An analysis of valence electronic structure from a viewpoint of resonance theory: tautomerization of formamide and diazadiboretidine

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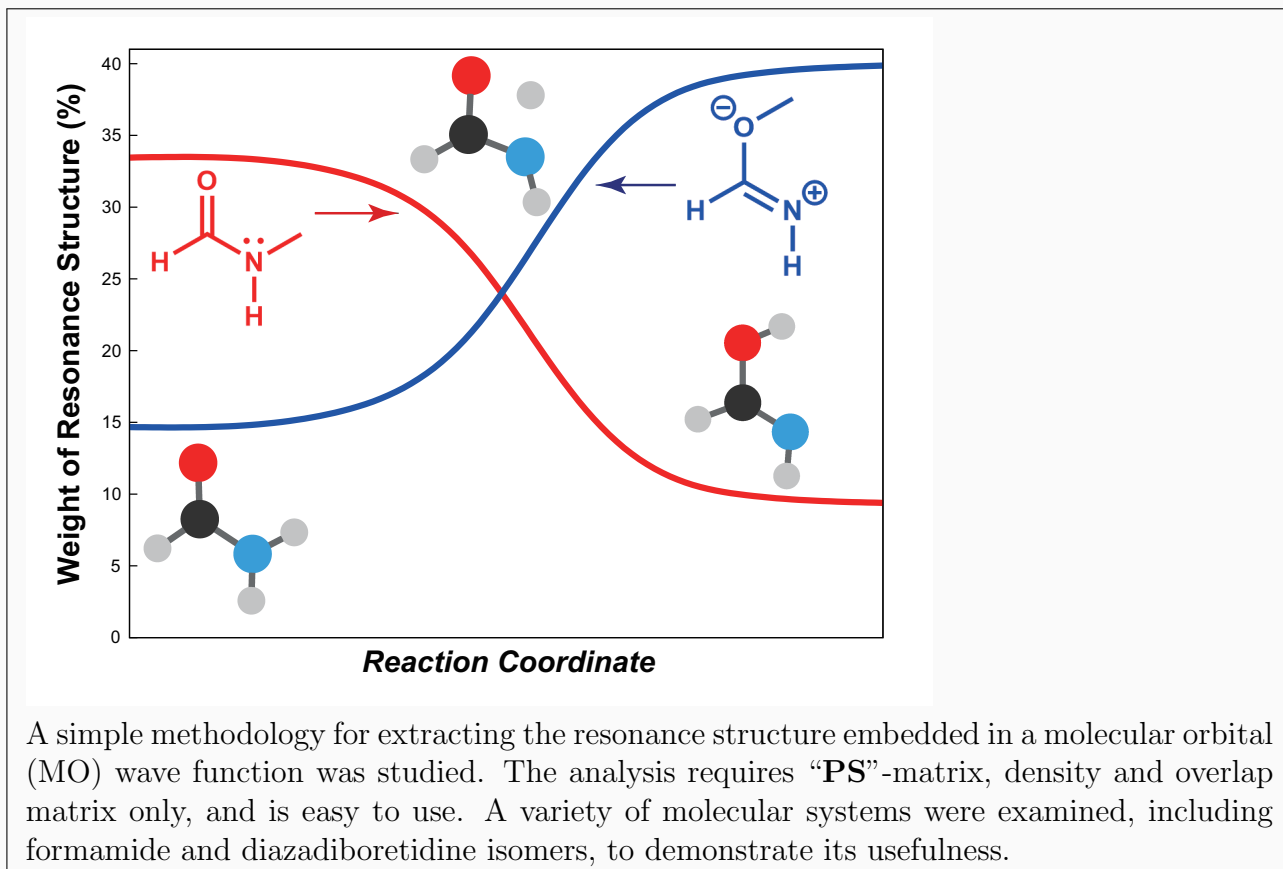
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Abstract

The resonance theory is still very useful in understanding the valence electron structure. However, such a viewpoint is not usually obtained by general-purpose quantum chemical calculations, instead requires rather special treatment such as valence bond methods. In this study, we propose a method based on second quantization to analyze the results obtained by general-purpose quantum chemical calculations from the local point of view of electronic structure and analyze diazadiboretidine and the tautomerization of formamide. This method requires only the "**PS**"-matrix, consisting of the density matrix (P-matrix) and overlap matrix, and can be computed with a comparable load to that of Mulliken population analysis. A key feature of the method is that, unlike other methods proposed so far, it makes direct use of the results of general-purpose quantum chemical calculations.

Keywords: Resonance theory, Second quantized operator, Linear combination of atomic orbital, Electronic structure ∎

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A simple methodology for extracting the resonance structure embedded in a molecular orbital (MO) wave function was studied. The analysis requires "**PS**"-matrix, density and overlap matrix only, and is easy to use. A variety of molecular systems were examined, including formamide and diazadiboretidine isomers, to demonstrate its usefulness.

INTRODUCTION

How do we understand the reason for the planarity of a peptide? One may bring up the idea
of resonance theory and try to rationalize it.
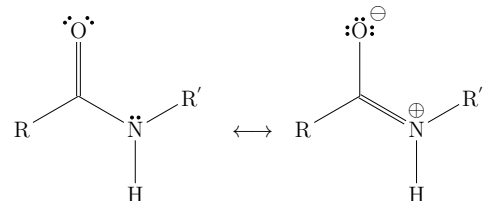
The contributing structures in the resonance can be attributed to the nature of chemical
bonds, which are localized in a moiety of the molecule. This traditional idea on the elec-
tronic structure is quite useful for understanding the origin of molecular properties and
reactivity. On the other hand, commonly used quantum chemical methods provide the elec-
tronic structure expressed in molecular orbital (MO). This is also insightful but cannot be
directly connected to the view of the resonance theory because MOs are intrinsically de-
localized over the molecule. Various methods have ever been invented for the analysis of
wave functions composed of delocalized MOs, including localized molecular orbital (LMO)
methods,[1] natural bond orbital (NBO) and natural resonance theory,[2] complete active space
valence bond methods[3] and other projection methods.[4] Some of these methods focus on the
idea that any MO wave function is represented as a superposition of atomic spin-orbital
based determinants. This is natural because the linear combination of atomic orbitals (AO)
is widely utilized approximation in modern quantum chemistry. Let us consider the wave
function of the form:

$$\Psi = |\cdots \phi_i \cdots \phi_j \cdots|$$
(1)

where ϕ_i is a molecular spin-orbital given as a linear combination of atomic spin-orbitals χ_μ.

$$\phi_i = \sum_\mu c_{i\mu} \chi_\mu$$
(2)

Substituting Eq. (2) into Eq. (1), we obtain

$$\Psi = \left| \cdots \left(\sum_\mu c_{i\mu} \chi_\mu \right) \cdots \left(\sum_\nu c_{j\nu} \chi_\nu \right) \cdots \right| = \sum_\mu c_{i\mu} \cdots \sum_\nu c_{j\nu} \cdots |\cdots \chi_\mu \cdots \chi_\nu \cdots| .$$
(3)

