DFVB: A Density-Functional-Based Valence Bond Method

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ABSTRACT: A new ab initio valence bond method with density-functional-based correlation correction, so-called DFVB, is presented. In the DFVB method, the dynamic correlation energy is taken into account by use of density correlation functional(s), while the static correlation energy is covered by the VBSCF wave function. Owing to incorporation of DFT methods, DFVB provides an economic route to improving the accuracy of ab initio VB theory. Various tests of the method are presented, including the spectroscopic parameters of a series of diatomic molecules, the dipole moments of the NF molecule for different electronic states, and the singlet−triplet gaps of the diradical species, chemical reactions barriers, and total charge-shift resonance energies. These tests show that DFVB is capable of providing high accuracy with relatively low computational cost by comparison to the currently existing post-VBSCF methods.

1. INTRODUCTION

As a chemical theory that uses the bond notion, one of the great advantages of valence bond (VB) theory is its visually intuitive wave function, which is expressed as a linear combination of chemically meaningful structures, and offering thereby insight along with a quantitative implementation of fundamental concepts. Since the 1980s, the computational efficiency of ab initio VB theory has been dramatically improved with the development of various accurate VB methods and orbital optimization algorithms.[1−11] The basic modern method of classical VB theory is called valence bond self-consistent field (VBSCF) theory, devised by Balint-Kurti and van Lenthe.[12,13] Different from the classical VB method, which does not optimize atomic orbitals (AOs) while building the VB structures, VBSCF optimizes both VB orbitals and structural coefficients simultaneously and uses the same set of purely localized hybrid atomic orbitals (HAOs) for all structures.

Since the VBSCF wave function is expressed as a linear combination of HAO-based Slater determinants, it is a multireference method. Thus, similar to the CASSCF method, VBSCF covers the static correlation but lacks dynamic correlation. Therefore, the quantitative applications of the VBSCF method are generally unsatisfactory. For example, for the O_2 molecule,[14] the VBSCF calculation with 12 VB structures using the cc-pVTZ basis set gives a bond dissociation energy (BDE) of 3.33 eV, thus covering only 64% of the experimental BDE value. The VBSCF-optimized bond length is 1.242 Å, longer than the experimental value by 0.034 Å.[14] Various higher level VB methods have been developed to improve the VBSCF accuracy, including BOVB,[15−18] VBCI,[19,20] and VBPT2.[21] The BOVB method accounts for part of the dynamic electron correlation by allowing different VB structures to have their own orbital sets, such that the resulting orbitals respond to the instantaneous fields of the individual VB structures. The other two methods, VBCI and VBPT2, belong to the post-VBSCF category, which uses the

VBSCF wave function as a reference and dynamic retrieves correlation energy using excited VB structures. The VBCI method does that by means of configuration interaction (CI), while VBPT2 employs perturbation theory (PT). Applications show their considerable successes in introducing dynamic correlation into VB theory.

Different from the post-VBSCF methods and high-level multireference MO methods, the KS-DFT[22−26] method provides an economic way for the dynamic correlation energy, describing an interacting system of electrons via its density. Due to the extremely high efficiency and reasonable accuracy, KS-DFT has become an extraordinarily successful approach in computational physics and chemistry since the 1990s. However, it is well known that the KS-DFT is unable to give reasonable results for the chemical problems that require a proper description of static correlation and hence are beyond the scope of the simple single-determinant description, including chemical reactions, bond dissociation curves, and poly radical systems, etc.[24−28]

One of the straightforward ways to cover static correlation is to incorporate a multireference-type wave function into density functional theory. In this manner, the dynamic correlation is considered by the correlation functional of DFT, while the static correlation effect is treated through a multireference approach. Extension of KS-DFT to multireference cases has been proposed by Savin,[29] Pérez-Jordá,[30−32] Roos,[33] Head-Gordon,[34,35] Cremer,[36−38] Filatov and Shaik,[39−42] Wu and VanVoorhis,[43] Rapacioli,[44] and Clementi et al.[45−51] Such DFT methods overcome to some extent the problems that originate in the use of a single determinant. However, a common problem of these multireference DFT (MR-DFT) type methods is the double-counting error arising from the fact that part of the correlation energy is counted twice, by the correlation already embedded in the energy of the Kohn−Sham

determinant, and the increment imparted by the added determinants. As proposed by Lie and Clementi et al.,[45,46] a practical way to avoid the error is that the active space of MCSCF or CASSCF is selected as small as possible.

