

Generalization of the New Resonance Theory: Second Quantization Operator, Localization Scheme, and Basis Set

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Abstract: We have recently proposed a method to evaluate the weights of resonance structures embedded in a molecular orbital by utilizing singlet-coupling scheme of an electron pair [*J. Phys. Chem. A* **2006**, *110*, 9028]. The method was formulated on the basis of the second quantization, in which a biorthogonal operator related to Mulliken population (MP) was used together with the Boys–Foster (BF) localization scheme. Our method is very easy to use; only a standard localization procedure is required to obtain the resonance weights. In addition, obtained results agreed well with our chemical intuition. In the present Article, the restrictions, namely MP and BF, were removed, and an operator related to Löwdin population (LP) and other various types of localization schemes were employed to examine the generality of the method. We found that computed resonance weights were virtually independent not only on the choice of these combinations but also on basis set. This new finding, the invariant nature in terms of resonance, may suggest that the present approach could be promising for analyzing molecular orbitals.

1. Introduction

The chemical bond is a central concept in chemistry. However, the presently available computational tools are not always related to the concept of the bond. In principle, there are two ways to obtain the electronic wave function: valence bond (VB) method and molecular orbital (MO) method. The former provides an understanding of the chemical bond in a relatively intuitive way, being related to the concepts of covalency, ionicity, and their resonance. Many modern electronic structure theories and their applications are based on the latter method. In this regard, a bridge between the two methods is indispensable. In other words, VB-based characterization of the MO wave function is highly desired to elucidate the nature of chemical bonding. Karafiloglou et al. are working vigorously to address this problem,¹ and several other methods for such purpose have been developed so far, including papers by Shaik et al.,² the pioneering work by Hiberty et al.,³ natural resonance theory (NRT)⁴ by

Weinhold et al., and the method based on CASSCF-type wave function by Hirao and co-workers.⁵ MOVb by Mo and Gao is a direct realization that fits the present purpose.⁶ Another type of analysis based on locally defined energy by Nakai et al. can also offer a detailed look inside at the electronic structure of a molecule and its bonds.⁷

Recently, we proposed a new analysis method to evaluate the weights of resonance structures and applied it to several molecular systems.⁸ All the results fit in with our chemical intuition. For instance, the method was combined with RISM-SCF,⁹ which provides microscopic information on the solvation effect based on statistical mechanics for molecular liquids, and the enhancement of the ionic contribution to electronic structure in solvated molecular system was adequately calculated.^{8b,c} Our method is very easy to use: Because of the simple strategy based on the second quantization of singlet-coupling in the target orbital, what we need to obtain the weights is only the density matrix of localized orbitals, and the additional computational cost is negligible. The results also showed excellent agreement with the past reports.^{8a}

In the original work,⁸ a biorthogonal operator related to Mulliken-population (MP) introduced by Mayer^{10,11} was

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employed together with the Boys-Foster (BF)¹² localized orbitals. In the present study, we erase these restrictions, and the protocol is extended to a generalized one that includes Löwdin population (LP) related operators¹³ with various localization schemes such as Edmiston–Ruedenberg (ER)¹⁴ and Pipek–Mezey (PM)¹⁵ methods. Furthermore, the basis set dependence is examined since it is usually believed to become a serious issue in this type of analysis. The obtained results shows remarkable invariance as explained below, establishing that the present analysis can deliver clear understanding of chemical bondings.

2. Theory

The first order density matrix (\mathbf{D}) _{$\nu\mu$} of wave function $|\Psi\rangle$ is given by eq 1

$$(\mathbf{D})_{\nu\mu} = \langle \Psi | a_{\nu}^+ a_{\mu}^- | \Psi \rangle \quad (1)$$

where a_{ν}^+ and a_{μ}^- are the creation and annihilation operators related to atomic orbitals (AOs) ν and μ , respectively.¹¹ In a similar manner, we can define density matrices for an orthonormalized orbital ψ_i ($i = 1, 2, \dots$), as follows:

$$(\mathbf{d}^i)_{\mu\nu} = \langle \psi_i | a_{\nu}^+ a_{\mu}^- | \psi_i \rangle \quad (2)$$

The matrix holds the idempotency

$$(\mathbf{d}^i)_{\mu\mu} = \frac{1}{2} \sum_{\nu} (\mathbf{d}^i)_{\mu\nu} (\mathbf{d}^i)_{\nu\mu} \quad (3)$$

and the number of electrons is conserved in each orbital in closed-shell system.