By following previous works, each term of atomic spin-orbital based matrix determinant, $|\cdots \chi_\mu \cdots \chi_\nu \cdots|$, is called AO determinant throughout this study. Eq. (3) is then formally rewritten as

$$\Psi = \sum_i K_i \Psi_i^{\mathrm{AO}} \tag{4}$$

where Ψ_i^{AO} is i-th AO determinant and K_i is its coefficient of the expansion. Note that, on calculation of the "weight" of each AO determinant, $|K_i|^2$ is not proper because commonly used AO basis functions are nonorthogonal, and the sum of $|K_i|^2$ can be changed. Instead, the following Chirgwin-Coulson weight[5]

$$w_i = K_i \left\langle \Psi | \Psi_i^{\mathrm{AO}} \right\rangle \tag{5}$$

satisfies the requirement and the weights sum up to unity for the normalized wave function.

$$\sum_i w_i = \langle \Psi | \Psi \rangle = 1 \tag{6}$$

Hiberty et al. focused on the expansion of Eq. (3) and proposed an analysis method of MO wave functions by regrouping them as valence bond (VB) type basis functions.[6–8] Bachler analyzed the photochemical reactions in terms of resonance structure.[9,10] AO determinant and VB function are not the same in general, but both are related to chemical resonance structures, representing the local electronic structures.

It would be pointed out that the Chirgwin-Coulson weight for the AO determinant in Eq. (5)(hereafter referred to "weight") is not widely evaluated for the analysis in usual computations despite the mathematical background is clear enough. Several reasons are conceivable. One is the nonorthogonality of AO determinants, making it complicated to formulate each weight in a compact form. While an approximate formula for Eq. (5) neglecting the overlap was reported,[9,10] attempts to deal with the nonorthogonality on this formulation so far have not been fully accomplished. The other is that a direct, simple computational procedure of the weight from the standard output of quantum chemistry is not well established. Indeed, the expansion of Eq. (3) is only formal, and it is not clear enough how to organize the large number of terms that appear. In the standard quantum chemical computations, many molecular properties are evaluated from the density

matrix ($\mathbf{P}$ matrix) and proper molecular integrals. A typical example is Mulliken population analysis,[11] in which only $\mathbf{P}$ and overlap ($\mathbf{S}$) matrices are required. In this study, these issues were resolved and a simple formula on the weight was derived by utilizing the biorthogonal, second quantized operator.

In addition to those mentioned above, many related studies have been reported. Through a series of studies, Karafiloglou contributed the methodological development for extracting local electronic structures from delocalized MO wave functions. Utilizing the Moffitt's theorem,[12] Karafiloglou et al. tried to efficiently formulate the weight.[13,14] He also invented an extension of population analysis called poly-electron population analysis,[15–19] and developed methods to represent each weight of resonance structures as an expectation value of a second quantized operator.[16–19,21–23] He and his coworkers especially focused on the orthonormal natural atomic orbitals (NAOs) and NBOs.[17–23] NAOs have been considered to have computational and conceptual advantages for understanding the characters of orbitals. Recently, another analysis scheme utilizing NAO basis was proposed.[24] Ikeda et al. also tried to analyze MO wave functions in terms of resonance structure utilizing second quantized operators.[25–27] They focused on a second quantized formalism especially for nonorthogonal atomic orbitals.[28–30]

In the present study, we followed the second quantized operator approach, and an alternative way for the analysis of MO wave function was derived. One of the advantages is that the weight is computed only with "$\mathbf{PS}$"-matrix. It provides a new procedure to analyze the results obtained with standard quantum chemical computations. The present study sheds new light and clarity on the relationship between molecular orbital calculation and the resonance theory. A practical way of connecting them is proposed, clarifying the relationships between many studies that have been carried out in this field so far, and linking them. In the following, we briefly outline the second quantized formalism in the next methodology section, especially on nonorthogonal orbital, and several chemical processes are analyzed in Section III to demonstrate the advantages of the present method.

METHODS

Second quantized formalism on nonorthogonal atomic spin-orbitals

We briefly outline the second quantized formalism of nonorthogonal orbitals only as much as required for the following discussions. See Refs. [30] and [31] for further details.

Atomic spin-orbitals χ_μ^σ (spin and spatial labels are denoted as σ and μ, respectively) used for standard MO calculations are nonorthogonal in spatial parts,

$$\left\langle \chi_\mu^{\sigma_1} \mid \chi_\nu^{\sigma_2} \right\rangle = \delta_{\sigma_1 \sigma_2} S_{\mu\nu} \neq \delta_{\sigma_1 \sigma_2} \delta_{\mu\nu}. \tag{7}$$

The creation operators $\chi_\mu^{\sigma+}$ and their adjoints $\chi_\mu^{\sigma-}$ obey the following anticommutation rule.

$$\left[\chi_\mu^{\sigma+}, \chi_\nu^{\sigma-} \right]_+ = \chi_\mu^{\sigma+} \chi_\nu^{\sigma-} + \chi_\nu^{\sigma-} \chi_\mu^{\sigma+} = S_{\mu\nu} \neq \delta_{\mu\nu} \tag{8}$$

The usual anticommutation rule is obtained by using operators related to a biorthogonal set of the atomic spin-orbitals. The biorthogonal functions for the atomic spin-orbitals are defined as functions which satisfy

$$\left\langle \varphi_\mu^\sigma | \chi_\nu^\sigma \right\rangle = \delta_{\mu\nu}. \tag{9}$$

This condition is satisfied when

$$\varphi_\mu^\sigma = \sum_\nu S_{\nu\mu}^{-1} \chi_\nu^\sigma \tag{10}$$

where $S_{\nu\mu}^{-1}$ is a matrix element of inverse of overlap matrix. Consider the creation operators $\varphi_\mu^{\sigma+}$ and their adjoints

$$\varphi_\mu^{\sigma-} = \left(\varphi_\mu^{\sigma+} \right)^\dagger = \sum_\nu S_{\mu\nu}^{-1} \chi_\nu^{\sigma-}. \tag{11}$$

The following anticommutation rule holds form Eqs. (8) and (11).

$$\left[\chi_\mu^{\sigma+}, \varphi_\nu^{\sigma-} \right]_+ = \delta_{\mu\nu} \tag{12}$$

Here we introduce an operator,

$$\hat{N}_\mu^\sigma = \chi_\mu^{\sigma+} \varphi_\mu^{\sigma-}. \tag{13}$$

Due to Eq. (12), this operator works as the particle number operator when acting on an AO determinant Ψ^{AO} , satisfying

$$\hat{N}_\mu^\sigma \Psi^{\text{AO}} = \begin{cases} \Psi^{\text{AO}} & \text{when} \quad \chi_\mu^\sigma \in \Psi^{\text{AO}} \\ 0 & \text{when} \quad \chi_\mu^\sigma \notin \Psi^{\text{AO}}. \end{cases} \tag{14}$$

When the operator $\hat{N}_\mu^\sigma$ acts on a linear combination of AO determinants of the form $\sum_i K_i \Psi_i^{\text{AO}}$,

$$\hat{N}_\mu^\sigma \sum_i K_i \Psi_i^{\text{AO}} = \sum_i n_i K_i \Psi_i^{\text{AO}} \tag{15}$$

where n_i is the occupancy of the atomic spin-orbital χ_μ^σ in the AO determinant Ψ_i^{AO}, i.e. $n_i = 1$ when Ψ_i^{AO} contains χ_μ^σ ($\chi_\mu^\sigma \in \Psi_i^{\text{AO}}$) and $n_i = 0$ when $\chi_\mu^\sigma \notin \Psi_i^{\text{AO}}$.