The VBSCF method is numerically quasi-identical to the molecular orbital (MO)-based CASSCF method if all structures for a given dimension of the active space are included. However, usually VB methods employ only a few structures that are essential for describing the system of interest and use strictly localized HAOs. The smaller and flexible active space of the VB methods compared to the CASSCF or MCSCF methods is beneficial for the task of perhaps overcoming the double-counting error. Accordingly, a hybrid method that combines VB methods with DFT functionals is achievable as shown in the present paper, which presents also some applications including to transition metal and organometallic molecules.

The idea of combining VB theory with DFT has been proposed, and different strategies have been implemented during the past decade, leading to various DFT methods, such as VBDFT(s) and VB-DFT. VBDFT(s)[52] is a Hückel-type semiempirical VB method scaled to density functional energies by utilizing the DFT energy of the spin-alternant determinant and a parameter λ. The method has shown its utility in the studies of ground and excited states of linear polyenes and relative systems.[53] The VB-DFT method describes the correlation energy of the core electrons by partitioning the system into two subsets: the core treated by DFT and the valence by VB theory. A multireference density functional theory in the framework of the valence bond model, called VBDFT,[54] was also described recently by Gao and Mo et al. The method is based on a block-localized density functional theory (BLDFT)[55] for construction of valence-bond-like diabatic states and suitable for study of electron transfer reactions and representation of reactive potential energy surfaces.

The aim of this paper is to develop a hybrid ab initio valence bond method with density-functional-based correlation correction, which we term DFVB, where the static electron correlation is described by ab initio VB theory while the dynamic electron correlation is considered by correlation functionals as an additional term. The paper is organized as follows: section 2 presents the theoretical details of the DFVB method. Computational results of various applications are illustrated and discussed in section 3. The paper is concluded with a summary and further perspective in section 4.

2. METHODOLOGY

A many-electron wave function in valence bond theory can be described as a linear combination of Heitler−London−Slater−Pauling (HLSP) wave functions, Φ_K

$$\Psi^{VB} = \sum_K C_K \Phi_K \tag{1}$$

where Φ_K corresponds to "classical" VB structure K and C_K is the linear coefficient.

The coefficients C_K in eq 1 can be conveniently determined by solving the secular equation $\mathbf{HC} = E\mathbf{MC}$, where the Hamiltonian and overlap matrices are defined as

$$H_{KL} = \langle \Phi_K | H | \Phi_L \rangle \tag{2}$$

$$M_{KL} = \langle \Phi_K | \Phi_L \rangle \tag{3}$$

Thus, the density $\rho^{VB}(r)$ is expressed as

$$
\begin{aligned}
\rho^{VB}(r) &= N \sum_{K,L} C_K C_L \int \Phi_L \Phi^*_K \, dx_2 \cdots dx_N \, d\sigma_1 \\
&= \sum_{\mu,\nu} \chi_\mu(r) P^{VB}_{\mu\nu} \chi^*_\nu(r)
\end{aligned}
\tag{4}
$$

In eq 4 N is the number of electrons of the system, x_i indicates the electron coordinate including spin index σ_i of electron i, χ_μ is the basis function employed in calculation, and $P^{VB}_{\mu\nu}$ is the matrix element of the VBSCF density matrix.

As the first modern classical VB method, VBSCF optimizes VB orbitals and structural coefficients simultaneously. If all VB structures for a given dimension of an active space are involved, VBSCF should be numerically quasi-identical to the MO-based CASSCF method. Thus, VBSCF mainly take the static correlation energy into account sufficiently, as does CASSCF with a limited active space.

In the KS-DFT approach, the total energy is expressed in the form

$$E^{KS\text{-}DFT}(\rho) = T_S[\rho] + J[\rho] + E_{Ne}[\rho] + E_{XC}[\rho] \tag{5}$$

where T_S is the noninteraction kinetic energy, J and E_{Ne} are Coulomb and nuclei−electron attraction, respectively, and E_{XC}, the exchange-correlation energy term, is defined as

$$E_{XC} = (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]) \tag{6}$$

Exchange-correlation energy should be involved in the exact exchange-correlation functional. However, the form of the exact exchange-correlation functional is still unknown. In practice, E_{XC} is provided approximately by the sum of exchange and correlation functionals. The current approximate correlation functionals have been mostly proposed for the dynamic correlation energy.[25]