$$2 = \sum_{\mu} (\mathbf{d}^i)_{\mu\mu} \quad (4)$$

From eqs 3 and 4, a simple equation is obtained:

$$1 = \frac{1}{4} \sum_{\mu} \sum_{\nu} (\mathbf{d}^i)_{\mu\nu} (\mathbf{d}^i)_{\nu\mu} = \sum_{M,N} W_{MN}^i \text{ where} \\ W_{MN}^i = \frac{1}{4} \sum_{\mu \in M} \sum_{\nu \in N} (\mathbf{d}^i)_{\mu\nu} (\mathbf{d}^i)_{\nu\mu} \quad (5)$$

M and N are atomic labels. By introducing spin variables σ_1 and σ_2 ($\sigma_1 \neq \sigma_2$), the quantity is also expressed as the expectation value of an operator

$$\frac{1}{4} (\mathbf{d}^i)_{\mu\nu} (\mathbf{d}^i)_{\nu\mu} = \langle \psi_i | a_{\nu}^{\sigma_1+} a_{\mu}^{\sigma_2+} a_{\nu}^{\sigma_2-} a_{\mu}^{\sigma_1-} | \psi_i \rangle \quad (6)$$

In the case of $\mu \neq \nu$, both $1/4 (\mathbf{d}^i)_{\nu\mu} (\mathbf{d}^i)_{\nu\mu}$ and $1/4 (\mathbf{d}^i)_{\nu\mu} (\mathbf{d}^i)_{\nu\mu}$ represent the weight of the state in which two electrons are singlet-coupled and shared by two AOs, μ and ν . In the case of $\mu = \nu$, $1/4 (\mathbf{d}^i)_{\mu\mu} (\mathbf{d}^i)_{\mu\mu}$ represents the weight of the state in which two electrons occupy the same AO (μ). Hence, $2W_{MN}^i = W_{MN}^i + W_{NM}^i$ is considered as the weight of the state in which two electrons in ψ_i are shared between M and N atoms, and W_{MM}^i is that of the state in which two electrons in ψ_i are belonging to the atom M.

Let us consider a localized molecular orbital (LMO) ψ_i^{local} ($i = 1, 2, \dots$), which has a two-center character between A and B atoms. Equations 5 and 6 are then

$$1 = \sum_{M,N} W_{MN}^i = W_{AA}^i + 2W_{AB}^i + W_{BB}^i + \\ \left\{ \begin{array}{l} \text{all other terms } (W_{MN}^i) \text{ in which} \\ (M, N) \text{ is not } (A \text{ or } B) \text{ at the same time} \end{array} \right\} \\ = W_{AA}^i + 2W_{AB}^i + W_{BB}^i + \bar{W}^i \quad (7)$$

One can notice that each term corresponds to the weights of ionic and covalent character in the bond between A and B. W_{AA}^i is the weight of the ionic structure ($A^- B^+$), W_{BB}^i is that of the ionic structure ($A^+ B^-$), and $2W_{AB}^i$ is that of the covalent structure ($A-B$). \bar{W}^i , sum of all the terms in braces corresponding to a many-body term, arises from the fact that LMO often penetrates into other than A and B atoms. As will be shown below, however, \bar{W}^i is actually very small because the concerned two electrons are usually localized in the area between A and B.

Total wave function of a molecule ($|\Psi\rangle$) is invariant to any unitary transformation among occupied orbitals, and the choice of the orthonormalized orbital is arbitrary. In general, each MO can be localized into either one-center (core orbital, lone-pair orbital, etc.) or two-center (bonding) orbitals. If electrons in different LMOs are independent of each other, the weights of resonance structures of the molecule are simply represented by multiplications of the weights of the two-center bonding orbitals (note that atomic index A and B must be related to the orbital i).

$$1 = \prod_i^{\text{LMOs}} (W_{AA}^i + 2W_{AB}^i + W_{BB}^i + \bar{W}^i) \quad (8)$$

Since the sum of the four terms in parentheses is always 1, normalization of the weights is always guaranteed. It is noteworthy that the contribution from the one-center orbital is regarded as unity because of $A = B$ with negligible \bar{W}^i . The alternative view is that the one-center contribution must be simply taken out because it does not participate in the formation of bondings. The separation between one- and two-center orbitals is readily defined, judging from the population assigned to each atom in the localized orbital. As a consequence, the resonance structure of a molecule can be computed by the combinational products of each bonding contribution.