Formulation of the weight of nonorthogonal AO determinant

Let us start with Ψ, which is any types of single MO determinants composed of Hartree-Fock (HF) or Kohn-Sham (KS) spin-orbitals, ϕ_i^σ.

$$\Psi = \left| \phi_i^\alpha \phi_j^\alpha \cdots \phi_k^\beta \phi_l^\beta \cdots \right| \tag{16}$$

The spin-orbital is given as a linear combination of atomic spin-orbitals as

$$\phi_i^\sigma = \sum_\nu c_{i\nu}^\sigma \chi_\nu^\sigma. \tag{17}$$

Note that, though we focus on single MO determinant wave functions as a simple case in the following, the extension to the correlated wave function such as configuration interaction (CI) wave functions is straightforward.

The weight for the N-electron AO determinant, $\left| \chi_a^\alpha \chi_b^\alpha \cdots \chi_c^\beta \chi_d^\beta \cdots \right|$, is obtained by two steps: The first step is to project out the component with its coefficient from Ψ. This is accomplished by acting the string of the projection operators $\hat{N}_\mu^\sigma$ on Ψ. Utilizing the Eq. (15), we can write the weight as follows.

$$w\left(\left| \chi_a^\alpha \chi_b^\alpha \cdots \chi_c^\beta \chi_d^\beta \cdots \right| \right) = \left\langle \Psi \left| \hat{N}_a^\alpha \hat{N}_b^\alpha \cdots \hat{N}_c^\beta \hat{N}_d^\beta \cdots \right| \Psi \right\rangle \tag{18}$$

Eq. (18) shows that the weight of an AO determinant is given as the expectation value concerning the projection operator. The second quantized representation of Mulliken population (gross atomic population) on atomic center A, derived by Mayer,[29,30] is written as

$$\sum_{a \in A} \left(\left\langle \Psi \left| \hat{N}_a^\alpha \right| \Psi \right\rangle + \left\langle \Psi \left| \hat{N}_a^\beta \right| \Psi \right\rangle \right). \tag{19}$$

This implies that the weight in the present study is closely related to the Mulliken population in terms of operator.

The second step is to compute Eq. (18). According to Eqs. (12) and (17), the creation operators $\phi_i^{\sigma+}$ creating an electron on the molecular spin-orbital satisfies the following anticommutation rule.

$$\left[\phi_i^{\sigma+}, \varphi_\mu^{\sigma-} \right]_+ = \sum_\nu c_{i\nu}^\sigma \left[\chi_\nu^{\sigma+}, \varphi_\mu^{\sigma-} \right]_+ = \sum_\nu c_{i\nu}^\sigma \delta_{\nu\mu} = c_{i\mu}^\sigma \tag{20}$$

Using Eq. (20), we obtain

$$\begin{aligned}
\hat{N}_\mu^\sigma \left| \Psi \right\rangle &= \hat{N}_\mu^\sigma \left| \phi_1^\sigma \phi_2^\sigma \cdots \phi_n^\sigma \right\rangle \\
&= \chi_\mu^{\sigma+} \varphi_\mu^{\sigma-} \phi_1^{\sigma+} \phi_2^{\sigma+} \cdots \phi_n^{\sigma+} \left| \text{vac} \right\rangle \\
&= c_{1\mu}^\sigma \left| \phi_1^\sigma \to \chi_\mu^\sigma \right\rangle - \chi_\mu^{\sigma+} \phi_1^{\sigma+} \varphi_\mu^{\sigma-} \phi_2^{\sigma+} \cdots \phi_n^{\sigma+} \left| \text{vac} \right\rangle \\
&= c_{1\mu}^\sigma \left| \phi_1^\sigma \to \chi_\mu^\sigma \right\rangle + \phi_1^{\sigma+} \left(\chi_\mu^{\sigma+} \varphi_\mu^{\sigma-} \right) \phi_2^{\sigma+} \cdots \phi_n^{\sigma+} \left| \text{vac} \right\rangle \\
&= \sum_{i=1}^n c_{i\mu}^\sigma \left| \phi_i^\sigma \to \chi_\mu^\sigma \right\rangle
\end{aligned} \tag{21}$$

where $\left| \phi_i^\sigma \to \chi_\mu^\sigma \right\rangle$ is the determinant in which the molecular spin-orbital ϕ_i^σ is replaced by the atomic spin-orbital χ_μ^σ in the original determinant $\left| \phi_1^\sigma \phi_2^\sigma \cdots \phi_n^\sigma \right\rangle$. Using Eq. (21) repeatedly, Eq. (18) becomes

$$\begin{aligned}
&w \left(\left| \chi_a^\alpha \chi_b^\alpha \cdots \chi_c^\beta \chi_d^\beta \cdots \right| \right) \\
&= \left\langle \Psi \left| \chi_a^{\alpha+} \varphi_a^{\alpha-} \chi_b^{\alpha+} \varphi_b^{\alpha-} \cdots \chi_c^{\beta+} \varphi_c^{\beta-} \chi_d^{\beta+} \varphi_d^{\beta-} \cdots \phi_i^{\alpha+} \phi_j^{\alpha+} \cdots \phi_k^{\beta+} \phi_l^{\beta+} \cdots \right| \text{vac} \right\rangle \\
&= \sum_{i,j,\cdots,k,l,\cdots} c_{ia}^\alpha c_{jb}^\alpha \cdots c_{kc}^\beta c_{ld}^\beta \cdots \left\langle \Psi \left| \Psi \left(\phi_i^\alpha \to \chi_a^\alpha, \phi_j^\alpha \to \chi_b^\alpha, \cdots, \phi_k^\beta \to \chi_c^\beta, \phi_l^\beta \to \chi_d^\beta, \cdots \right) \right\rangle \right.
\end{aligned}$$
$$\tag{22}$$

