

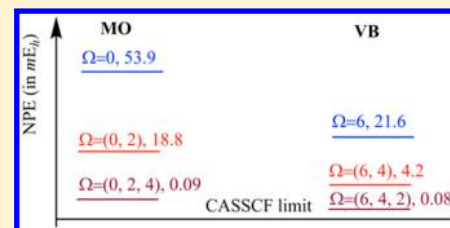
# Seniority Number in Valence Bond Theory

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## S Supporting Information

**ABSTRACT:** In this work, a hierarchy of valence bond (VB) methods based on the concept of seniority number, defined as the number of singly occupied orbitals in a determinant or an orbital configuration, is proposed and applied to the studies of the potential energy curves (PECs) of  $H_8$ ,  $N_2$ , and  $C_2$  molecules. It is found that the seniority-based VB expansion converges more rapidly toward the full configuration interaction (FCI) or complete active space self-consistent field (CASSCF) limit and produces more accurate PECs with smaller nonparallelity errors than its molecular orbital (MO) theory-based analogue. Test results reveal that the nonorthogonal orbital-based VB theory provides a reverse but more efficient way to truncate the complete active Hilbert space by seniority numbers.



## I. INTRODUCTION

The seniority number ( $\Omega$ ), which is defined as the number of singly occupied orbitals in a Slater determinant or an orbital configuration, was originated in the nuclear and condensed matter physics.<sup>1,2</sup> Recently, the concept of seniority number aroused the interest of theoretical chemists. The seniority-based MCSCF studies of Bytautas et al.<sup>3</sup> showed that, for the molecules exhibiting strong correlation, the seniority-based selection procedure is much more efficient for constructing compact configuration interaction (CI) expansions than the traditional particle–hole excitation-based scheme. Alcoba et al.<sup>4–6</sup> also investigated the convergence behaviors of the seniority-based CI approach toward the full CI (FCI) limits with various types of orbitals. At the lowest level with the  $\Omega = 0$  sector only, the seniority-based CI method is reduced to the doubly occupied CI (DOCI) method, first formulized by Weinhold and Wilson.<sup>7</sup> Because the DOCI method has a simple form of two-body reduced density matrix, it has been studied extensively.<sup>7–9</sup> Moreover, after introducing some approximations, many other computationally less-expensive methods, such as APIroG,<sup>9–15</sup> GVB,<sup>16</sup> PEMSCF,<sup>17–20</sup> and seniority-based p-CCD<sup>21,22</sup> might be deduced from the DOCI method.

Valence bond (VB) theory, as one of electronic structure theories, provides an intuitive tool for understanding the nature of chemical bonding. To this end, the total wave function is expressed in terms of Heitler–London–Slater–Pauling (HLSP) functions, which represent the Lewis structures (that is to say, covalent and ionic ones) faithfully. In VB theory, by using the valence bond self-consistent field (VBSCF) method,<sup>23</sup> the static correlation effect is taken into account innately, because it is a multideterminant approach, while the dynamic correlation can be described by using post-VBSCF approaches, such as VBCI<sup>24</sup> and VBPT2.<sup>25,26</sup>

Many useful chemical concepts, such as the partial ionic character of chemical bond, the electronegativity of atoms, and

the resonance effect, can be well-interpreted through the analysis of the VB wave function. The ionicity of a VB structure can be defined as the number of doubly occupied orbitals, assumed to be  $\omega$  in this paper. As a HLSP function is written as a linear combination of atomic orbital (AO)-based Slater determinants, which share the same orbital occupancy, one may have a simple linear relationship between ionicity and seniority number ( $\Omega$ ),

$$\Omega + 2\omega = N \quad (1)$$

where  $N$  is the number of electrons.

In seniority-based MO methods, for closed-shell molecules, the main components of the total wave function come from the doubly occupied determinants. As such, the DOCI method, which is the lowest level of the seniority-based CI, provides a valuable initial wave function for higher- $\Omega$  CI calculations. Meanwhile, contributions from other determinants generally decrease as the seniority numbers increase. However, in the VB method, the most significant contributions to the wave function are usually from structures that involve the maximum number of covalent bonds, and each covalent bond is represented by the spin coupling of two electrons in two singly occupied orbitals. As such, generally speaking, HLSP functions with the largest seniority number are the most important for the wave function. Meanwhile, contributions from other VB structures in the total wave function decreases as the seniority number decreases. Even for systems comprised of different electro-negative atoms, a good VB wave function with hybrid atomic orbitals (HAOs) can usually be obtained after involving the monoionic structures in the expansion. Especially, the overlap-enhanced orbital (OEO)-based VB method, such as spin-coupled valence bond (SCVB),<sup>27</sup> can give a proper description for the static electronic correlation even with covalent

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structures only. Therefore, different from the seniority-based MO methods, the seniority-based VB approach should truncate the Hilbert space in a reverse manner, that is to say, from the maximum  $\Omega$  value to the minimum  $\Omega$  value. The purpose of the paper is to set up a hierarchy of VB methods by the truncation technique, based on the seniority number criteria. To this end, the convergence behavior of seniority-based VBSCF toward FCI/CASSCF limit will be explored, and various types of VB orbitals are adopted in the test calculations.