In eq 5, what we need is to compute the density matrix elements related to localized orbital ψ_i^{local} , $(\mathbf{d}^i)_{\nu\mu}$. Now we have two issues that need to be selected in the actual computation of this quantity. One is the choice of the operator described in eq 1, and the other is orbital localization scheme to obtain ψ_i^{local} . For the former choice, both the nonorthogonal and orthogonal AO based operators are examined in this study: nonorthogonal-AO creation operator χ_{ν}^+ and its biorthogonal-AO annihilation operator ϕ_{μ}^- related to MP,^{10,11} which were introduced in our original work, and the operators, l_{ν}^+ and l_{μ}^- , related to LP.¹³

$$\text{Mulliken type: } (\mathbf{d}^i)_{\nu\mu} = (\mathbf{p}^i \mathbf{S})_{\nu\mu} (a_{\nu}^+ = \chi_{\nu}^+ \text{ and } a_{\mu}^- = \phi_{\mu}^-) \quad (9)$$

$$\text{Löwdin type: } (\mathbf{d}^i)_{\nu\mu} = (\mathbf{S}^{1/2} \mathbf{p} \mathbf{S}^{1/2})_{\nu\mu} (a_\nu^+ = l_\nu^+ \text{ and } a_\mu^- = l_\mu^-) \quad (10)$$

\mathbf{S} is the overlap matrix and $(\mathbf{p}^i)_{\nu\mu}$ is an element constituting \mathbf{P} -matrix (\mathbf{P}) for given orbital i .^{10,13}

$$(\mathbf{p}^i)_{\mu\nu} = 2(\mathbf{C}^L)_{\mu i} (\mathbf{C}^{L*})_{vi} \quad (11)$$

$(\mathbf{C}^L)_{\mu i}$ is the LCAO coefficient of LMO i . The standard \mathbf{P} -matrix is computed by summing over all the occupied orbitals, and only the total sum is invariant under the transformation from canonical orbitals (being delocalized) to other localized ones.

$$\begin{aligned} (\mathbf{P})_{\mu\nu} &= \sum_i^{\text{occ}} (\mathbf{p}^i)_{\mu\nu} \\ &= 2 \sum_i^{\text{occ}} (\mathbf{C})_{\mu i} (\mathbf{C}^*)_{vi} = 2 \sum_j^{\text{occ}} (\mathbf{C}^{L1})_{\mu j} (\mathbf{C}^{L1*})_{vj} \quad (12) \\ &= 2 \sum_k^{\text{occ}} (\mathbf{C}^{L2})_{\mu k} (\mathbf{C}^{L2*})_{vk} = \dots \end{aligned}$$

For the choice of localization as the second option, three major schemes were examined in this article: Boys-Foster (BF), Edmiston-Ruedenberg¹⁴ (ER), and Pipek-Mezey¹⁵ (PM) localization. Hence, the original analysis is generalized in terms of these various combinations of two options. Hereafter, the combination is respectively called BF-, ER- and PM-weights based on the MP (Mulliken) or LP (Löwdin) population related operator. Additionally, the basis set dependence could be crucial from the standpoint of the invariance of the theory. A series of basis sets implemented in the GAMESS program package,²⁰ DZ, DZP, TZ, TZP, and TZP+,¹⁷ were used for the purpose of a systematic investigation, and further large basis sets were also employed. It is noted that 5d orbitals were used throughout the study since Löwdin population analysis with 6d orbitals is not rotationally invariant.^{18,19} All calculations were performed with program code GAMESS²⁰ modified by us.

3. Results and Discussion

3.1. H₂: A Basal Examination. At first, the weights of resonance structures of H₂ were calculated. This is a basal examination and the so-called minimum requirements in this type of analysis. Because the occupied orbital is unique in this two-electron system, the orbital transformation is not necessary, meaning it is unrelated to the localization scheme. Another special character of this system is that weights do not depend on the choice of basis set at all due to the high symmetry.

The obtained weight of covalent structure H–H was 50%, and that of each ionic structure H⁺ H[−] and H[−] H⁺ was, respectively, 25%. These properly exhibit a well-known fact that the electronic structure of H₂ in the Hartree–Fock wave function possesses half-covalent and half-ionic character.

3.2. H₂O and NH₃. Second, the H₂O molecule is examined. After carrying out standard MO computations, the orbitals were localized by BF, ER, and PM procedures