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with the similar notation to that in Eq. (21). The overlap of the two determinants in Eq. (22) is calculated as,

$$
\left\langle \Psi \mid \Psi \left(\phi_i^\alpha \to \chi_a^\alpha, \phi_j^\alpha \to \chi_b^\alpha, \cdots, \phi_k^\beta \to \chi_c^\beta, \phi_l^\beta \to \chi_d^\beta, \cdots \right) \right\rangle
$$

$$
= \begin{vmatrix}
\langle \phi_i^\alpha | \chi_a^\alpha \rangle & \langle \phi_i^\alpha | \chi_b^\alpha \rangle & & \langle \phi_i^\alpha | \chi_c^\beta \rangle & \langle \phi_i^\alpha | \chi_d^\beta \rangle & \\
\langle \phi_j^\alpha | \chi_a^\alpha \rangle & \langle \phi_j^\alpha | \chi_b^\alpha \rangle & \cdots & \langle \phi_j^\alpha | \chi_c^\beta \rangle & \langle \phi_j^\alpha | \chi_d^\beta \rangle & \cdots \\
& \vdots & \ddots & & \vdots & \ddots \\
\langle \phi_k^\beta | \chi_a^\alpha \rangle & \langle \phi_k^\beta | \chi_b^\alpha \rangle & & \langle \phi_k^\beta | \chi_c^\beta \rangle & \langle \phi_k^\beta | \chi_d^\beta \rangle & \\
\langle \phi_l^\beta | \chi_a^\alpha \rangle & \langle \phi_l^\beta | \chi_b^\alpha \rangle & \cdots & \langle \phi_l^\beta | \chi_c^\beta \rangle & \langle \phi_l^\beta | \chi_d^\beta \rangle & \cdots \\
& \vdots & \ddots & & \vdots & \ddots
\end{vmatrix}
$$

$$
= \begin{vmatrix}
\langle \phi_i^\alpha | \chi_a^\alpha \rangle & \langle \phi_i^\alpha | \chi_b^\alpha \rangle & \\
\langle \phi_j^\alpha | \chi_a^\alpha \rangle & \langle \phi_j^\alpha | \chi_b^\alpha \rangle & \cdots \\
& \vdots & \ddots
\end{vmatrix}
\begin{vmatrix}
\langle \phi_k^\beta | \chi_c^\beta \rangle & \langle \phi_k^\beta | \chi_d^\beta \rangle & \\
\langle \phi_l^\beta | \chi_c^\beta \rangle & \langle \phi_l^\beta \chi_d^\beta \rangle & \cdots \\
& \vdots & \ddots
\end{vmatrix} .
\tag{23}
$$

Substituting Eqs. (23) into Eq. (22), and replacing the matrix elements with

$$
\langle \phi_i^\sigma | \chi_\mu^\sigma \rangle = \sum_\nu c_{i\nu}^{\sigma*} \langle \chi_\nu^\sigma | \chi_\mu^\sigma \rangle = \sum_\nu c_{i\nu}^{\sigma*} S_{\nu\mu},
\tag{24}
$$

we obtain

$$
w \left(\left| \chi_a^\alpha \chi_b^\alpha \cdots \chi_c^\beta \chi_d^\beta \cdots \right| \right)
$$

$$
= \sum_{i,j,\cdots} c_{ia}^\alpha c_{jb}^\alpha \cdots
\begin{vmatrix}
\sum_\mu c_{i\mu}^{\alpha*} S_{\mu a} & \sum_\mu c_{i\mu}^{\alpha*} S_{\mu b} & \\
\sum_\mu c_{j\mu}^{\alpha*} S_{\mu a} & \sum_\mu c_{j\mu}^{\alpha*} S_{\mu b} & \cdots \\
& \vdots & \ddots
\end{vmatrix}
\sum_{k,l,\cdots} c_{kc}^\beta c_{ld}^\beta \cdots
\begin{vmatrix}
\sum_\mu c_{k\mu}^{\beta*} S_{\mu c} & \sum_\mu c_{k\mu}^{\beta*} S_{\mu d} & \\
\sum_\mu c_{l\mu}^{\beta*} S_{\mu c} & \sum_\mu c_{l\mu}^{\beta*} S_{\mu d} & \cdots \\
& \vdots & \ddots
\end{vmatrix}
$$

$$
= \begin{vmatrix}
\sum_\mu P_{a\mu}^\alpha S_{\mu a} & \sum_\mu P_{a\mu}^\alpha S_{\mu b} & \\
\sum_\mu P_{b\mu}^\alpha S_{\mu a} & \sum_\mu P_{b\mu}^\alpha S_{\mu b} & \cdots \\
& \vdots & \ddots
\end{vmatrix}
\begin{vmatrix}
\sum_\mu P_{c\mu}^\beta S_{\mu c} & \sum_\mu P_{c\mu}^\beta S_{\mu d} & \\
\sum_\mu P_{d\mu}^\beta S_{\mu c} & \sum_\mu P_{d\mu}^\beta S_{\mu d} & \cdots \\
& \vdots & \ddots
\end{vmatrix}
$$

$$
= \begin{vmatrix}
(\mathbf{P}^\alpha \mathbf{S})_{aa} & (\mathbf{P}^\alpha \mathbf{S})_{ab} & \\
(\mathbf{P}^\alpha \mathbf{S})_{ba} & (\mathbf{P}^\alpha \mathbf{S})_{bb} & \cdots \\
& \vdots & \ddots
\end{vmatrix}
\begin{vmatrix}
(\mathbf{P}^\beta \mathbf{S})_{cc} & (\mathbf{P}^\beta \mathbf{S})_{cd} & \\
(\mathbf{P}^\beta \mathbf{S})_{dc} & (\mathbf{P}^\beta \mathbf{S})_{dd} & \cdots \\
& \vdots & \ddots
\end{vmatrix}
\tag{25}
$$

where $\mathbf{S}$ is the overlap matrix with the (μ, ν)-element $S_{\mu\nu}$ and $\mathbf{P}^\sigma$ is the density matrix (P matrix) with the (μ, ν)-element

$$P_{\mu\nu}^\sigma = \sum_i^{\mathrm{occ}} c_{i\mu}^\sigma c_{i\nu}^{\sigma*}. \tag{26}$$

For the HF wave function of two electrons, the weight of $\left|\chi_a^\alpha \chi_b^\beta\right|$ is

$$w\left(\left|\chi_a^\alpha \chi_b^\beta\right|\right) = (\mathbf{P}^\alpha \mathbf{S})_{aa}(\mathbf{P}^\beta \mathbf{S})_{bb}. \tag{27}$$

When the restricted HF (RHF) wave function is used for this two-electron system, $(\mathbf{P}^\alpha \mathbf{S})_{aa}(\mathbf{P}^\beta \mathbf{S})_{bb} = \frac{1}{4}(\mathbf{PS})_{ab}(\mathbf{PS})_{ba}$ holds where $\mathbf{P} = 2\mathbf{P}^\alpha = 2\mathbf{P}^\beta$. Therefore, Eq. (27) is equivalent to the formula utilized for the analysis of MOs by Ikeda et al.[25–27]