The paper is organized as follows: In section II, the seniority-based VB method is presented. Section III presents test calculations on the potential energy curves (PECs) of  $H_8$ ,  $N_2$ , and  $C_2$ . A short summary is presented in section IV.

## II. THEORY AND METHODOLOGY

**A. Valence Bond Theory and the Partitioning of the Hilbert Space.** In VB theory, the general many-electron wave function is expressed in terms of VB functions,

$$\Psi = \sum_K C_K \Phi_K \quad (2)$$

where  $\Phi_K$  may be either a spin-coupled HLSP function, or a tableau function,<sup>28–30</sup> if the spin-free form of quantum chemistry is used. In the VBSCF method, the structural coefficients and orbitals, which are used to construct the VB functions, are simultaneously optimized to minimize the energy of chemical systems.

In spin-free quantum chemistry, as state functions, HLSP functions are written as the product of spatial and spin factors, where the spatial factor is a successive product of orbitals, and the spin factor is a spin eigenfunction. In other words, the spatial factor depends on the orbital configuration, which specifies orbital occupancy, while the spin factor is dependent on the spin-coupling scheme. As mentioned above, the definition of seniority number is based on the orbital occupancy. Thus, the spatial factor can be further classified according to seniority numbers. Therefore, a HLSP function may be identified by three indices—seniority number ( $\Omega$ ), orbital configuration ( $A$ , which belongs to the same seniority number  $\Omega$ ), and component of spin eigenfunction ( $\kappa$ ). Thus, the total wave function (eq 2) can be written as

$$\Psi = \sum_{\Omega} \sum_A \sum_{\kappa} C_{\Omega A \kappa} \Phi_{\Omega A \kappa} \quad (3)$$

Equation 3 is the most general form of wave function for a system of  $N$  electrons in  $n$  orbitals, and it is equivalent to the MO-based CASSCF wave function if OEOs are used. For a system of  $N$  electrons in  $N$  orbitals, eq 3 is reduced to the SCVB wave function, if only one orbital configuration with the maximum seniority number ( $\Omega = \Omega_{\max}$ ) is involved.

Equation 3 provides a strategy for truncating wave function according to the seniority number  $\Omega$ . As mentioned above, because of the fact that VB structures with larger  $\Omega$  values are usually more important, the truncating procedure should start with the maximum seniority number, and subsequently add structures with smaller seniority numbers. Clearly, this procedure operates in a manner opposite to that of the seniority-based CI approach in MO theory.

In this paper, different truncation levels associated with seniority numbers are examined to investigate the convergence performance of the VBSCF method. In other words, the total electronic wave function is of the form

$$\Psi_{(\Lambda)} = \sum_{\Omega} \sum_A \sum_{\kappa} C_{\Omega A \kappa} \Phi_{\Omega A \kappa} \quad (\Lambda = \Omega_{\max}, \Omega_{\max} - 2, \dots, 2S) \quad (4)$$

where the summation of  $\Omega$  is over  $\Lambda, \Lambda + 2, \dots, \Omega_{\max}$ ;  $S$  is the total spin number; and

$$\Omega_{\max} = \begin{cases} N & (N \leq n) \\ 2n - N & (N > n) \end{cases} \quad (5)$$

**B. Dimensions of the Orbital Configuration, and Seniority-Labeled and Full Hilbert Spaces.** In this section, the numbers of determinants and spin-adapted VB functions in the orbital configuration, and the seniority number labeled subspaces and the full Hilbert space will be formulized. As can be seen in the following text, the number of configurations can be reduced by spin-adaption and seniority number truncation.

For a given orbital configuration with seniority number  $\Omega$ , the number of singly occupied  $\alpha$  and  $\beta$  electrons are  $(\Omega/2) + S$  and  $(\Omega/2) - S$ , respectively. So, the number of determinants with seniority number  $\Omega$  in an orbital configuration (OC) subspace, is written as

$$N_{OC}^{Det} = \binom{\Omega}{\Omega/2 + S} = \binom{\Omega}{\Omega/2 - S} \quad (6)$$

For a given seniority number  $\Omega$ , the number of orbital configurations is

$$N_{\Omega}^{OC} = \binom{n}{\omega} \binom{n - \omega}{\Omega} \quad (7)$$

where  $\omega$  is the number of doubly occupied orbitals, known as ionicity in VB theory.