Despite the apparent lack of static correlation in the single-determinant KS-DFT approach, the method describes the dynamic correlation energy very well at a low cost, compared to the post-HF methods. As mentioned above, VBSCF mainly includes static correlation, and hence, its accuracy is not satisfactory. To improve the computational accuracy, a practical strategy for the VBSCF method is to correct dynamic correlation by adding DFT correlation energy, leading to an improved VB method, herein called density functional valence bond (DFVB), i.e.

$$E^{DFVB}[\rho^{VB}] \approx E^{VBSCF} + E_C[\rho^{VB}] \tag{7}$$

where correlation energy E_C is the functional of the VBSCF density, ρ^{VB}. We emphasize that strictly speaking, dynamic and static correlations cannot be divided explicitly, and thus, eq 7 is approximate. Since DFT includes some static correlation, the double-counting error (DCE) will exist in the DFVB method, as in the CAS-DFT method, which is a case of MR-DFT that combines CASSCF with dynamic correlation functionals.

Different from the CAS-DFT methods, which involve all excited configurations with a given active space in the calculation, the VBSCF wave function is usually very compact and includes only a few structures that are important for the system of interest. Thus, the DCE may be less serious compared to CAS-DFT.

Implementation of the DFVB method is shown in Scheme 1, where the correlation functionals are determined by the VB

Scheme 1. Procedure of the the DFVB Method
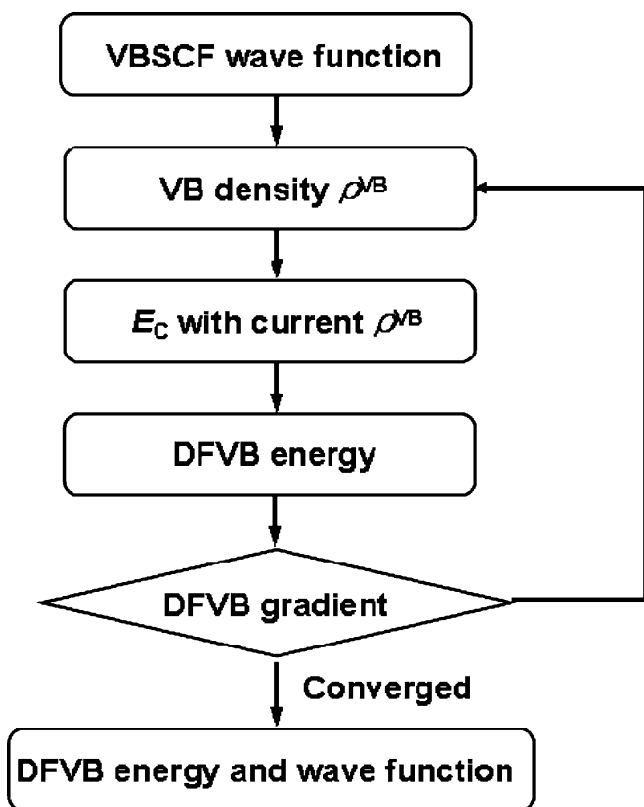
density and added to VBSCF energy, and thus, the dynamic correlation is taken into account in a self-consistent manner determined by the VB density. Optimization of DFVB wave function is achieved during the SCF procedure. The computation is consistently iterative until convergence is achieved.

It is well known that VBSCF is size consistent; however, the popular correlation functionals are not. To obtain size-consistent DFVB energy, the correction strategy for the correlation energy proposed by Pérez-Jordá et al.[31,32] is used in the current DFVB implementation. In this strategy, instead of the functional of ρ_α and ρ_β, the correlation energy is a functional of $\rho_<$ and $\rho_>$

$$E_C = E_C[\rho_<, \rho_>] \tag{8}$$

where $\rho_<$ and $\rho_>$ are defined as

$$\rho_< = \sum_{n_i \geq 1} |\phi_i|^2 + \sum_{n_i < 1} n_i |\phi_i|^2 \tag{9}$$

$$\rho_> = \sum_{n_i \geq 1} (n_i - 1)|\phi_i|^2 \tag{10}$$

where n_i is the occupation number of the ith natural orbital ϕ_i, which can be obtained by diagonalizing the VB density matrix.

This paper employs two types of correlation functionals for DFVB: the Lee–Yang–Parr (LYP) functional[56] and the Perdew–Wang (PW) correlation functional,[57,58] leading to two DFVB methods, denoted as DFVB(LYP) and DFVB(PW).