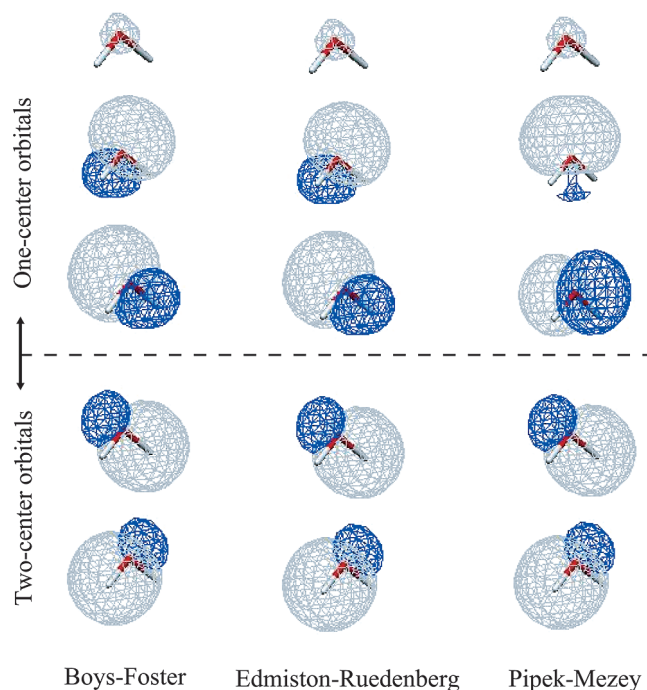


Figure 1. Three one-center and two two-center BF-, ER-, and PM-orbitals of H₂O. TZP basis sets were used.

(Figure 1). Independent of the basis set choice, three one-center ($i = 1, 2, 3$) and two two-center ($i = 4, 5$) orbitals were obtained by each localization method. Regarding one-center orbitals, the core orbital is common to all the procedures. The distinct difference is the PM localization produced one in-plane and one out-of-plane lone pair orbital, whereas BF and ER localizations gave two equivalent lone pair orbitals. But for the two-center orbitals, all the three localization procedures provide very similar orbitals corresponding to the two O–H bonds (OH₁ and OH₂). The weights of resonance structures of H₂O are calculated from $(\mathbf{p}^i)_{\nu\mu}$ of the two two-center orbitals, which participate the bond formation.

$$1 = (W_{\text{OO}}^4 + 2W_{\text{OH}_1}^4 + W_{\text{H}_1\text{H}_1}^4 + \bar{W}^4)(W_{\text{OO}}^5 + 2W_{\text{OH}_2}^5 + W_{\text{H}_2\text{H}_2}^5 + \bar{W}^5) \quad (13)$$

By opening the brackets, the weights are calculated as shown in Figure 2. The upper panel shows results obtained from the MP operator while the lower panel shows results from the LP one using various basis sets. The six combinations are possible at the choice of the localization (BF, ER, and PM) together with the operator (MP and LP), but the ER-weights were not shown in the figure. This is because they are virtually the same as the BF-weights, and the differences were always less than 0.1% in all the resonance structures. All in all, the most important resonance structure was **2**, in which one O–H bond was ionic and the other is covalent. The next is the totally covalent structure **1**, which is comparable with a totally ionic structure **4**. As illustrated in the figure, BF- and PM-weights are almost the same, meaning that the three localization procedures provide essentially the same results. This may not be surprising because BF, ER, and PM two-center orbitals look very similar, as shown in Figure 1. Essentially, two operators

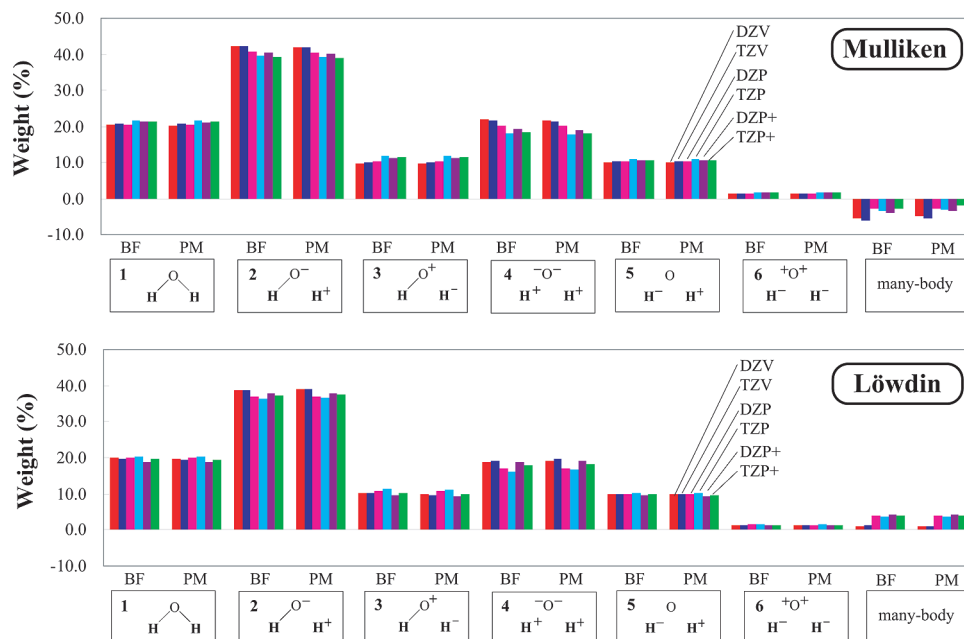


Figure 2. Weights (%) of resonance structures of H₂O evaluated with Mulliken and Löwdin operators.