It is obvious that no common determinants appear in two different orbital configurations. Thus, the number of determinants in the seniority-labeled space can be simply given by

$$N_{\Omega}^{Det} = N_{\Omega}^{OC} N_{OC}^{Det} \quad (8)$$

This expression can finally be written as a multinomial coefficient as

$$\begin{aligned} N_{\Omega}^{Det} &= \frac{n!}{\omega!(\Omega/2 + S)!(\Omega/2 - S)!(n - \omega - \Omega)!} \\ &= \binom{n}{\omega, \Omega/2 + S, \Omega/2 - S, n - \omega - \Omega} \end{aligned} \quad (9)$$

From eq 9, one can see that  $N_{\Omega}^{Det}$  is the number of all possible ways to chose  $\omega$  doubly occupied orbitals,  $\Omega/2 + S$  and  $\Omega/2 - S$  singly occupied orbitals for  $\alpha, \beta$  electrons, and  $n - \omega - \Omega$  unoccupied orbitals from the total of  $n$  orbitals. The number of determinants in the full Hilbert space is given by summing over all possible values of  $\Omega$  in eq 9,

$$N_{CAS}^{Det} = \binom{n}{N/2 + S} \binom{n}{N/2 - S} \quad (10)$$

Clearly, eq 10 can be interpreted as the number of ways of choosing  $(N/2 + S)$  from  $n$  orbitals for  $\alpha$  electrons and then choosing  $(N/2 - S)$  from  $n$  orbitals for  $\beta$  electrons.

Meanwhile, for a given orbital configuration, the number of HLSP functions, as spin-adapted functions, can be obtained by using the Weyl formula,<sup>31,32</sup>

**Table 1.** Total CASSCF Energies, Deviations from CASSCF, and Nonparallelity Errors (NPEs) for H<sub>8</sub> Linear Chain Molecule with Seniority-Based MCSCF<sup>a</sup>

R (Å)	CASSCF <sup>b</sup> (E <sub>h</sub> )	Molecular Orbital Theory <sup>b</sup>			Valence Bond Theory		
		Ω = 0	Ω = (0, 2)	Ω = (0, 2, 4)	Ω = 8	Ω = (8, 6)	Ω = (8, 6, 4)
0.7	−4.166 794	33.247	8.357	0.136	12.232	0.814	0.158
1.0	−4.414 546	33.977	9.619	0.068	8.743	1.280	0.027
1.2	−4.355 115	34.027	9.497	0.441	5.933	1.112	0.021
1.5	−4.218 948	32.405	9.875	0.743	2.678	0.628	0.010
2.0	−4.064 602	20.854	5.803	0.193	0.420	0.190	0.000
2.2	−4.034 862	14.783	3.880	0.019	0.173	0.060	0.000
3.0	−3.997 913	2.054	0.468	0.092	0.003	0.000	0.000
NPE	0	31.923	9.151	0.675	12.229	1.280	0.158

<sup>a</sup>The deviations and NPEs are given in units of mE<sub>h</sub>. <sup>b</sup>Data taken from ref 3.

$$N_{\text{OC}}^{\text{VB}} = \frac{2S+1}{\Omega/2+S+1} \binom{\Omega}{\Omega/2-S} = \left( \frac{2S+1}{\Omega/2+S+1} \right) N_{\text{OC}}^{\text{Det}} \quad (11)$$

The number of HLSP functions with seniority number Ω is written as

$$N_{\Omega}^{\text{VB}} = N_{\text{OC}}^{\text{VB}} N_{\Omega}^{\text{OC}} \quad (12)$$

Substituting eqs 6 and 11 into eq 12 yields

$$N_{\Omega}^{\text{VB}} = \frac{2S+1}{\Omega/2+S+1} \binom{n}{\omega, \Omega/2+S, \Omega/2-S, n-\omega-\Omega} \quad (13)$$

Comparing eqs 9 and 13, one has

$$N_{\Omega}^{\text{VB}} = \left( \frac{2S+1}{\Omega/2+S+1} \right) N_{\Omega}^{\text{Det}} \quad (14)$$

Finally, by using the Weyl formula<sup>31,32</sup> again, the number of HLSP functions in the full Hilbert space is expressed as

$$N_{\text{CAS}}^{\text{VB}} = \frac{2S+1}{n+1} \binom{n+1}{n-N/2+S} \binom{n+1}{N/2-S} \quad (15)$$

Note that eqs 10–15 are valid not only for HLSP functions, but also for configuration state functions (CSFs), since both of them are spin-adapted functions.