3. TEST APPLICATIONS

The DFVB method at the VBSCF level has been implemented in the XMVB module[59−61] for the GAMESS package.[62] All calculations were performed in the gas phase. For the studied atoms and molecules, two basis sets, cc-pVTZ and cc-pVDZ, are employed, where the cc-pVTZ basis set is used for C and O, H_2, HF, HCl, Li_2, F_2, Cl_2, ClF, NF, N_2, O_2, and CH_2 while the cc-pVDZ basis set for trimethylenemethane (TMM) and Stuttgart RSC 1997 ECP basis set for Au_2.[63,64] For the Menshutkin reaction $NH_3 + CH_3Cl \rightarrow [NH_3CH_3]^+ + Cl^-$ and the identity S_N2 reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$, we used the 6-31G* and 6-31+G* basis sets, respectively, as in previous VB studies.[65,66] Study of the rotational barrier of $(CO)_4Fe$-(C_2H_4) used the Lanl2dz basis set for Fe and 6-31G* for the other atoms.

Geometries of the diatomic molecules except Au_2 are optimized by the DFVB/cc-pVTZ method, while the diradicals CH_2 and TMM are optimized by the CASPT2/cc-pVTZ level. The geometry of Au_2 is optimized by the MP2 method. The geometries in the Menshutkin and the identity S_N2 reactions are optimized at the MP2/6-31G* and MP2/6-31+G* levels, respectively. The geometry of the $(CO)_4Fe(C_2H_4)$ complex is optimized by the B3LYP method.

For comparison, we performed also calculations by CASPT2 and three density functionals: one hybrid functional (B3LYP[67−69]) and two GGA functionals (PW91[57,58,70,71] and BLYP[56,72,73]).

All geometry optimizations and DFVB calculations were performed in the GAMESS[62] program package with a modified XMVB[60] module.

A. Selection of VB Structures. One of the great advantages of VB theory is its very compact wave function in terms of several fundamental VB structures. For the simple diatomic molecules, such as H_2, HF, and F_2, three VB structures for the single σ bond, one covalent structure and two ionic structures, are sufficient for description of the wave function. However, for the molecules with multiple bonding or strong diradical character, such as NF, N_2, and O_2, the VB structure sets are more extensive. As used in the VB previous studies of NF,[74] O_2,[75] and N_2[21] molecules, there are two strategies in selection of the most important VB structures for the studied systems, one quantitative and the other qualitative. The quantitative strategy consists of performing a VBSCF calculation of the complete active set of VB structures and subsequently selecting a restricted set of VB structures on the basis of their weights or coefficients in the total wave function. The qualitative procedure consists of selecting a restricted set of VB structures based on chemical grounds, so as to describe the various bonds of the electronic states in a consistent way. As we showed in the past, the two selection procedures lead to the same VB structure set for the studied molecules.

Selection of the VB structures used in previous studies is a balance between the computational accuracy and the cost for VBSCF and post-VBSCF calculations. The double-counting error may be introduced in DFVB calculations with the same VB structure set. Test calculations show that all of the VB structure sets used in the previous studies perform well with the DFVB calculations except for the N_2 molecule. For N_2, it is shown that the set of 17 VB structures,[21] S1−S17, shown in Scheme 2, introduces relatively large double-counting error. Further analysis shows that the 6 VB structures, S12−S17, which are ionic for the two of the three bonds, and are hence di-ionic, involve relatively large dynamic correlation in short equilibrium bond distances, and thus should be removed for DFVB calculation. As such, for the N_2 molecule, the VB set, S1−S11 will be used in calculation.
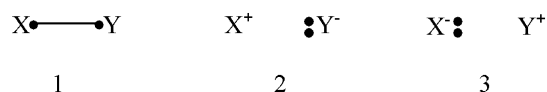
Scheme 2. Seventeen VB Strcutrues Used for the N_2 Molecule[a]
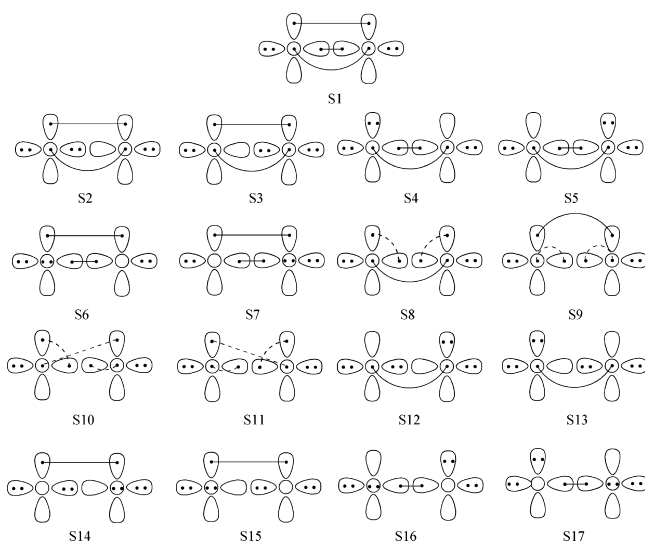
[a]Only S1—S11 are used to reduce correlation double counting.

