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A New Analysis of Molecular Orbital Wave Functions Based on Resonance Theory

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A new method to evaluate the weights of resonance structures from molecular orbital wave function is proposed, which is based on the second quantization of singlet-coupling. The present method is useful to analyze molecules of which the electronic structures are well localizable. The evaluation is carried out through localization of molecular orbitals followed by algebraic calculation of density matrices. This method is applied to H_2O, H_3O^+, and BH_3. The calculated weights of covalent and ionic structures are in excellent agreement with those of the previous works and our chemical intuition.

We have traditionally considered that molecules are built up of atoms that link each other through chemical bonding. The nature of the chemical bond has been discussed in terms of resonance between covalent and ionic-type interactions in many cases. The concepts of covalency, ionicity, and resonance still play important roles in chemistry, because these enable us to classify the various molecules according to the nature of the chemical bond. In this sense, it is highly desirable to present a method by which results of electronic structure calculations of molecules are interpreted with these chemical concepts.

Most of modern ab initio calculations are based on the molecular orbital (MO) method. However, it is hard to obtain the weights of covalency and ionicity from the wave function calculated by the MO method, because MOs are delocalized over the whole molecule, and the wave function is quite different from the valence bond wave function that directly describes covalent−ionic resonance. Various methods have been developed to make up for deficiencies in the MO method. Good examples are population analysis[1−3] and bond order indexes.[4−6] One goal of extension of these developments is to calculate the weights of each resonance structure from the wave function.

Many evaluation methods of weights of resonance structures from the wave function have been developed over a long period. The most important of this research was reported by Hiberty et al.[7] They constructed complete sets of valence bond wave functions from atomic orbital basis sets, and then, a Hartree−Fock (HF) wave function was expanded with these valence bond wave functions. This is one of the important pioneering works, though not practical enough. Recently, natural resonance theory[8] (NRT), which was based on natural bond orbital (NBO) analysis,[3] has been developed by Glendening and Weinhold. Additionally, Karafiloglou reported another method to calculate weights of resonance structures from NBO analysis.[9] In this paper, we would like to present a new method to calculate the weights of resonance structures from HF wave function. The range of application of the present method is limited to the molecular orbital wave functions in which each MO can be localized to either one- or two-center orbitals. At the present stage, it is difficult to apply the method to molecules involving more than three-center LMOs, such as conjugated molecules. However, for molecules for which the electronic structures are well localizable, the method is a simple and useful tool to link MOs with the concept of resonance.

The first-order density matrix $(PS)_{\mu\nu}$ of the LCAO-MO determinant $|\Psi\rangle$ is given by eq 1

$$(PS)_{\mu\nu} = \langle\Psi|\chi_\nu{}^{+}\varphi_\mu{}^{-}|\Psi\rangle = 2\sum_{i}^{\mathrm{occ}}\sum_{n} C_{\mu,i}C_{n,i}S_{n\nu} \qquad (1)$$

where χ_ν^+ is creation operator related to atomic orbital (AO) basis χ_ν and φ_μ^- is annihilation operator related to the biorthogonal AO basis φ_μ. $C_{\mu,i}$ is the LCAO coefficient of MO i, and $S_{\mu\nu}$ is the element of the overlap matrix.

$|\Psi\rangle$ is invariant to localization (unitary transformation) among doubly occupied orbitals. When we use localized MOs (LMOs) $\phi_i^{\mathrm{local}} = \sum_\mu L_{\mu,i}\chi_\mu$, we can define local density matrices for the orbital i ($i = 1,2,...$) as follows

$$(PS)^i_{\mu\nu} = 2\sum_n L_{\mu,i}L_{n,i}S_{n\nu} \qquad (2)$$

where $L_{\mu,i}$ is LCAO coefficient of LMO i. It is noted that these local density matrices hold the idempotency and the number of electrons is conserved in each LMO.

$$(PS)^i_{\mu\nu} = \frac{1}{2}\sum_n (PS)^i_{\mu n}(PS)^i_{n\nu} \qquad (3)$$

$$2 = \sum_\mu (PS)^i_{\mu\mu} \qquad (4)$$

According to eqs 3 and 4, we can obtain a simple equation

$$1 = \frac{1}{4}\sum_\mu\sum_\nu (PS)^i_{\mu\nu}(PS)^i_{\nu\mu} = \sum_M\sum_N w^i_{MN} \qquad (5)$$

$$w^i_{MN} = \sum_{\mu\in M}\sum_{\nu\in N}\frac{1}{4}(PS)^i_{\mu\nu}(PS)^i_{\nu\mu} \qquad (6)$$

