A geminal method based on the generalized electron pairing
applied to the Heisenberg model of hydrocarbons

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1 In the approximate valence bond (VB) description of
2 molecular electronic structures, the resonating VB effect
3 might be incorporated in an efficient manner by mixing the
4 triplet component into conventional singlet geminals. We
5 developed a variational optimization scheme for this
6 *generalized pairing* type wave function in the framework of
7 the spin Hamiltonian model. With numerical verifications,
8 we found the resonance stabilization is partially described
9 through the contamination of higher spin states for molecules
10 such as non-Kekulé hydrocarbons.

11 Keywords: Valence bond theory, Geminal theory,
12 Heisenberg spin Hamiltonian

13 The valence bond (VB) theory, based on the Lewis's
14 electron pair concept, is an appealing chemical theory
15 providing insights into molecular electronic structures from a
16 perspective different from delocalized molecular orbitals.[1–3]
17 The Heisenberg model, or classical VB model, is quite useful
18 to qualitatively understand electronic structures from a
19 viewpoint of localized chemical bonds. Notably, the
20 Ovchinnikov's rule,[4] which predicts the ground state spin
21 multiplicity of hydrocarbons, is derived from the Heisenberg
22 model. This spin Hamiltonian theory was extensively applied
23 to conjugated hydrocarbons.[5–14] The accumulated results
24 show that the neutral ground and low-lying excited states of
25 many conjugated hydrocarbons are well described by this
26 simple spin Hamiltonian model. Theoretical developments in
27 the classical VB theory were reviewed by Klein et al.[15]

28 In the rigorous VB model, however, the number of
29 resonance structures combinatorically increases as the
30 number of electrons in the system increases; we need to
31 consider a huge number of VB basis functions even for
32 medium-sized molecules. This fact complicates the
33 computation and interpretation of VB wave functions. The
34 situation is essentially the same in both *ab initio*[16–18] and
35 qualitative VB theories. Due to these circumstances, one
36 representative resonance structure is often used to describe
37 the electronic state in simple terms. (Chemists may
38 unconsciously make a selection for the chemical structure
39 formula of a conjugated hydrocarbon.) This approximation in
40 the VB method is called *perfect pairing* (PP). If a simple
41 method to correct the resonating VB effect ignored in this
42 approximation is established, it is expected to efficiently
43 improve the numerical accuracy of the compact trial wave
44 function while maintaining a clear chemical picture.

45 We mention the theory of many-electron wave functions
46 based on the two-electron unit or *geminal*,[19–21] a fundamental
47 basis of our present study. Several researchers devised
48 methods to efficiently correct the geminal product type wave
49 functions by partially relaxing the spin symmetry of

50 geminals.[22–25] Furthermore, Surján, Szabados and their
51 coworkers developed a perturbation theory[26] and spin-
52 projection techniques[27–30] to improve spin-unrestricted
53 geminals. Some other directions to extend geminal product
54 wave functions can be found in refs [31–33]. Notably, in the
55 field of quantum Monte Carlo, the idea of *generalized pairing*
56 (GP),[34,35] or fully extended spin functions in geminals, was
57 proposed to capture the electron correlation. By mixing the
58 triplet functions into standard singlet-type geminals, inter-
59 geminal correlation effect is expected to be incorporated in
60 an efficient manner. To the best of our knowledge, however,
61 the GP concept has not been well tested especially for
62 polyatomic molecular systems. In addition, its chemical
63 meaning does not seem to be fully understood.

64 In this work, a new method to incorporate the resonating
65 VB effect into the simple PP wave function was devised and
66 numerically tested in the framework of the Heisenberg model.
67 We propose a variational optimization scheme for GP type
68 wave functions and the chemical meaning is clarified for
69 unsaturated hydrocarbons.

70 In what follows, we present the formulation and method
71 for the computation of GP type VB wave functions based on
72 the variational principle. The Heisenberg spin Hamiltonian
73 considered here is

$$H = \sum_{\mu < \nu} J_{\mu\nu} \mathbf{S}_\mu \cdot \mathbf{S}_\nu \qquad (1)$$