### III. TEST CALCULATIONS

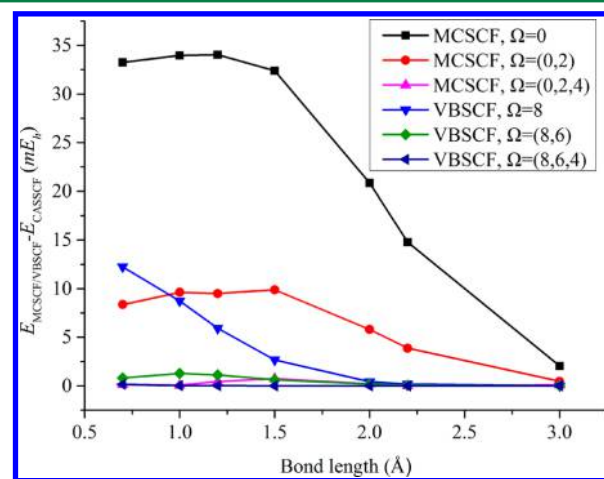
Several calculations are performed to test the performance of the seniority-based VB methods. To compare the performance of seniority-based MO and VB approaches, the PEC calculations of N<sub>2</sub> and H<sub>8</sub> molecules are calculated using the same geometries and the same cc-pVDZ<sup>33</sup> basis set taken from ref 3; and the PEC calculation of C<sub>2</sub> molecule is tested using the 6-31G(d) basis set.<sup>34,35</sup>

All VB calculations are performed with the Xiamen Valence Bond (XMBV) program<sup>36–39</sup> on a workstation with an Intel Xeon X5450 CPU. To obtain basis set integrals and nuclear repulsion energy, preliminary ROHF calculations are carried out using the GAMESS package.<sup>40</sup>

**A. H<sub>8</sub>.** Pure hydrogen networks are often used as examples for testing novel electronic structure methods, especially for sophisticated *ab initio* methods targeted to strong correlation problems.<sup>3,41–51</sup> Although H<sub>2n</sub> molecules share very simple electronic structures, the potential energy surface calculations become challenging for single-reference-based methods. As the

first example, the symmetric dissociation PEC of the linear H<sub>8</sub> chain is calculated using a seniority-based VBSCF approach. In this model, the H–H distances are kept equivalent along the dissociation PEC. To compare our results with the seniority-based and the traditional particle–hole excitation-based MCSCF results done by Bytautas et al.,<sup>3</sup> the same H–H distances, active space of distributing eight electrons in eight orbitals and the cc-pVDZ basis set are used; and the nonparallelity errors (NPEs), defined as the difference between the maximum and minimum errors from the CASSCF benchmark along the PEC, are obtained.

Table 1 shows the total CASSCF energies, deviations from CASSCF results, and NPEs for H<sub>8</sub> linear chain molecule with seniority-based VBSCF approach, alongside the MCSCF results of Bytautas et al.<sup>3</sup> Figure 1 plots the PECs. Obviously, the

**Figure 1.** 1Σ<sub>g</sub><sup>+</sup> ground state PECs for the H<sub>8</sub> molecule.

seniority-based VB approach is superior to the analogue MO one. At the short H–H distance (0.7 Å), the lowest level of seniority-based VB method (Ω = 8) gives an error of 12.2 mE<sub>h</sub>, which is about one-third of that of MO analogue (33.2 mE<sub>h</sub>). Meanwhile, this ratio becomes even smaller as the bond distance increases. In fact, the seniority-based VB method, even at its lowest level, is able to recover almost all static correlation energy at the dissociation limit; however, its MO analogue still has a significant error (ca. 2.1 mE<sub>h</sub>) at an H–H distance of 3.0 Å. If the seniority sector with a lower Ω value (Ω = 6) is also involved in the VBSCF wave function, the energies are much improved for all H–H distances; and the values of error are only about one tenth of the MO analogue with Ω = (0, 2)



sector. In fact, the VB energies with  $\Omega = (8, 6)$  sector are close to the MO ones with  $\Omega = (0, 2, 4)$  sector, as can be seen from Figure 1. The NPE value of the VB with  $\Omega = (8, 6)$  is  $\sim 1.3$  mE<sub>h</sub>, which is significantly better than the MO calculation using  $\Omega = (0, 2)$  seniority sectors with an NPE of ca. 9.2 mE<sub>h</sub>. When the di-ionic structures ( $\Omega = 4$ ) are included in the VB wave function, the energies are improved even further, namely that the largest error along the PEC is 0.16 mE<sub>h</sub> only at the H–H distance of 0.7 Å. Because this VB method gives the exact CASSCF energy at the dissociation limit, the NPE value of  $\Omega = (8, 6, 4)$  is also only 0.16 mE<sub>h</sub>.

Moreover, it is interesting to note that, even near the equilibrium geometries, the seniority-based VB method is as efficient as the traditional particle–hole excitation-based CI scheme; while the previous MO studies<sup>3</sup> showed that, in these cases, the excitation-based CI scheme is superior to the seniority-based one, when the correlation is essentially dynamic.