deliver very similar results, but the weights of **2** and **4** evaluated with the Löwdin type were slightly smaller than those with the Mulliken type, which is consistent with a general trend that polarization is slightly enhanced in MP; for example, populations of the oxygen atom calculated with MP and LP (TZP basis sets) were, respectively, 8.615 and 8.397. Another important difference is found in the many-body term arising from the product of \bar{W}^i . The contribution is negligibly small, but the sign is different between two operators. This can be readily understood in terms of a well-known fact that MP analysis often gives negative population due to the nonorthogonality of AOs. However, it must be emphasized that these differences were very small, and two operators provided essentially the same results. Thus, the present procedure seems to be virtually independent from the choice of eq 9 or 10.

All the basis sets provide almost similar results, and the dependence is very small. The differences in the weights are less than 5%. It might sound paradoxical when remembering that the present analysis is related to MP (or LP) analysis, which is usually regarded to exhibit considerable basis-set dependence. Actually, the Mulliken charge of oxygen varies from -0.799 (DZ) to -0.615 (TZP). However, the paradox can be dispelled from the viewpoint of fraction F defined as the ratio of the assigned charge of oxygen to the total electron number in the system: the difference in electron number between the DZ and TZP results, 0.184, corresponds to less than 2% of the total number ($0.184/10 \times 100$). The change in electronic structure often looks remarkable from the point of view of commonly used counting of electron numbers assigned to a specific atom, but it can look changeless when a different viewpoint is introduced. The weights of resonance structure, which characterizes the electronic structure of the whole molecule, is obviously related to the ratio, not to direct number-counting. In fact, the basis set dependence of the weights shows a good correlation with F (Figure 3). In other words,

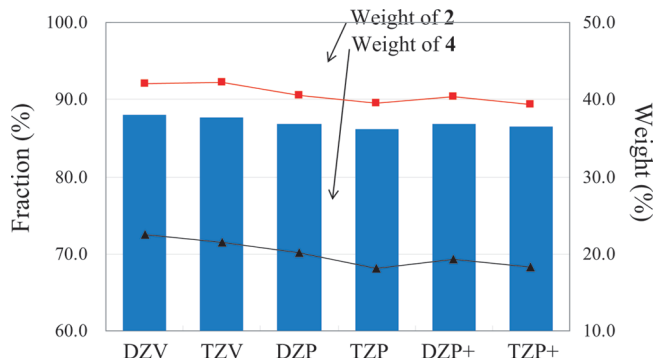


Figure 3. Basis set dependence of F , which is the fraction between number of electrons and Mulliken population of oxygen (bar). The weights of resonance structures **2** and **4** (lines), calculated by BF-localization.

Table 1. Weights of Covalent and Ionic Bond (%) in H₂O by Larger Basis Sets^a

basis set	1	2	3	4	5	6
cc-pVDZ	24.27	32.97	17.85	11.20	12.13	3.28
cc-pVTZ	22.92	37.82	13.88	15.60	11.46	2.10
cc-pVQZ	21.98	39.64	12.18	17.88	10.98	1.69
aug-cc-pVDZ	25.07	32.69	19.23	10.65	12.53	3.69
aug-cc-pVTZ	22.83	34.86	14.95	13.31	11.41	2.45
aug-cc-pVQZ	21.01	37.48	11.78	16.71	10.51	1.65

^a BF and MP operator was used. See Figure 2 for the index of the resonance structures.

the viewpoint of resonance structure could offer a robust way to understand the electronic structure of molecules. Table 1 lists the results from much larger basis sets. Again, the obtained weights are virtually independent of the basis set choice. Since the Mulliken population evaluated with these basis sets varies to a considerable degree, the resonance weights also show slight variation. Even so, all the standard deviations of each weight are less than 3.0%.