75 where $J_{\mu\nu}$ is the exchange interaction constant and $J_{\nu\mu} = J_{\mu\nu}$ (μ
76 $< \nu$) is satisfied for convenience. The spin operator acts on the
77 orthogonal basis functions χ_μ placed on the atomic sites. We
78 assume $J_{\mu\nu} > 0$, i.e., antiferromagnetism. The constant
79 parameters are assumed to include some non-orthogonality
80 effects, which are generally important for the VB description.
81 The spin operator can be represented as

$$\mathbf{S}_\mu \cdot \mathbf{S}_\nu = \frac{1}{2}\left(a_\nu^{\beta+} a_\mu^{\alpha+} a_\mu^{\beta-} a_\nu^{\alpha-} + a_\mu^{\beta+} a_\nu^{\alpha+} a_\nu^{\beta-} a_\mu^{\alpha-} \right)$$

82
$$+ \frac{1}{4}\left(a_\mu^{\alpha+} a_\nu^{\alpha+} a_\nu^{\alpha-} a_\mu^{\alpha-} - a_\mu^{\alpha+} a_\nu^{\beta+} a_\nu^{\beta-} a_\mu^{\alpha-} \right. \qquad (2)$$

$$\left. - a_\mu^{\beta+} a_\nu^{\alpha+} a_\nu^{\alpha-} a_\mu^{\beta-} + a_\mu^{\beta+} a_\nu^{\beta+} a_\nu^{\beta-} a_\mu^{\beta-} \right)$$

83 where $a_\mu^{\sigma+}$ and a_μ^{σ} are creation and annihilation operators for
84 spinorbital χ_μ^σ (having spatial part χ_μ and spin part σ),
85 respectively.
86 The tested trial wave functions for 2N-electron systems are
87 written as

88 $\Phi = \hat{A}[\psi_1(x_1, x_2)\psi_2(x_3, x_4)\cdots\psi_N(x_{2N-1}, x_{2N})]$ (3)

89 where ψ_i is an antisymmetrized geminal, $\hat{A}$ is the
90 antisymmetrizer between geminals, and x_n shows the spatial

1 coordinate r_n and spin coordinate. The PP wave function Φ_{PP}
2 for the singlet state is simply constructed using normalized
3 singlet geminals as ψ_i in eq (3),

$$\psi_i^{PP} = \left| \chi_\mu^\alpha \chi_\nu^\beta \right| - \left| \chi_\mu^\beta \chi_\nu^\alpha \right| \qquad (\mu, \nu \in i). \tag{4}$$

5 The notation $\mu, \nu \in i$ means χ_μ and χ_ν are exclusively involved
6 in the geminal labeled i. Higher spin states can be described
7 by replacing the singlet geminals with proper spin functions.
8 Correspondence between Φ_{PP} and a chemical structure is
9 obvious by linking the atomic sites where χ_μ and χ_ν in each
10 geminal are placed on. The exact VB wave function can be
11 represented as a superposition of all the linearly independent
12 PP functions.
13 By extending the geminal to include the general spin
14 functions,

$$\psi_i^{GP} = \sum_{\sigma_1 \sigma_2} C_{\mu\nu}^{\sigma_1\sigma_2} \left| \chi_\mu^{\sigma_1} \chi_\nu^{\sigma_2} \right| \qquad (\mu, \nu \in i), \tag{5}$$

16 we give the GP wave function Φ_{GP} as an extension of the
17 corresponding Φ_{PP}. The geminal expansion coefficients
18 $C_{\mu\nu}^{\sigma_1\sigma_2}$ are variational parameters. Note that the so-called
19 strong orthogonality condition,

$$\int \psi_i(r_1, r_2)\psi_k(r_1, r_3)dr_1 = 0 \qquad (i \neq k), \tag{6}$$

21 which makes the variational solution tractable, is already
22 satisfied for Φ_{PP} and Φ_{GP}. Due to the strong orthogonality, the
23 structures of one- and two-electron density matrices become
24 quite simple. Non-zero elements of the density matrices for
25 Φ_{GP} are written as

$$P_{\mu\mu}^{\sigma_1\sigma_2} = \left\langle \Phi_{GP} \left| a_\mu^{\sigma_2+} a_\mu^{\sigma_1} \right| \Phi_{GP} \right\rangle$$
$$= \sum_{\sigma_3} C_{\mu\nu}^{\sigma_1\sigma_3} C_{\mu\nu}^{\sigma_2\sigma_3} \qquad (\mu, \nu \in i), \tag{7}$$