To further test the accuracy of the seniority-based VB wave functions, the occupation numbers of the natural orbitals, together with those of the CASSCF benchmark for an H–H distance of 2.5 Å, are evaluated, presented in Table 2. This table

**Table 2. Occupation Numbers of the Natural Orbitals for H<sub>2</sub> Molecule Evaluated by Seniority-Based VBSCF with Semilocalized OEOs at an H–H Distance of 2.5 Å**

orbital	$\Omega = 8$	$\Omega = (8, 6)$	$\Omega = (8, 6, 4)$	$\Omega = (8, 6, 4, 2)$	$\Omega = (8, 6, 4, 2, 0)$
1 $\sigma_g^+$	1.3769	1.3773	1.3774	1.3774	1.3774
1 $\sigma_u^+$	1.3321	1.3323	1.3324	1.3324	1.3324
2 $\sigma_g^+$	1.2584	1.2582	1.2583	1.2583	1.2583
2 $\sigma_u^+$	1.1654	1.1627	1.1627	1.1627	1.1627
3 $\sigma_g^+$	0.8389	0.8415	0.8414	0.8414	0.8415
3 $\sigma_u^+$	0.7433	0.7435	0.7434	0.7434	0.7434
4 $\sigma_g^+$	0.6662	0.6661	0.6660	0.6660	0.6660
4 $\sigma_u^+$	0.6189	0.6185	0.6184	0.6184	0.6184

shows that, at the lowest level, the seniority-based VB approach already produces the occupation numbers very close to the CASSCF benchmark, with the largest errors of 0.0027 and 0.0026, respectively, coming from the near half filling frontier 2 $\sigma_u^+$  and 3 $\sigma_g^+$  orbitals. As more lower seniority sectors are involved into the VB wave function, these differences become almost negligible. The natural orbitals in terms of basis functions and their scheme views are also obtained and are presented in the Supporting Information.<sup>52</sup> From Table S1 and Figure S1 in ref 52, it can also be seen that there is little difference between the natural orbitals obtained by seniority-based VB methods and by the CASSCF method. These results suggest that the seniority-based VB approach produces not only accurate energy but also good wave function for difficult strongly correlated systems.

To investigate the compactness of wave functions, Table 3 collects the numbers of determinants, CSFs in the MO method, and VB structures in VB method for various seniority numbers for the active space containing eight electrons and eight orbitals. From Table 3, it can be seen that although at the lowest level—namely, that  $\Omega = 8$  for VBSCF and  $\Omega = 0$  for MCSCF—both wave functions involve the same number of determinants, MCSCF includes more CSFs than VB structures in VBSCF. Generally speaking, at the lower levels of seniority-based CI methods, VB theory provides more compact wave

**Table 3. Numbers of Determinants ( $N_{\Omega}^{\text{Det}}$ ) and Spin-Adapted Functions ( $N_{\Omega}^{\text{CSF}}$  and  $N_{\Omega}^{\text{VB}}$  for MO and VB Theories, Respectively) for Various Seniority-Labeled Sectors in the Active Space Containing Eight Electrons and Eight Orbitals**

$\Omega^{\text{MO}}$	$N_{\Omega}^{\text{CSF}}$	$N_{\Omega}^{\text{Det}}$	$N_{\Omega}^{\text{VB}}$	$\Omega^{\text{VB}}$
0	70	70	14	8
2	560	1120	280	6
4	840	2520	840	4
6	280	1120	560	2
8	14	70	70	0

functions, compared to its MO analogue, in addition to its efficiency.

**B. N<sub>2</sub>.** The nitrogen molecule has been studied via numerous high-level *ab initio* methods,<sup>3,25,26,44,45,47,51,53–55</sup> because of its strong correlation character. The ground state of the molecule shares the symmetry of  $^1\Sigma_g^+$ . Once again, for the comparison of the performance of the seniority-based VB and MO approaches, the PEC of N<sub>2</sub> molecule is investigated by using the same cc-pVDZ basis function, the active space of distributing 10 electrons in 8 orbitals and the same N–N distance as that in ref 3.

The total CASSCF energies, the deviation from CASSCF, and NPE for N<sub>2</sub> molecule with seniority-based VBSCF approach are collected in Table 4, alongside the results of Bytautas et al.;<sup>3</sup> the plot of the energy errors of the seniority-based approaches is presented in Figure 2. The results show clearly that the seniority-based VB approach is much better than its MO analogue. At the lowest level of both approaches, the NPEs are 21.6 and 53.9 mE<sub>h</sub> for VB with  $\Omega = 6$  and MO with  $\Omega = 0$ , respectively. Moreover, it can be seen from Figure 2 that the VB method also produces lower energies along the full dissociation curve and, thus, more-accurate PEC than its MO correspondence. When one more seniority sector ( $\Omega = 4$ ) is included in the VB wave functions, we see again that it produces a smaller NPE value (see Table 4) and better PEC (see Figure 2). Inasmuch as the seniority-based VB ( $\Omega = 6, 4, 2$ ) and MO ( $\Omega = 0, 2, 4$ ) wave functions are both very accurate, the difference of performance between these two approaches becomes very small; nevertheless, VB theory is still slightly superior to the MO approach, with respect to the NPE values.