The next example is NH₃. By the localization, two one-center (the core and lone-pair of nitrogen) and three two-

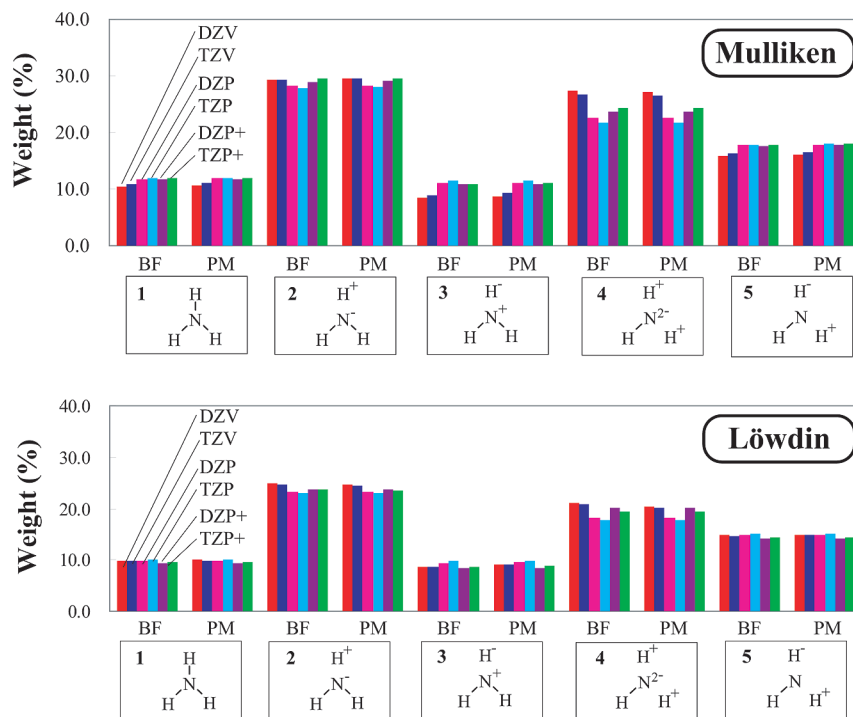


Figure 4. Weights (%) of important resonance structures of NH_3 evaluated with Mulliken and Löwdin operators.

center N–H orbitals were obtained, and weights were calculated from the latter ones. Three orbitals respectively obtained by BF, ER, and PM localizations look similar to the case of H_2O (not shown), and all the weights are also independent to the localization schemes, the operators, as well as the choice of basis sets. In Figure 4, some structures with high weights are selectively shown. The most important structure was **2**, which consisted of two covalent (N–H) and one ionic (N^-H^+) bonds. Next was **4**, which consisted of one covalent (N–H) and two ionic (N^-H^+) bonds. Both **2** and **4** have the character of a negatively charged nitrogen atom, and the weights calculated with Löwdin type were slightly smaller than those with Mulliken type. This feature is again related to the difference in these population analysis.

3.3. H_2CO . Next, the double bond $\text{C}=\text{O}$ in H_2CO was the focus. In the above-mentioned molecules, bonding orbitals look very similar independent of the localization schemes. The situation is different in the case of a double bond (see Figure 5). BF and ER localization provide two equivalent σ – π mixed orbitals, exhibiting so-called “banana bond” character (BF1, BF2 and ER1, ER2, respectively), while PM localization provides one σ (PM1) orbital and one π orbital (PM2). In other words, the generality is not obvious compared to the previous cases.

Figure 6 shows calculated BF- and PM-weight from the two orbitals in a similar manner. In all cases, the most important resonance structure is **2**, which comprises one ionic bond and one covalent bond, and the next is **1**, which is a doubly bonded resonance structure. These results accord with common knowledge of polarized character in a $\text{C}=\text{O}$ bond. One of the most interesting findings is that the weight does not depend upon the choice of operator as well as upon the localization scheme again, even though orbitals BF1 and BF2 looks very different from PM1 and PM2. Total weights are

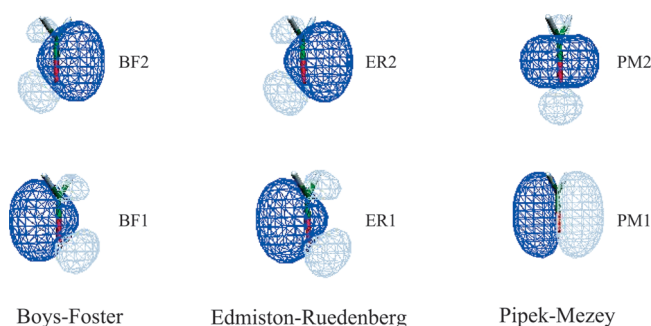


Figure 5. Two two-center BF-, ER-, and PM-orbitals of H_2CO , corresponding to the $\text{C}=\text{O}$ bond. TZP basis sets were used.

virtually the same among all the combinations, and the difference is less than few percents.