$$\Gamma_{\mu\nu,\mu\nu}^{\sigma_1\sigma_2,\sigma_3\sigma_4} = \left\langle \Phi_{GP} \left| a_\mu^{\sigma_3+} a_\nu^{\sigma_4+} a_\nu^{\sigma_2} a_\mu^{\sigma_1} \right| \Phi_{GP} \right\rangle$$
$$= \begin{cases} C_{\mu\nu}^{\sigma_1\sigma_2} C_{\mu\nu}^{\sigma_3\sigma_4} & (\mu, \nu \in i) \\ P_{\mu\mu}^{\sigma_3\sigma_1} P_{\nu\nu}^{\sigma_4\sigma_2} & (\mu \in i, \nu \in k, i \neq k) \end{cases}, \tag{8}$$

$$\Gamma_{\mu\nu,\nu\mu}^{\sigma_1\sigma_2,\sigma_3\sigma_4} = \left\langle \Phi_{GP} \left| a_\nu^{\sigma_3+} a_\mu^{\sigma_4+} a_\nu^{\sigma_2} a_\mu^{\sigma_1} \right| \Phi_{GP} \right\rangle$$
$$= \begin{cases} -C_{\mu\nu}^{\sigma_1\sigma_2} C_{\mu\nu}^{\sigma_4\sigma_3} & (\mu, \nu \in i) \\ -P_{\mu\mu}^{\sigma_4\sigma_1} P_{\nu\nu}^{\sigma_3\sigma_2} & (\mu \in i, \nu \in k, i \neq k) \end{cases}. \tag{9}$$

29 We note ionic terms do not appear in the trial wave function
30 because the present formulation is based on the spin
31 Hamiltonian in eq (1). If ionic terms appear in *ab initio* cases,
32 the non-diagonal and other elements of density matrices
33 might have non-zero values as shown, e.g., in ref [21]. In the
34 right-hand-side of eq (7), ν comes from the same geminal μ
35 belongs to.
36 Then, the energy expectation value is expressed as follows:

$$E = \left\langle \Phi_{GP} \left| H \right| \Phi_{GP} \right\rangle$$
$$= \sum_{\mu < \nu} J_{\mu\nu} \left(-\frac{1}{2}\Gamma_{\nu\mu,\mu\nu}^{\alpha\beta,\alpha\beta} - \frac{1}{2}\Gamma_{\mu\nu,\nu\mu}^{\beta\alpha,\beta\alpha} - \frac{1}{4}\Gamma_{\nu\mu,\mu\nu}^{\alpha\alpha,\alpha\alpha} \right.$$
$$\left. -\frac{1}{4}\Gamma_{\nu\mu,\mu\nu}^{\beta\beta,\beta\beta} + \frac{1}{4}\Gamma_{\nu\mu,\mu\nu}^{\beta\alpha,\alpha\beta} + \frac{1}{4}\Gamma_{\nu\mu,\mu\nu}^{\alpha\beta,\beta\alpha} \right)$$
$$= \sum_i \sum_{\mu < \nu \in i} J_{\mu\nu} \left\{ C_{\mu\nu}^{\alpha\beta} C_{\mu\nu}^{\beta\alpha} + \frac{1}{4}\left(C_{\mu\nu}^{\alpha\alpha}\right)^2 + \frac{1}{4}\left(C_{\mu\nu}^{\beta\beta}\right)^2 \right.$$
$$\left. -\frac{1}{4}\left(C_{\mu\nu}^{\alpha\beta}\right)^2 - \frac{1}{4}\left(C_{\mu\nu}^{\beta\alpha}\right)^2 \right\} + \frac{1}{2}\sum_\mu \sum_{\sigma_1\sigma_2} \tilde{h}_{\mu\mu}^{\sigma_1\sigma_2} P_{\mu\mu}^{\sigma_2\sigma_1}$$

37
(10)
38 where the one-electron effective potential is written as

39
$$\tilde{h}_{\mu\mu}^{\sigma_1\sigma_2} = \begin{cases} \dfrac{1}{4}\sum_{k(\neq i)}\sum_{\lambda \in k} J_{\mu\lambda}\left(P_{\lambda\lambda}^{\alpha\alpha} - P_{\lambda\lambda}^{\beta\beta}\right) & (\sigma_1 = \sigma_2 = \alpha) \\ \dfrac{1}{4}\sum_{k(\neq i)}\sum_{\lambda \in k} J_{\mu\lambda}\left(P_{\lambda\lambda}^{\beta\beta} - P_{\lambda\lambda}^{\alpha\alpha}\right) & (\sigma_1 = \sigma_2 = \beta) \\ \dfrac{1}{2}\sum_{k(\neq i)}\sum_{\lambda \in k} J_{\mu\lambda} P_{\lambda\lambda}^{\sigma_1\sigma_2} & (\sigma_1 \neq \sigma_2) \end{cases}. \tag{11}$$