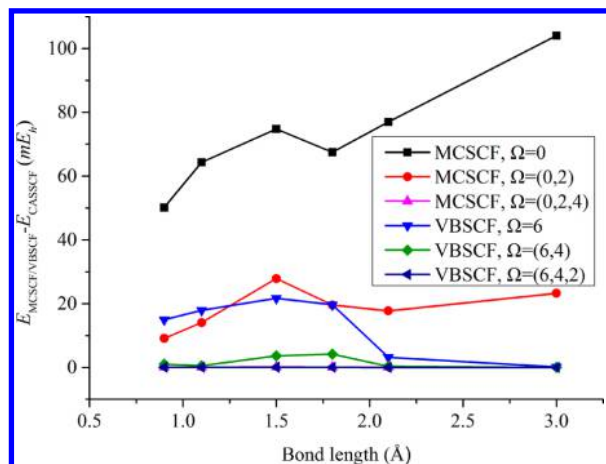
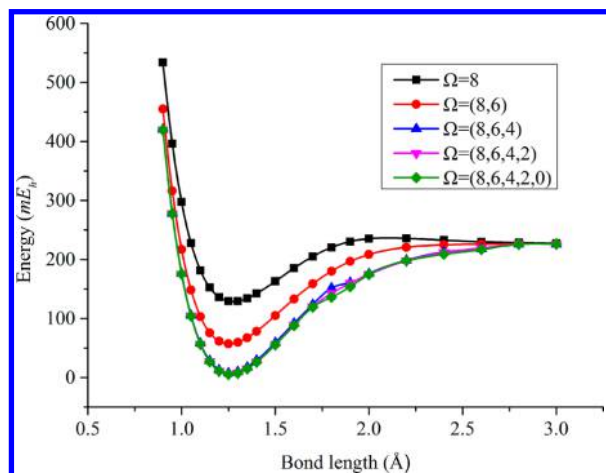
**C. C<sub>2</sub>.** The C<sub>2</sub> molecule, especially its PEC of dissociation, was proved to be a challenge for single-reference methods. Because of the difficulty arising from the complicated coupling patterns of the eight valence electrons and its interesting chemical bonding,<sup>45,56–60</sup> the C<sub>2</sub> molecule has been investigated by a variety of high-level *ab initio* methods.<sup>26,61–65</sup>

In this work, the PEC of C<sub>2</sub> molecule is taken as the final example. The same geometries and 6-31G(d) basis functions are taken from ref 61. In the CASSCF and VB calculations, the active space comprises of eight electrons and eight orbitals. Two sets of orbitals, HAOs and OEOs, are applied. The advantage of HAOs is that they are strictly localized and thus the defined VB structures can be interpreted unambiguously in the classical Lewis electron pair bonding pattern, while the use of OEOs provides more compact wave function and lower total energy. The PECs of C<sub>2</sub> molecule are displayed in Figures 3 and 4 for HAOs and OEOs, respectively. It is obvious that all seniority-based VB methods give correct dissociation into two carbon atoms in their ground states  $^3\text{P}(1s^2 2s^2 2p^2)$ , regardless of whether strictly localized HAOs or semilocalized OEOs are used. Meanwhile, to obtain an accurate PEC, seniority sector of

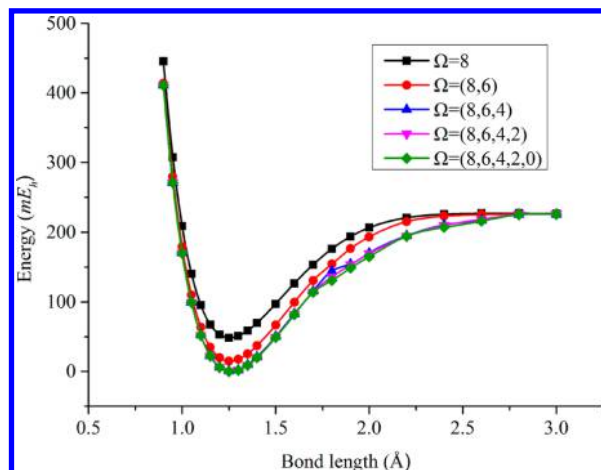
**Table 4.** Total CASSCF Energies, Deviations from CASSCF, and Nonparallelity Errors (NPEs) for N<sub>2</sub> Linear Chain Molecule with Seniority-Based MCSCF<sup>a</sup>