Table 2 compares the localized orbitals in terms of respective weight components defined in eq 5, together with their population calculated by the MP operator. It is unsurprising that BF and ER give virtually the same weights, probably due to their similarity of orbitals. At the same time, PM1 and PM2 are slightly different from those of BF and ER, which are located in the middle of the two PMs. The weights are then calculated from these values, for example,

BF

$$1: \text{C}=\text{O} \quad 0.4774 \times 0.4774 = 22.79\%$$

$$2: \text{C}^+-\text{O}^- \quad 0.4774 \times 0.3834 \times 2 = 36.61\%$$

PM

$$1: \text{C}=\text{O} \quad 0.4989 \times 0.4505 = 22.48\%$$

$$2: \text{C}^+-\text{O}^- \quad 0.4989 \times 0.4286 + 0.4505 \times 0.3313 = 36.31\%$$

The obtained weights are a little different though they are derived in different ways. It should be noted that all

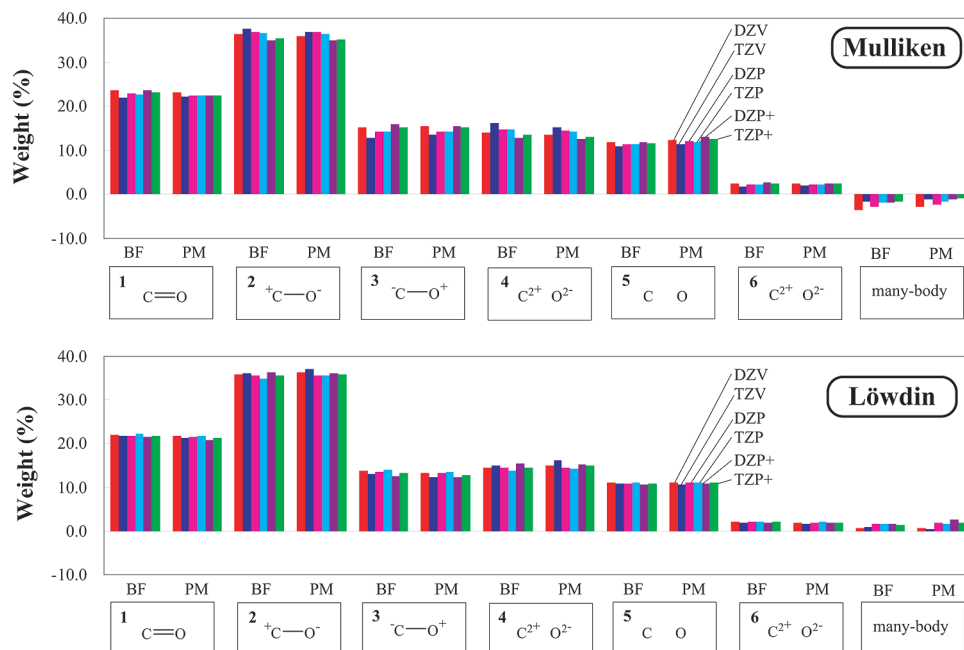


Figure 6. Weights (%) of resonance structures of H_2CO evaluated with Mulliken and Löwdin operators.

Table 2. Weights of Covalent and Ionic Bonds in H_2CO Calculated by All the Localization Schemes^a

	W_{CC}	weights/% $2W_{\text{CO}}$	W_{OO}		C	O	population H	H
BF1	14.86	47.74	38.34		0.7710	1.2384	-0.0047	-0.0047
BF2	14.86	47.74	38.34		0.7710	1.2384	-0.0047	-0.0047
				subtotal	1.5420	2.4768	-0.0094	-0.0094
ER1	14.91	47.74	38.23		0.7722	1.2365	-0.0044	-0.0044
ER2	14.91	47.74	38.23		0.7722	1.2365	-0.0044	-0.0044
				subtotal	1.5444	2.4730	-0.0088	-0.0088
PM1	18.78	49.89	33.13		0.8668	1.1511	-0.0089	-0.0089
PM2	11.84	45.05	42.86		0.6881	1.3094	0.0013	0.0013
				subtotal	1.5549	2.4605	-0.0077	-0.0077

^a Computed with the MP operator, and TZP basis sets were used.

the localized orbitals are linked through unitary transformation, but the numbers shown here (weight and its components) are not necessarily the same because the summation in eq 5 is limited over a specific atom (M and/or N) and the transformation is not completed.