In a similar manner, for the four-electron system, the weight is given by,

$$w\left(\left|\chi_a^\alpha \chi_b^\alpha \chi_c^\beta \chi_d^\beta\right|\right) = \begin{vmatrix} (\mathbf{P}^\alpha \mathbf{S})_{aa} & (\mathbf{P}^\alpha \mathbf{S})_{ab} \\ (\mathbf{P}^\alpha \mathbf{S})_{ba} & (\mathbf{P}^\alpha \mathbf{S})_{bb} \end{vmatrix} \begin{vmatrix} (\mathbf{P}^\beta \mathbf{S})_{cc} & (\mathbf{P}^\beta \mathbf{S})_{cd} \\ (\mathbf{P}^\beta \mathbf{S})_{dc} & (\mathbf{P}^\beta \mathbf{S})_{dd} \end{vmatrix}$$
$$= \{(\mathbf{P}^\alpha \mathbf{S})_{aa}(\mathbf{P}^\alpha \mathbf{S})_{bb} - (\mathbf{P}^\alpha \mathbf{S})_{ab}(\mathbf{P}^\alpha \mathbf{S})_{ba}\}\{(\mathbf{P}^\beta \mathbf{S})_{cc}(\mathbf{P}^\beta \mathbf{S})_{dd} - (\mathbf{P}^\beta \mathbf{S})_{cd}(\mathbf{P}^\beta \mathbf{S})_{dc}\}, \tag{28}$$

and for six-electron system,

$$w\left(\left|\chi_a^\alpha \chi_b^\alpha \chi_c^\alpha \chi_d^\beta \chi_e^\beta \chi_f^\beta\right|\right) = \begin{vmatrix} (\mathbf{P}^\alpha \mathbf{S})_{aa} & (\mathbf{P}^\alpha \mathbf{S})_{ab} & (\mathbf{P}^\alpha \mathbf{S})_{ac} \\ (\mathbf{P}^\alpha \mathbf{S})_{ba} & (\mathbf{P}^\alpha \mathbf{S})_{bb} & (\mathbf{P}^\alpha \mathbf{S})_{bc} \\ (\mathbf{P}^\alpha \mathbf{S})_{ca} & (\mathbf{P}^\alpha \mathbf{S})_{cb} & (\mathbf{P}^\alpha \mathbf{S})_{cc} \end{vmatrix} \begin{vmatrix} (\mathbf{P}^\beta \mathbf{S})_{dd} & (\mathbf{P}^\beta \mathbf{S})_{de} & (\mathbf{P}^\beta \mathbf{S})_{df} \\ (\mathbf{P}^\beta \mathbf{S})_{ed} & (\mathbf{P}^\beta \mathbf{S})_{ee} & (\mathbf{P}^\beta \mathbf{S})_{ef} \\ (\mathbf{P}^\beta \mathbf{S})_{fd} & (\mathbf{P}^\beta \mathbf{S})_{fe} & (\mathbf{P}^\beta \mathbf{S})_{ff} \end{vmatrix}. \tag{29}$$

Now the weight of an AO determinant is readily computed with Eq. (25) by using overlap and P-matrix. Especially when an orthonormal atomic orbital basis set is used, "$\mathbf{PS}$"-matrix in Eq. (25) is replaced by the matrix $\mathbf{P}^\sigma$. Eq. (25) is applicable not only to the closed-shell system but also to different orbitals for different spins (DODS) type such as unrestricted HF (UHF) wave function, as previously recognized.[9] This expression will also be useful for the extension to multi-configurational wave functions.

Resonance theory

Eq. (25) can be associated with the analysis of MO wave functions in terms of resonance theory, but further considerations are necessary for actual computations. As an example, consider the two electron AO determinant $\left|\chi_a^\alpha \chi_b^\beta\right|$ where atomic spin-orbitals χ_a^α and χ_b^β belong to atomic centers A and B, respectively ($\chi_a^\alpha \in$ A and $\chi_b^\beta \in$ B). This is associated with the resonance structure denoted as A($\uparrow$)B($\downarrow$) where up (α) and down (β) spins belong to A and B respectively. The weight of the covalent type resonance structure A–B is then given by $w\left(\left|\chi_a^\alpha \chi_b^\beta\right|\right) + w\left(\left|\chi_b^\alpha \chi_a^\beta\right|\right)$. Analogously, $w\left(\left|\chi_a^\alpha \chi_a^\beta\right|\right)$ and $w\left(\left|\chi_b^\alpha \chi_b^\beta\right|\right)$ can be regarded as the weight of the ionic type resonance structures A^-–B^+ and A^+–B^-, respectively. Similarly, the proper linear combination of AO determinants is considered on the conversion to a linearly independent set of VB type function.

For the computations with extended basis sets, the weight is simply extended to[8–10]

$$\sum_{a\in A, b\in B, c\in C, d\in D,\ldots} w\left(\left|\chi_a^\alpha \chi_b^\alpha \cdots \chi_c^\beta \chi_d^\beta \cdots\right|\right). \tag{30}$$

In our treatment, an important property is satisfied between weight of resonance structures and Mulliken population: weighted sum of numbers of valence electrons on an atom in all resonance structures is equal to the Mulliken population of the atomic center in the valence space. A more detail discussion about that can be found in Supporting Information (SI).

Applications for the analysis of resonance structures

This section is devoted to demonstrating the chemical application of the present methodology. All the calculations and the subsequent analysis were conducted with the GAMESS program package[32] modified by us.

Assessments on *trans*-butadiene and ozone

First of all, we study the *trans*-butadiene and ozone molecules, which are 4π-electron systems. They have been the subject of many studies, including the pioneering work of Hiberty, and

is typical of those on resonance theory. The details are reported in SI. As expected, our results are virtually the same as those by Hiberty when the minimal basis sets (STO-3G) is employed. Note that their VB structures, Kekulé and 1,4-diradical structure of butadiene correspond to the three contributing structures in the present work. Both of them can be equivalent by taking proper linear combinations.

The present method is easy to be applied to the computations with standard, extended basis sets. As can be seen in Tables S1 and S2, the differences in weights due to the basis sets are within 1-2% when the sufficiently large basis set is used. It is interesting that the DODS treatment for ozone shows considerable difference from the spin-restricted function. In all cases, the method provides adequate computational results, in agreement with previous results and our chemical intuition. It should be emphasized that the present method is equivalent to Hiberty's one only concerning with three-center four-electron systems. While the present method is based on "$\mathbf{PS}$"-matrix, reflecting the uniqueness of expansion with AO-determinant, this is not the case for Hiberty's method since the dependent VB type basis set is not uniquely determined. For the details, see SI.

Tautomerism of formamide and formamidic acid

Tautomerism of formamide and formamidic acid represented in the conventional reaction formula (Figure 1) is a simple chemical reaction accompanied with the migration of a hydrogen atom. The tautomerism is considered as a change of distribution of π-electrons in the three atomic center in conjunction with geometry change. It should be stressed again that the present method only requires the "$\mathbf{PS}$"-matrix obtained in the usual quantum chemical calculations. It enables us to compute the weights very readily, meaning that the analysis of the reaction is also easy almost without additional computations.

The transition state and intrinsic reaction coordinate (IRC) in this process are determined with the standard manner at RB3LYP[33–35]/6-31G(d).[36] Then, each weight is computed along the IRC using Eqs. (28) and (30). The structures of this system are shown in Figure 2 (**1a-1f**). Firstly, we show each weight of the resonance structures (**1a–1f**) in formamide (at the geometry optimized by RHF/6-31G(d) for comparison) in Table 1. The results by HF, KS and the previous *ab initio* VB (VBSCF)[37] calculations are shown in the table.