R (Å)	CASSCF <sup>b</sup> (E <sub>h</sub> )	Molecular Orbital Theory <sup>b</sup>			Valence Bond Theory		
		$\Omega = 0$	$\Omega = (0, 2)$	$\Omega = (0, 2, 4)$	$\Omega = 6$	$\Omega = (6, 4)$	$\Omega = (6, 4, 2)$
0.9	-108.889381	50.120	9.103	0.048	14.953	0.988	0.074
1.1	-109.103396	64.257	14.062	0.042	17.941	0.506	0.055
1.5	-108.943238	74.762	27.879	0.125	21.687	3.616	0.080
1.8	-108.827857	67.428	19.581	0.064	19.685	4.175	0.035
2.1	-108.786568	76.957	17.730	0.039	3.134	0.346	0.012
3.0	-108.777536	104.025	23.244		0.109	0.004	0.001
NPE	0	53.905	18.776	0.086	21.578	4.171	0.080

<sup>a</sup>The deviations and NPEs are given in units of mE<sub>h</sub>. <sup>b</sup>Data taken from ref 3.

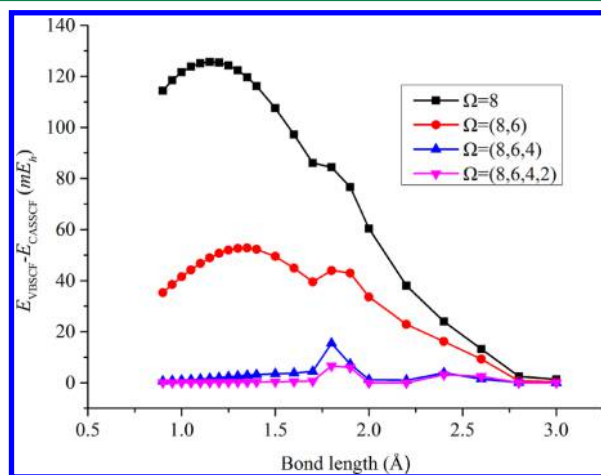
**Figure 2.** <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state PECs for N<sub>2</sub> molecule.**Figure 3.** <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state PECs for C<sub>2</sub> molecule by seniority-based VBSCF using HAOs. The CASSCF energy (−75.617339 E<sub>h</sub>) at the equilibrium bond length (1.25 Å) is chosen as zero.

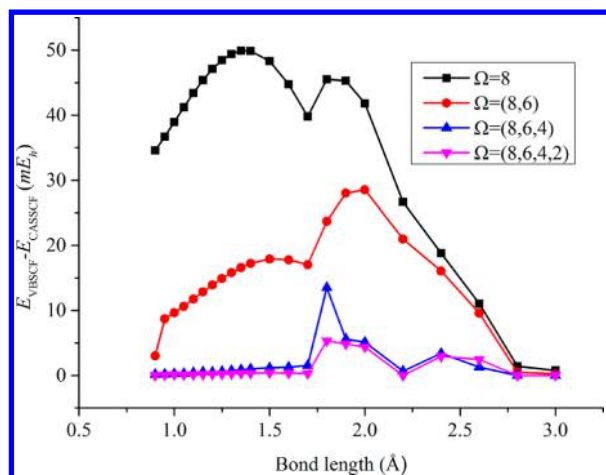
$\Omega = (8, 6, 4)$  is required for both types of orbitals. Inasmuch as including smaller seniority sector,  $\Omega = (2, 0)$ , into the wave function improves the quality of the ground state PEC very little, it is clear that the higher-order ionic structures are not important. It can also be seen that the lowest level of seniority-based VB ( $\Omega = 8$ ) with HAOs or OEOs does not represent the ground state well near the equilibrium geometry. However, the OEO-based one is much better, since it produces a well even deeper than HAO-based one with seniority sector of  $\Omega = (8,$

**Figure 4.** <sup>1</sup>Σ<sub>g</sub><sup>+</sup> ground state PECs for C<sub>2</sub> molecule by seniority-based VBSCF using OEOs. The CASSCF energy (−75.617339 E<sub>h</sub>) at the equilibrium bond length (1.25 Å) is chosen as zero.

6). Meanwhile, when  $\Omega = 6$  is included in the OEO-based wave function, its curve is further improved.