Another viewpoint is the population of the localized orbitals. In the table, two orbitals were chosen for each localization scheme, and as can be seen, though the populations assigned to PM1 and PM2 are different from each other, the sum of them is very close to that of BF and of ER. It is noted that the Mulliken population is invariant against unitary transformations of the occupied orbitals, and the gross populations are 5.8310 (carbon), 8.3206 (oxygen), and 0.9242 (hydrogen), respectively. There are two σ -orbitals in carbon and hydrogen, and three one-center (core and lone pair) orbitals in oxygen. If each of them is ideally occupied by exactly two electrons, 1.8310, 2.3206, and -0.0758 are assigned to the population of these two orbitals, which are reasonably close to those of localized orbitals shown in the table. This may suggest that the valence space extracted by all the localization scheme are well separated from the core and lone-pair orbitals, and the obtained valence-space, which

is the direct sum of the space spanned by the two orbitals, is very similar each other.

Unfortunately, the formal proof of this invariance seems to be impossible because the agreement is more like qualitative sense. All the numbers look essentially equivalent but are not exactly the same. According to our experience, the invariance about the localization scheme is always found in every case, even in a more complicated compound such as a triple-bond-containing molecule, and the obtained result always matches our chemical intuition for the examined molecules. Hence, the following two facts are worth pointing out. One is that the present analysis is related to MPA that is invariant against unitary transformations. The other point is the present measuring rule, namely, fraction. As mentioned above, an understanding in terms of the ratio seems to be robust enough, and even the basis set dependence of MPA becomes less prominent.

3.4. Some Other Molecules. Finally, two examples are shown. One is a substituent effect to H_2CO , namely XYCO . The same procedures were employed to evaluate the weight using PM localization to select one π and one σ orbital. As shown in Table 3, polarization of the C–O bond properly reproduced, and the contribution from C^+-O^- becomes

Table 3. Selected Weights of Covalent and Ionic Bonding (%) in Substituted H₂CO^a

X	Y	C=O	C ⁺ —O ⁻	C—O ⁺	C ²⁺ —O ²⁻	C O	C ²⁻ —O ²⁺
H	H	22.47	36.30	14.36	14.20	11.97	2.22
H	F	22.47	37.66	14.29	14.80	12.72	2.13
F	F	22.25	38.05	14.33	14.77	13.38	2.09
F	Me	22.29	38.24	14.04	15.18	12.94	2.05
H	Me	22.32	37.17	14.05	14.76	12.24	2.11
Me	Me	22.24	37.75	13.89	15.10	12.46	2.05

^a PM localization and MP operator were used with TZP basis set.

greater by inductive effect compared to the original H₂CO. Interestingly, the contributions from a pure double bond hardly change by the substitution.

The next example is formamide. In relation to the understanding of the nature of an amide bond, its resonance structure was extensively studied by Mo et al.²¹ Since the present analysis is built up from separated chemical bonds, treatment of conjugation is not simple. For the sake of simplicity, the following procedure was adopted in the present study. By BF localization, two π orbitals were obtained, and these four electrons are considered to be related to the resonance structure. But the lone-pair electron on the nitrogen atom is also included in this set. Hence, after computing the weights by multiplying the contributions from C—O and C—N bonds, as described above, this contribution (C⁺ N⁻) was subtracted to obtain the final resonance structure. Using the MP operator with 6-31G(d) basis set, the following weights were obtained: **1**, 28.0%; **2**, 25.6%; **3**, 15.9%; **5**, 7.7%; **6**, 2.5%. (The index was defined by Mo et al. in their work.²¹ Since O...N direct interaction is not taken into account, the contribution from **4** does not explicitly appear in the present treatment.) Although this procedure is rather *ad hoc*, the qualitative trend derived shows good agreement with their report.

Nevertheless, the present method is good at analyzing bonds localized at a specific region. The description of conjugated electrons system is relatively poor, and further improvement is highly desired.

4. Conclusions

In the present work, our recently proposed method is generalized to evaluate the weight of resonance structures by taking the various combinations of the operator and the localization scheme. The method is applied to analyze the electronic structure of H₂, H₂O, NH₃, and H₂CO, and the basis set dependency of the method is also examined. Though the chosen operator, namely Mulliken-type or Löwdin-type, is kind of responsible for the weight, it can be concluded that the result is virtually independent from the combination as well as from the choice of basis sets. This suggests that understanding through resonance structure offers a robust and adequate description of molecular electronic structure. Furthermore, our method is very easy to use, and only standard localization procedure is required to obtain the resonance weights. From these results, the method could be a promising tool for analyzing molecular orbitals. On the other hand, it is

difficult to apply the method when successful localization is not performed. For example, the electron in the transition state of a reaction inherently spreads over the reaction system, and the one- or two-center orbital picture is no longer valid. Extension to correlated wave function is also interesting. Further work along this line is currently in progress and will be reported elsewhere.

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