40 Since the total energy is represented as the sum of the energy
41 attributed to each geminal and interaction energies between
42 two geminals, variational optimization of the wave function
43 is accomplished by the self-consistent optimization of each
44 geminal under the field created by other geminals.[20, 21,36] The
45 two-electron effective Hamiltonian to determine the
46 expansion coefficients in the geminal i constructed with the
47 orbitals χ_μ and χ_ν is given as

$$H^i = \sum_{\sigma_1\sigma_2} \left(\tilde{h}_{\mu\mu}^{\sigma_1\sigma_2} a_\mu^{\sigma_1+} a_\mu^{\sigma_2} + \tilde{h}_{\nu\nu}^{\sigma_1\sigma_2} a_\nu^{\sigma_1+} a_\nu^{\sigma_2} \right) + J_{\mu\nu}\mathbf{S}_\mu \cdot \mathbf{S}_\nu. \tag{12}$$

49 We evaluated the effective Hamiltonian matrix elements
50 $H_{\mu\nu,\mu\nu}^{\sigma_1\sigma_2,\sigma_3\sigma_4}$ for the antisymmetrized two-electron functions
51 $\left| \chi_\mu^{\sigma_1} \chi_\nu^{\sigma_2} \right|$ and $\left| \chi_\mu^{\sigma_3} \chi_\nu^{\sigma_4} \right|$. These four-by-four matrix
52 elements are gathered in **Table 1**. It can be observed that
53 different spin parts are allowed to mix in each geminal
54 through the effective one-electron potential. The sequential
55 optimization of each geminal is performed as follows. Firstly,
56 we give initial guess values for the geminal expansion
57 coefficients and compute the density matrices based on eqs
58 (7), (8) and (9). Since the effective one electron potential is
59 evaluated with the density matrices, we can also compute the
60 elements of the two-electron effective Hamiltonian matrix.
61 By sequentially diagonalizing the Hamiltonian matrices,
62 geminal expansion coefficients are updated. This process is
63 repeated until the self-consistency is achieved. For the
64 present purpose, optimization of one-electron orbitals
65 constructing each geminal is not performed.
66 We demonstrate several systems where the instability is
67 caused in Φ_{PP}, and GP solutions were obtained. The
68 Heisenberg model requires only the information of the
69 linkage between the atomic sites, or molecular graph. Since a
70 molecular graph is identified with the carbon skeleton of a
71 conjugated hydrocarbon, we refer to the graph by the name

of the corresponding compound. Through our preliminary calculations, we found the instability does not appear in Φ_{PP} of alternant hydrocarbons such as ethylene, butadiene, benzene, anthracene, and so on. This made us realize again that the PP is a good approximation for many conjugated hydrocarbons.

Firstly, we consider four atomic sites arranged on four vertices of a square, representing cyclobutadiene (CBD) molecule. Two PP functions schematically shown in **Figure 1** construct a complete basis for this four-electron system. These correspond to the Kekulé structures. We write Φ_{PP} and Φ_{GP} corresponding to the structure **X** as PP(X) and GP(X), respectively. Non-zero values of the exchange interactions were assumed only between adjacent sites; $J_{12} = J_{34} = \varepsilon J$ and $J_{14} = J_{23} = J$ where J is a constant and ε is a real parameter.
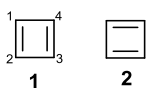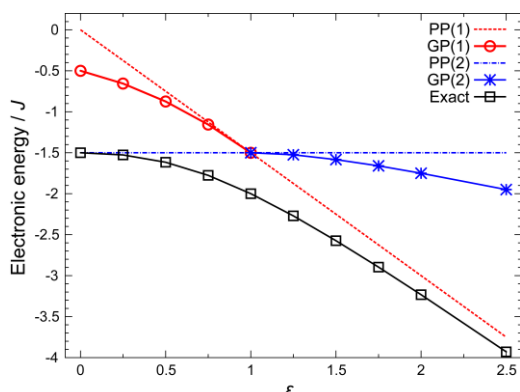

Figure 1. Two perfect pairing structures of CBD. Numbering for the atomic sites is also shown.