Tested exchange-correlation functionals are B3LYP, BLYP,[34,35] CAM-B3LYP,[38] PBE0,[39] PBE,[40,41] M06-2X[42] and ωB97X.[43] The covalent structure (**1a**) and ionic structure (**1b**) have large weights. It has been known in *ab initio* VB theory that the structure **1b** in which polarization to oxygen is occurring has a large weight in addition to the large weight of structure **1a**. We found that the computed weights show a similar tendency as those from the VB functions constructing the VBSCF wave function, although direct comparison can not be made, strictly speaking. In the present method, the weight of ionic structure (**1b**) seems to be overestimated probably because the wave function is constructed by a single determinant. We found functional dependence on the weights is moderate in this molecule.

The change of the weight along the IRC is shown in Figure 3. Near the transition state (IRC = 0.0), the character changes drastically. In particular, the weight of **1a** and **1d** largely change from 33.5% to 9.4% and from 14.7% to 39.9%, respectively. Thus, this reaction process is characterized as the change of electronic state from **1a** to **1d**, justifying the representation by the standard chemical reaction formula. The weight of structure **1b** constantly large around 31.0–35.9% in this process. The weight of **1e** little changes but slightly increases near the transition structure where the O-C-N bond angle slightly decreases. The tendencies that each weight of **1f** and **1c** slightly increases and decreases in this process also seem to be reasonable. Looking at chemical reactions as continuous changes of resonance structures, we can capture the entire character of the change in the electronic state. As demonstrated above, this *a posteriori* analysis accompanied with MO or KS calculations will be useful for understanding of chemical reaction processes.

Electronic delocalization in 1,3,2,4- and 1,2,3,4-diazadiboretidine

The electronic properties of 1,3,2,4-diazadiboretidine (**2**) and 1,2,3,4-diazadiboretidine (**3**) recently attract researchers' attentions.[44] The analysis of nucleus-independent chemical shift (NICS) and energetic difference from the reference acyclic system showed that the electrons in **2** show more delocalized character than in **3**. It seems to be difficult to make a systematic comparison of the degree of delocalization of $\pi-$electron systems on the basis of delocalized MOs. In fact, *ab initio* VB (VBCI) computation was applied to analyze **2**.[45]

As pointed out previously,[44,45] the planar geometries do not correspond to energy min-

imum in both molecules. However, imposing planarity constraints simplifies the discussion due to the $\sigma - \pi$ separation, and will be useful for understanding the electronic properties of them. Following this treatment, we analyzed the planar **2** and the planar **3** with D_{2h} and C_{2v} symmetry, respectively. The geometries of both molecules were optimized by HF/6-31G(d,p), then their weights of resonance structures were calculated with HF and KS methods with the same basis set at the common geometries. Various exchange-correlation functionals were tested for **2**, and the B3LYP functional was used for **3**. At the optimized structure of **2**, the B-N bond length is 1.443Å. The N-N, B-B, and B-N bond lengths are 1.442, 1.775, and 1.401Å, respectively in **3**.

Both compounds are treated as four-center four-electron system in the analysis. All the structures (**2a**–**2i** and **3a**–**3m**) of these systems considered are shown in Figures 4 and 5, respectively. The corresponding weights are shown in Tables 2 and 3, respectively for **2** and **3**. Previous *ab initio* VB (VBCI) results of **2**[45] are also shown in Table 2 for comparison. Concerning the results of **2**, the weight of **2g** in which four electrons are localized on two nitrogen atoms is especially large. Also, the weight of **2c** in which delocalization to boron is occurring is large to the same extent. The results of B3LYP in the present method is quite similar to those by the VBCI. The HF seems to overestimate the weight of **2g**, probably due to the lack of the electron correlation. We found hybrid functionals tend to behave between the pure GGA functional and HF in terms of the weight, as expected. Unfortunately, VB calculation for **3** has not been reported so far, but the above results suggest that the present analysis is comparable to that by *ab initio* VB methods, and sufficiently reliable. On the results of **3**, the weight of **3j** (58.93% by HF and 49.11% by B3LYP) is larger than the weight of **2g** (52.35% by HF and 41.60% by B3LYP) both by B3LYP and by HF. Additionally, the weight of **3d** (33.60% by HF and 38.11% by B3LYP) is smaller compared with **2c** (39.03% by HF and 44.98% by B3LYP). Though there are contributions from other structures in **2** and **3**, their weights are relatively small (difference of total contributions is about 1%) and will not affect the discussion here. By these comparison through the present analysis of **2** and **3**, we found the degree of the delocalization is larger in the former molecule. This observation by directly analyzing delocalized MOs is consistent with the previous results by other analysis method mentioned above.[44]

CONCLUSIONS

Any MO wave functions could be uniquely expanded with AO determinants. As has been recognized so far, estimating the weights of each AO determinant constructing the wave function give us insights to the electronic structures of molecules. In this study, we focused on a second quantized formalism of nonorthogonal orbitals and formulated the well-defined weight of each AO determinant constructing single-determinant wave function. As a result, we derived the simplest formula on the weight of AO determinant as Eq. (25) using density matrix and overlap matrix only. Through the present study, a very clear and easy-to-use analysis methodology for delocalized MO wave functions in terms of resonance structure was established. In principle, any numbers of electrons can be treated, and the analysis in terms of resonance theory is possible with the given set of valence bond functions.

The derived formula was numerically verified through the analysis of simple π-electron systems. The present methodology combined with standard quantum chemical calculations will be useful to analyze electronic properties of molecules and chemical reaction processes.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Figure 1: Tautomerism of formamide and formamidic acid represented in the conventional chemical reaction formula.

Figure 2: Resonance structures of formamide.

Figure 3: The changes of the weights of resonance structures in the 4π-electron system along the IRC for the isomerization of formamide to formamidic acid calculated with B3LYP/6-31G(d). The corresponding resonance structures (**1a**–**1f**) are shown in Figure 2.

Figure 4: Resonance structures of 1,3,2,4-diazadiboretidine (**2**).

Figure 5: Resonance structures of 1,2,3,4-diazadiboretidine (**3**).

