}}^{B}}\sum_{j=N_{\mathrm{occ}}^{A}+1}^{N_{\mathrm{occ}}^{A}+N_{\mathrm{occ}}^{B}}(\mathcal{S}^{-1})_{ij}\mathbf{t}_{iB}\tilde{\mathbf{t}}_{jB}\\&=\sum_{i=N_{\mathrm{occ}}^{A}+1}^{N_{\mathrm{occ}}^{A}+N_{\mathrm{occ}}^{B}}\sum_{j=N_{\mathrm{occ}}^{A}+1}^{N_{\mathrm{occ}}^{A}+N_{\mathrm{occ}}^{B}}(\mathbf{R}_{BB})_{ij}\tilde{\mathbf{t}}_{jB}\mathbf{M}^{BA}\mathbf{M}^{AB}\mathbf{t}_{iB}.\end{aligned} \tag{A16}$$

It is these terms that contribute to the electron delocalization over the molecular units in the Löwdin gross population.

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