Figures 5 and 6 display the energy error curves of HAO- and OEO-based VB calculations. These two figures demonstrate again that with seniority sectors of  $\Omega = (8, 6, 4)$ , both HAO- and OEO-based VB approaches are able to provide an accurate wave function for PEC. Interestingly, because of the avoided crossing of the X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> and B<sup>1</sup>Σ<sub>g</sub><sup>+</sup> states near the C–C bond

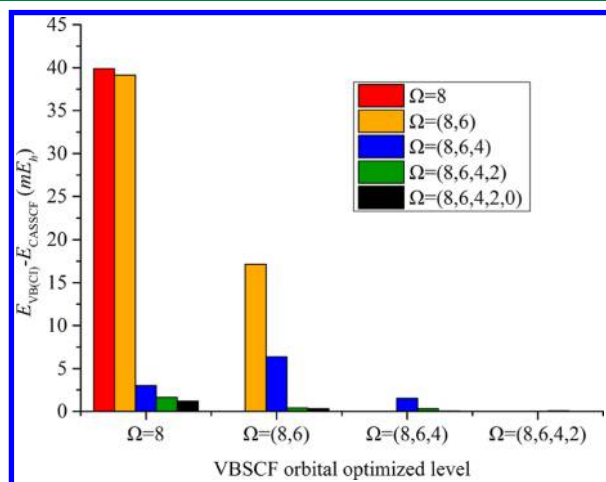
**Figure 5.** Energy error curves for C<sub>2</sub> molecule by seniority-based VBSCF using HAOs.



**Figure 6.** Energy error curves of  $C_2$  molecule by seniority-based VBSCF using OEOs.

distance of 1.8 Å,<sup>26,56</sup> there is a swell in the CC bond length region of 1.7–2.0 Å for the error curves of  $\Omega = (8, 6, 4)$  in Figures 5 and 6.

To pursue the accuracy of VBSCF calculation, more and more VB structures should be involved in the calculation, resulting in very expensive computational cost. One practical and efficient strategy is to combine VBSCF with a CI technique. Namely, first, the orbitals are optimized by VBSCF at a lower level with larger seniority numbers; and then without further orbital optimization, a CI calculation is performed by including more VB structures with smaller seniority numbers. Unlike our previous VBCI method,<sup>24,66,67</sup> where the excited structures were generated by replacing the occupied orbitals by virtual ones, in this VB approach, all structures belong to the active Hilbert space. Figure 7 displays



**Figure 7.** Deviation of seniority-based VB energy from CASSCF ( $-75.503767 E_h$ ) for  $C_2$  molecule at the bond length of 1.7 Å. The orbitals are optimized by the seniority-based VBSCF method with the seniority number restrictions on the determinants shown on the x-axis.

the results of this VB calculation at the CC bond distance of 1.7 Å. The data reveal that optimizing the orbitals at the lowest level of seniority-based VB method ( $\Omega = 8$ ), and then including two more seniority sectors is able to give a result with an error of only ca. 3 mE<sub>h</sub>, with respect to the CASSCF limit. This result

demonstrates clearly that this VB approach may be useful, based on the seniority number.

## IV. CONCLUSIONS

In this paper, the concept of seniority number ( $\Omega$ ), which is defined as the number of singly occupied orbitals in a determinant or an orbital configuration, was incorporated into valence bond (VB) theory. As a result, a hierarchy of VB methods beyond the single configuration spin-coupled VB method was developed. In this scheme, the complete active space is divided into subspaces classified by the seniority number. It was found that the seniority number in VB theory shares a clear chemical concept, i.e., the ionicity of a VB structure, and thus the seniority-based truncation may be applied intuitively to the VB approach.

Different from the MO-based methods, the truncation criterion for VBSCF is observed to operate in a reversed way, starting from a maximum value of seniority number and adding VB structures with lower  $\Omega$  values to increase the CI level. Test examples show that the seniority-based VB method shares the following advantages over its MO analogues. First, at the same level of truncation, VB method produces a lower total energy than the MO analogue. Meanwhile, the number of VB structures is much smaller than the number of determinants or even CSFs in MO theory. Secondary, the seniority-based VB expansion converges more rapidly toward FCI/CASSCF limit than the MO analogue. Third, for the PECs of model systems with strongly correlated problem, seniority-based VB approach gives more-accurate results, as the nonparallelity errors are much smaller than the MO ones.

In addition, a practical VB approach is presented. In this approach, the nonorthogonal orbitals at a lower level with large seniority numbers are optimized and followed by a configuration interaction calculation by involving VB structures with smaller seniority numbers without further orbital optimization. The test results show that this strategy improves the results effectively at a lower computational cost.

Furthermore, the seniority-based VBSCF method can provide a compact reference wave function for post-VBSCF methods, such as VBCI and VBPT2. Thus, not only static correlations but also dynamic correlations are taken into account in VB approaches.

Finally, it is worthwhile to note that, although the seniority-based VB approach is more efficient in convergence to CASSCF than its MO analogues, its computational cost is still expensive, because of the use of nonorthogonal VB orbitals. Fortunately, the situation was improved by using our recently developed reduced density matrix-based VB approaches.<sup>26,38,68,69</sup> Some aspects along this line are under investigation, and the results will be published elsewhere in the future.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jctc.5b00416.

Natural orbitals of the  $H_8$  molecule and total energies of the  $C_2$  molecule (PDF)

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## Notes

The authors declare no competing financial interest.

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