Figure 1
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1a

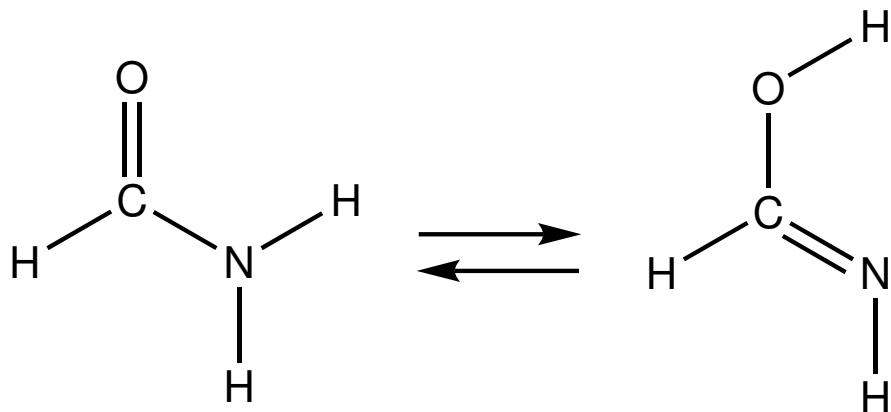**1b**

1c

1d

1e

1f
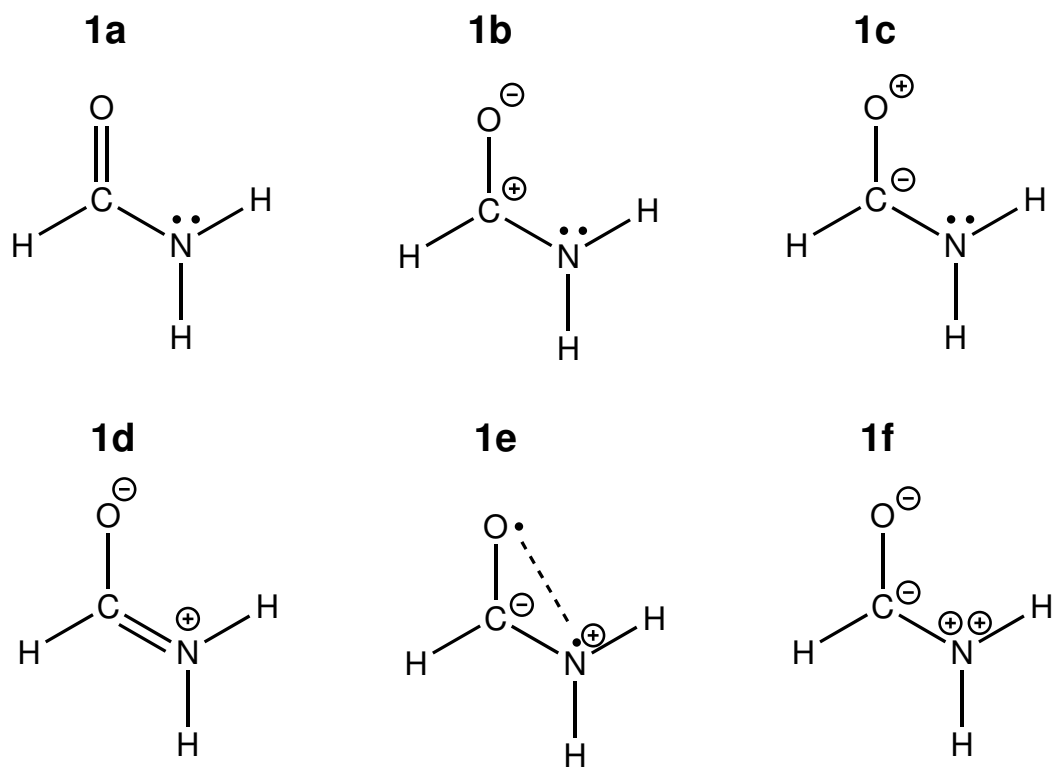
Figure 2
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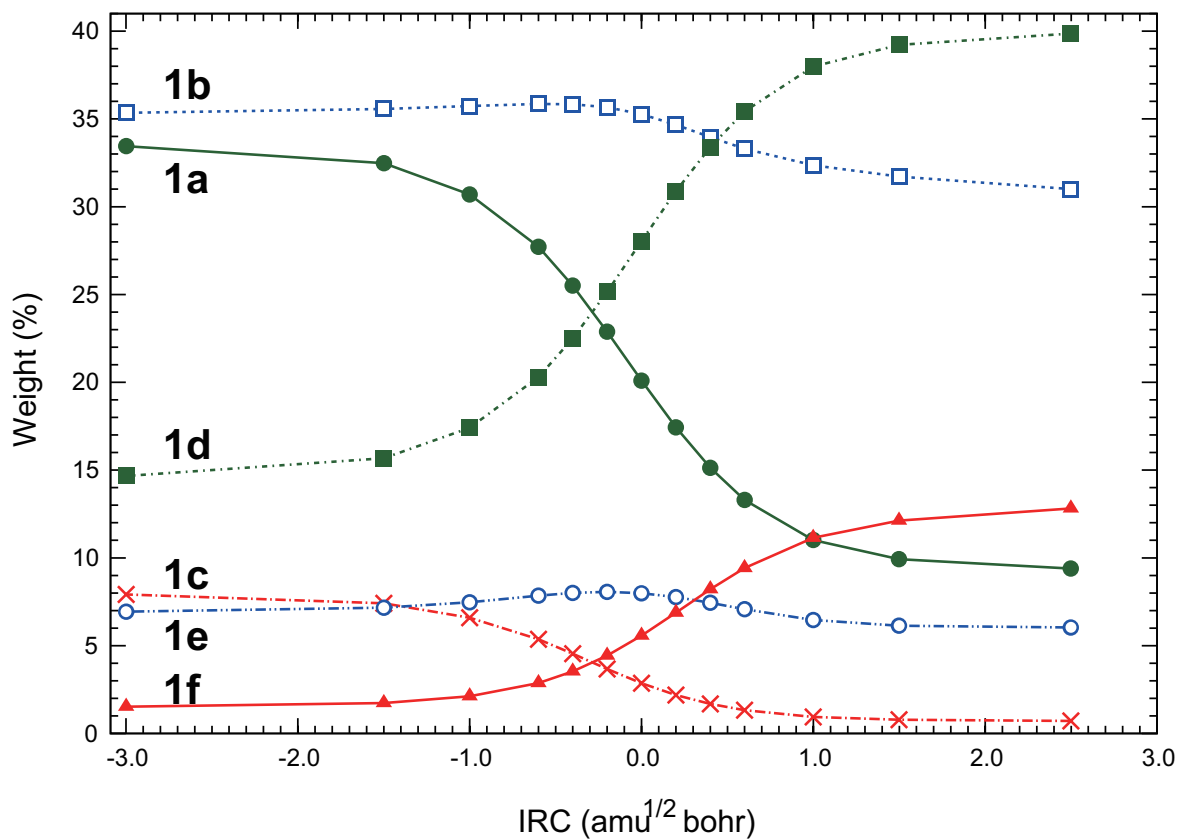
Figure 3
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2a

HN—BH
HB—NH

2b

HN—BH
HB—NH

2c

HN—BH
HB—NH

2d

HN—BH
HB—NH

2e

HN—BH
HB—NH

2f

HN—BH
HB—NH

2g

HN—BH
HB—NH

2h

HN—BH
HB—NH

2i

HN—BH
HB—NH
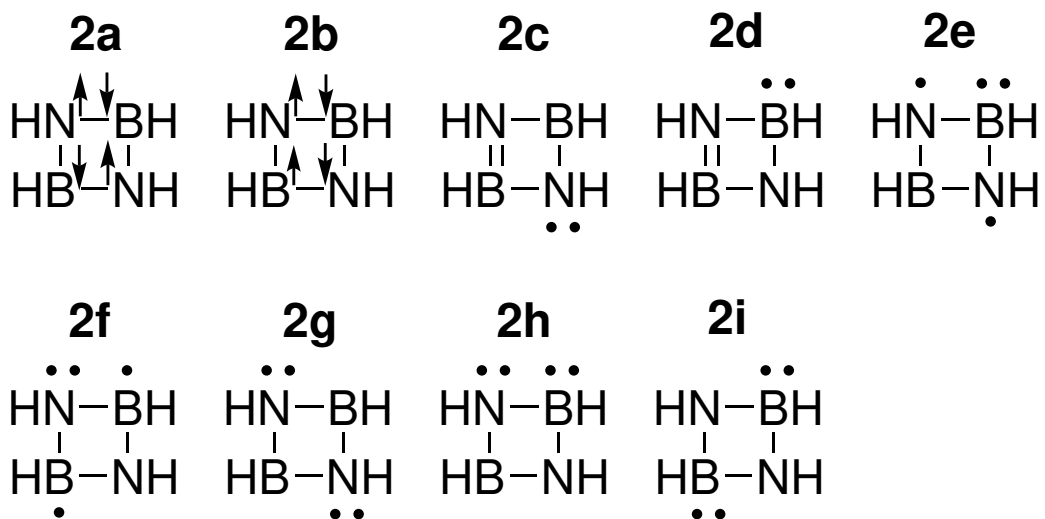
Figure 4
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3a **3b** **3c** **3d** **3e**