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TABLE 1: Weights of Each Resonance Structure in H_2O Computed with 6-31G(d,p)

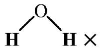
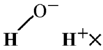
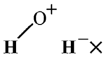
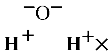
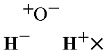
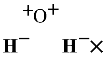
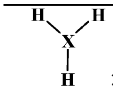
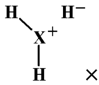
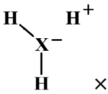
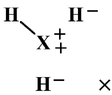
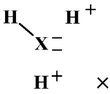
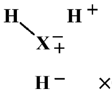
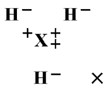
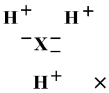
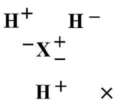
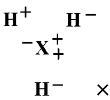
	Weight
 ×1	0.212
 ×2	0.399
 ×2	0.112
 ×1	0.188
 ×2	0.106
 ×1	0.015
Other	-0.032
Total	1.000

TABLE 2: Weights of Resonance Structures of BH_3 and H_3O^+ Calculated with Various Basis Sets[b]

	Hiberty[a])	BS1	BS2	BS3	BS4
 ×1	0.127	0.128	0.133	0.132	0.137
	0.086	0.077	0.038	0.057	0.067
 ×3	0.216	0.219	0.241	0.237	0.231
	0.045	0.048	0.015	0.029	0.039
 ×3	0.165	0.167	0.164	0.166	0.183
	0.291	0.279	0.214	0.248	0.259
 ×3	0.120	0.126	0.146	0.142	0.130
	0.006	0.010	0.002	0.005	0.008
 ×3	0.072	0.073	0.068	0.069	0.082
	0.333	0.334	0.402	0.363	0.334
 ×6	0.186	0.191	0.199	0.198	0.206
	0.114	0.116	0.057	0.085	0.101
 ×1	0.023	0.024	0.030	0.028	0.024
	0.000	0.001	0.000	0.000	0.000
 ×1	0.010	0.011	0.009	0.010	0.012
	0.127	0.134	0.252	0.177	0.143
 ×3	0.042	0.042	0.041	0.041	0.046
	0.072	0.070	0.053	0.062	0.065
 ×3	0.054	0.055	0.060	0.059	0.058
	0.012	0.012	0.004	0.007	0.010
Other	-0.015	-0.035	-0.091	- 0.084	-0.109
	-0.086	-0.081	-0.037	- 0.032	-0.025
Total	1.000	1.000	1.000	1.000	1.000
	1.000	1.000	1.000	1.000	1.000

[a] The results by Hiberty et al.[7] [b] In each structure, upper and lower values represent X = B and X = O, respectively. BS1, BS2, BS3, and BS4 are, respectively, STO-3G, 6-31G, 6-31G(d,p), and 6-311G(d,p).

Importantly, $(PS)^i_{\mu\nu}(PS)^i_{\nu\mu}$ is expressed as the expectation value of an operator.

$$\frac{1}{4}(PS)^i_{\mu\nu}(PS)^i_{\nu\mu} = \langle \phi_i^{\mathrm{local}} | \chi_\nu^{\sigma_i +} \chi_\mu^{\sigma_2{}^{+}+} \varphi_\nu^{\sigma_2 -} \varphi_\mu^{\sigma_1 -} | \phi_i^{\mathrm{local}} \rangle \quad (7)$$

In the case of $\mu \neq \nu$, the sum of $^1/_4(PS)^i_{\mu\nu}(PS)^i_{\nu\mu}$ and $^1/_4(PS)^i_{\nu\mu}(PS)^i_{\mu\nu}$ represents the weight of the electronic structure in which two electrons are singlet-coupled between AOs μ and ν. In the case of $\mu \neq \nu$, $^1/_4(PS)^i_{\mu\mu}(PS)^i_{\mu\mu}$ is that of the electronic structure in which two electrons occupy the same AO μ. Thus, $2w^i_{MN} = w^i_{MN} + w^i_{NM}$ represents the weight of the electronic structure in which two electrons in ϕ_i^{local} are shared between M and N atoms, and w^i_{MM} represents that of the electronic structure in which two electrons in ϕ_i^{local} belong to atom M. When ϕ_i^{local} is a two-center LMO between A and B atoms, two electrons are localized in the bond between A and B, and we can convert eq 5 to eq 8.