Electronic energy changes of this system for the scaling parameter ε are shown in **Figure 2**. When ε is zero, the four-site model can be considered as two isolated ethylene molecules forming bonds 1-4 and 2-3. The PP(2) gave the exact energy while the PP(1) gave the energy value of zero. In this context, as ε is increased from zero, the two ethylene molecules get closer. When ε becomes larger than one, two bonds are recoupled to form stronger bonds 1-2 and 3-4. The PP(1) becomes more stable than PP(2) in this region. Namely, this four-site system can be considered as a model for the bond recombination process. Because the more stable PP wave function exists, PP(1) and PP(2) are not proper representations of the system in the regions $0 \leq \varepsilon \leq 1$ and $1 \leq \varepsilon$, respectively. Notably, the GP type solutions of GP(1) and GP(2) appeared in these regions. In the present case, there exists the PP wave function more stable than the GP solutions. The appearance of a GP solution means the instability of a certain PP function, not always indicating the existence of the globally stable geminal product wave function. We mention the ground and low-lying excited states of CBD were described by Voter and Goddard with their generalized resonating valence bond (GRVB) wave function.[37] Mixing of the two PP structures leads to the resonant and anti-resonant singlet states. They showed the rectangular distortion of CBD stabilizes the resonant state and destabilizes the anti-resonant state. As the structure distorts, each state becomes similar to a different PP function. The instability of the present PP wave function, related to the emergence of GP solution, can also be understood from the putative behaviors of resonant and anti-resonant states.

Table 1. Matrix elements $H^{\sigma_1\sigma_2,\sigma_3\sigma_4}_{\mu\nu,\mu\nu}$ for the effective two-electron Hamiltonian. The rows and columns represent the types of spin functions $\sigma_1\sigma_2$ and $\sigma_3\sigma_4$, respectively. Only the upper triangular part is shown.

|	$\alpha\beta$	$\beta\alpha$	$\alpha\alpha$	$\beta\beta$
$\alpha\beta$	$\tilde{h}^{\alpha\alpha}_{\mu\mu} + \tilde{h}^{\beta\beta}_{\nu\nu} - \dfrac{1}{4}J_{\mu\nu}$	$\dfrac{1}{2}J_{\mu\nu}$	$\tilde{h}^{\beta\alpha}_{\nu\nu}$	$\tilde{h}^{\alpha\beta}_{\mu\mu}$
$\beta\alpha$		$\tilde{h}^{\beta\beta}_{\mu\mu} + \tilde{h}^{\alpha\alpha}_{\nu\nu} - \dfrac{1}{4}J_{\mu\nu}$	$\tilde{h}^{\beta\alpha}_{\mu\mu}$	$\tilde{h}^{\alpha\beta}_{\nu\nu}$
$\alpha\alpha$			$\tilde{h}^{\alpha\alpha}_{\mu\mu} + \tilde{h}^{\alpha\alpha}_{\nu\nu} + \dfrac{1}{4}J_{\mu\nu}$	0
$\beta\beta$				$\tilde{h}^{\beta\beta}_{\mu\mu} + \tilde{h}^{\beta\beta}_{\nu\nu} + \dfrac{1}{4}J_{\mu\nu}$

Figure 2. The electronic energies of the four-site model system in the unit of J for the scaling parameter ε. See text for the notations. The exact energies are also shown.

As ε is moved away from the value of one, the difference between the PP and GP energies becomes large, while the difference between the GP and exact energies also becomes large. This behavior is due to the increasing spin contamination in the GP wave function. The expectation values of the total S^2 operator for GP(1) are shown in **Figure 3**. Due to the symmetry of the system, it is sufficient to consider only the behavior at $0 \leq \varepsilon \leq 1$. At $\varepsilon = 0$, the GP wave function is the spin alternant (SA) determinant (i.e., the Néel state in the literature of solid state physics), giving the value of two for $\langle S^2 \rangle$. At $\varepsilon = 1$, the GP wave function degenerates to the PP wave function. The expectation value $\langle S^2 \rangle$ changes monotonically as ε increases. We found the numerically computed $\langle S^2 \rangle$ is proportional to ε at $0 \leq \varepsilon \leq 1$. The result implies that the proportion of the triplet component contained with different signs in each geminal is proportional to $\varepsilon^{1/4}$. In

4

our present formulation, the S_z spin-symmetry is not constrained. Thus, we obtained degenerate GP solutions in the S_z space, depending on the initial guess for the geminal expansion coefficients.
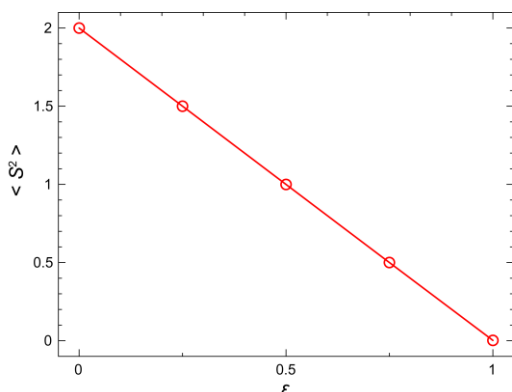
Figure 3. The expectation value of the total S^2 operator for the generalized pairing solution of GP(1). See text for the notations.