HN–BH HN–BH HN–BH HN–BH HN–BH
HN–BH HN–BH HN–BH HN=BH HN=BH

3f **3g** **3h** **3i** **3j**

HN–BH HN–BH HN–BH HN–BH HN–BH
HN–BH HN–BH HN–BH HN–BH HN–BH

3k **3l** **3m**

HN–BH HN–BH HN–BH
HN–BH HN–BH HN–BH
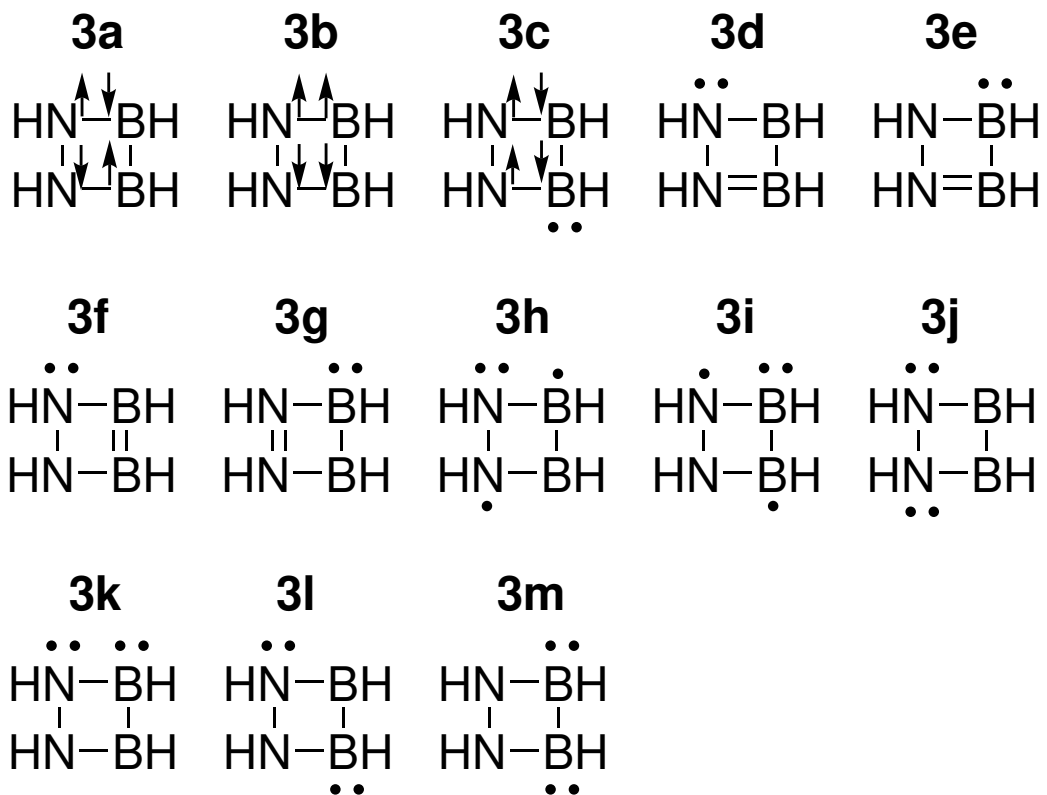
Figure 5
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Structure	B3LYP	BLYP	CAM-B3LYP	PBE0	PBE	M06-2X	ωB97X	HF	VBSCF
1a	33.71	33.51	34.03	33.64	33.40	34.20	34.01	33.21	46.1
1b	35.27	33.26	36.14	35.65	33.11	36.19	36.64	43.32	31.8
1c	8.06	8.44	8.01	7.94	8.43	8.08	7.89	6.36	2.3
1d	14.42	15.23	13.83	14.33	15.33	13.65	13.65	11.68	13.1
1e	6.89	7.67	6.51	6.76	7.73	6.45	6.33	4.48	6.5
1f	1.48	1.74	1.32	1.44	1.77	1.29	1.27	0.79	0.2
Others	0.16	0.15	0.15	0.24	0.23	0.14	0.21	0.17	–
Total	100	100	100	100	100	100	100	100	100

Table 1: Weight of resonance structures (%) of formamide calculated with 6-31G(d).

Taken from Table II in Ref. [37]

Structure	Degeneracy	HF	B3LYP	BLYP	CAM-B3LYP	PBE0	PBE	M06-2X	ωB97X	VBCI
2a	2	0.35	0.36	0.35	0.36	0.37	0.37	0.37	0.37	–
2b	4	1.82	3.04	3.49	2.83	2.94	3.50	2.68	2.62	–
2c	4	39.03	44.98	46.36	44.22	44.56	46.32	43.65	43.37	48.8
2d	4	0.13	0.19	0.22	0.18	0.20	0.22	0.18	0.18	–
2e	2	1.82	3.04	3.49	2.83	2.94	3.50	2.68	2.62	–
2f	2	1.82	3.04	3.49	2.83	2.94	3.50	2.68	2.62	–
2g	1	52.35	41.60	38.45	43.21	42.25	38.26	44.39	44.76	40.4
2h	4	1.82	3.04	3.49	2.83	2.94	3.50	2.68	2.62	–
2i	1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	–
Others		0.86	0.71	0.65	0.71	0.88	0.81	0.67	0.83	–
Total		100	100	100	100	100	100	100	100	100

Table 2: Weight of resonance structures (%) of 1,3,2,4-diazadiboretidine (**2**) calculated with 6-31G(d,p).

Taken from Figure 5 in Ref [45]. Instead of structures **2a**–**2c**, Kekulé type bases are included in their VB expansion, and their weights are alternatively reported there.

Structure	Degeneracy	HF	B3LYP
3a	2	2.39	3.70
3b	2	0.00	0.00
3c	2	2.37	3.65
3d	4	33.60	38.11
3e	4	0.68	1.42
3f	4	-0.09	-0.11
3g	4	-0.09	-0.11
3h	4	-0.61	-0.55
3i	4	-0.01	-0.02
3j	1	58.93	49.11
3k	2	0.00	0.00
3l	2	2.39	3.70
3m	1	0.02	0.07
Others		0.41	1.03
Total		100	100

Table 3: Weight of resonance structures (%) of 1,2,3,4-diazadiboretidine (**3**) calculated with 6-31G(d,p).