$$1 = w^i_{AA} + 2w^i_{AB} + w^i_{BB} + \bar{w}^i \quad (8)$$

The term $\bar{w}^i$ is the sum of all w^i_{MN} in which (M, N) is not (A or B) at the same time. This term corresponds to a higher-body correlation term and is virtually very small as shown below. The weights of ionic and covalent bonds between A and B can be calculated by using eq 8. w^i_{AA} represents the weight of the ionic structure (A^-B^+), w^i_{BB} represents that of the ionic structure (A^+B^-), and $2w^i_{AB}$ represents that of the covalent structure ($A-B$). If each MO can be localized into either one-center or two-center orbital, the weights of the resonance structures of a whole molecule can be obtained by multiplication of the weights of the participating two-center bonding between two atoms.

$$1 = \prod_{i}^{\text{LMOs}} \{w_{AA}^{i} + 2w_{AB}^{i} + w_{BB}^{i} + \bar{w}^{i}\} \qquad (9)$$

The choice of w^i in each LMO i is actually related to choice of valence bond configuration. Because sum of the values in {} is 1 in eq 9, the total sum of the weights calculated by the present procedure is always 1. It is confident that all the weights continuously and reasonably change with respect to nuclear coordinate even if the symmetry is broken.

This method was applied to H_2O, BH_3, and H_3O^+. Two two-center LMOs for H_2O and three for BH_3 and H_3O^+ are selected. All calculations were performed with the program code GAMESS modified by us.

At first, we apply the method to the H_2O (H1−O−H2) molecule using 6-31G(d,p) basis sets.[10] We obtained two two-center valence LMOs, ϕ_4^{local} and ϕ_5^{local}, and then calculated the weights of covalent and ionic bonds for OH1 and OH2 using eqs 6 and 8. In the present case, eq 9 is written as

$$1 = \{w_{\text{OO}}^{4} + 2w_{\text{OH1}}^{4} + w_{\text{H1H1}}^{4} + \bar{w}^{4}\}\{w_{\text{OO}}^{5} + 2w_{\text{OH2}}^{5} + w_{\text{H2H2}}^{5} + \bar{w}^{5}\} \qquad (10)$$

For example, the weight of the structure $H1^+O^-$−H2 was obtained as $w_{\text{OO}}^{4} \times 2w_{\text{OH2}}^{5}$. The weights of all resonance structures are shown in Table 1. “Other” represents the sum of all terms containing $\bar{w}^i$. The most important structure is H^+O^-−H for which the weight is 0.399. The weights of the ionic structures which consist of O^-H^+ are larger than that of O^+H^-. This result agrees well with our chemical intuition. It is noted that the “Other” term is very small.

The results of BH_3 and H_3O^+ are shown in Table 2. The results by our method with STO-3G basis sets are in excellent agreement with those by Hiberty et al.[7] Characteristic differences are observed between BH_3 and H_3O^+. In BH_3, the most important resonance structure consists of two covalent bonds (B−H) and one ionic (B^+H^-) bond. On the other hand, in H_3O^+, the most important resonance structure consists of one covalent bond (O−H) and two ionic bonds (O^-H^+). These results are consistent with the fact that the electronegativity of oxygen is larger than that of boron.

In both, the results from various basis sets are little different. Thus, the weights computed by the present method minimally depend on the selection of basis sets.

In this paper, the method was used in conjunction with Mulliken type of (PS) matrices. However, the analysis by this method can be successfully combined with density matrices based on Löwdin orbitals in the case of simple molecule. Both Löwdin and Mulliken types of density matrices produced qualitatively similar results. The comparison between two kinds of density matrices and the inspection of the basis set dependency will be presented in the forthcoming paper.

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Supporting Information Available: LMOs of H_2O and w_{OO}^{i}, w_{HH}^{i}, and $2w_{\text{OH}}^{i}$ for two-center LMOs in H_2O. The weights of resonance structures for distorted H_2O molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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