Secondly, we discuss simple non-Kekulé molecules, tetramethylenemethane (TMM) and tetramethyleneethane (TME), as examples. The molecular graph of TMM (**3**) and four PP structures of TMM (**4**–**7**) are shown in **Figure 4**. We assumed the non-zero value of the exchange interaction constant J only between the adjacent atomic sites. Although TME has two types of bonds, our current interest lies in its non- Kekulé molecular topology, so we used a single constant parameter for simplicity. The ground electronic state of TMM is triplet, while that of TME is singlet. The PP wave function of the triplet TMM is constructed with the singlet and triplet geminals. We found Φ_{PP} of these non-Kekulé molecules are not stable and broken symmetry solutions are obtained by the variational calculations.
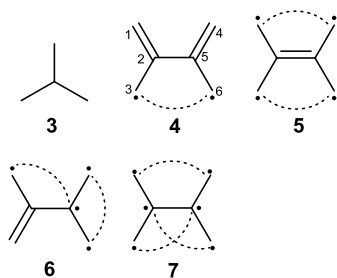
Figure 4. The molecular graph of TMM (**3**) and four perfect pairing structures of TME (**4**–**7**). Dashed lines show the singlet coupling between non-adjacent atomic sites. Numbering for the atomic sites is also shown.

The electronic energies of TMM calculated with the SA, PP, GP and exact wave functions are gathered in **Table 2**. We found Φ_{GP} gives lower energy than the SA determinant and Φ_{PP}. The expectation value $\langle S^2 \rangle$ of Φ_{GP} was the intermediate of those for SA and Φ_{PP}. The GP energy accounts for 58.6 % of the resonance energy, which is here defined as the difference between the energies of the exact and the most stable PP wave function. This implies that the resonating VB

effect is partially incorporated in the GP wave function while the spin contamination cannot be ignored in terms of energy.

The energies of four PP structures of TME (**4**–**7**) and those of corresponding GP wave functions are shown in **Table 3**. The expectation value $\langle S^2 \rangle$ of the four GP are also given. Among the PP wave functions, PP(4) gives the lowest energy because there are two bonds 1-2 and 4-5 in the structure. Concerning the GP wave functions, GP(4) was the most stable; it is considered as the globally stable geminal product. The exact energy was $-2.1642J$; GP(4) accounts for 71.3% of the resonance energy. Projection techniques for restoring of the spin symmetry will be one promising approach to further improve the GP wave functions.

Table 2. The electronic energies in the unit of J for TMM (**3**) described with the SA, PP, GP and exact wave functions. The expectation values of the total S^2 operator are also shown.

	Energy / J	$\langle S^2 \rangle$
SA	−0.75	3
PP	−0.75	2
GP	−0.9571	2.2929
Exact	−1.25	2

Table 3. The electronic energies in the unit of J for TME described with PP (**4**–**7**) and corresponding GP wave functions. The expectation values $\langle S^2 \rangle$ for the GP wave functions are also shown.

	PP	GP	$\langle S^2 \rangle$
4	-1.5	-1.6908	1.4505
5	-0.75	-1.3680	2.5528
6	-0.75	-1.4571	2.2929
7	0	-1.2500	3.0000

In summary, we developed a new method to variationally optimize the generalized electron pairing type VB wave function, and verified it in the Heisenberg model. By numerical computations, chemical implications of the spin-symmetry broken wave function were explored. We found the mixing of higher spin states stabilizes the wave function in the case when a certain PP wave function is not a proper representation of the system; non-Kekulé molecule is a typical example. This instability of the perfect paring is consistent with our empirical knowledge in chemistry. The present method might also be applied to chemically interesting open-shell conjugated molecules.[37] And lastly, the tested trial wave function will also be useful as an *ab initio* model and a reference to describe complex molecular electronic structures.

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