Hence, for H_2, Li_2, HF, HCl, F_2, Cl_2, ClF, and Au_2 molecules, the three VB structures for the single σ bond, shown in Scheme 3, are used. For NF, O_2 molecules, Menshutkin reaction,

Scheme 3. Three VB Structures Selected for Descrbing Single σ Bonds

identity S_N2 reaction, and the rotational barrier of $(CO)_4Fe$-(C_2H_4), the same VB structures as in the previous VB studies[1,14,21,74] are involved. For TMM, CH_2, O, and C, the selected VB structures for the full valence space are employed.

B. Bond Dissociation Curve of H_2. The potential energy curve (PEC) of the H_2 molecule is the simplest test for the dissociation behavior of a single bond for different methods. Additionally, this molecule has served also as an example for discussing size consistency of the MR-DFT-type methods.[34,35,43] Figure 1 shows the dissociation curves of the H_2
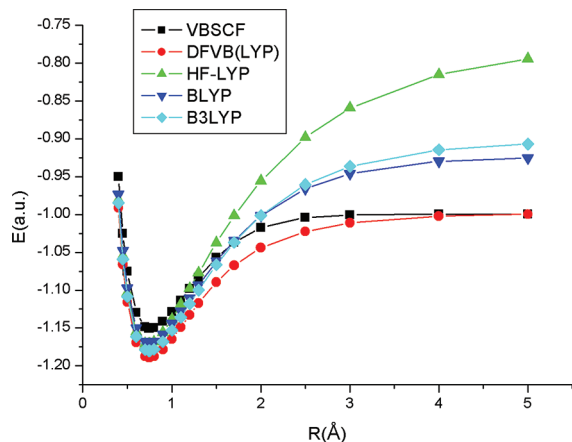
Figure 1. Dissociation curve for the H_2 molecule by VBSCF, DFVB, and DFT methods with the cc-pVTZ basis set.

molecule by various methods, DFVB(LYP), VBSCF, BLYP, HF-LYP, and B3LYP. All methods are spin restricted. It is shown that VBSCF dissociates the H_2 molecule to the correct dissociation limit. Due to the lack of dynamic correlation, the VBSCF produces the highest energy value, compared to the other methods, near the equilibrium bond length. However, amended by the LYP correlation functional with size-consistency correction,[31] DFVB is not only able to produce the correct dissociation limit but also to give quite a good description at the equilibrium geometry compared with VBSCF. By comparison, restricted HF-LYP, BLYP, and B3LYP calculations are unable to produce a correct dissociation limit. Our DFVB results are very similar with those by some MR-DFT-type methods.[34,35,43] The DFVB(PW) method performs similar to DFVB(LYP) and hence is not shown in the figure.

C. Singlet–Triplet Gaps of Diradical Systems. Table 1 shows the singlet–triplet gaps of the diradical systems, including atoms C and O and molecules O_2, NF, CH_2, and TMM (Figure 2 shows geometries). It is not surprising that the KS-DFT method fails for these species due to the strong multireference character of these diradicals. In general, VBSCF gives satisfactory results with the mean absolute error (MAE) value of 4.7 kcal/mol. With the correlation functionals embedded, DFVB gives improvement for the singlet–triplet gaps, compared to the VBSCF method, especially at the DFVB(PW) level. The MAE value is 4.8 kcal/mol by DFVB(LYP) and 1.8 kcal/mol by DFVB(PW). It can be seen that the accuracy of DFVB matches those of the high-level multireference MO methods such as CASPT2 and MRCC.[76−78]

D. Spectroscopic Constants and Dipole Moments. The spectroscopic constants of various diatomic molecules, including equilibrium bond distances (R_e, in Angstroms), vibrational frequencies (ω_e, in cm^{-1}), and bond dissociation energies (BDE, in kcal/mol), calculated by usage of DFVB methods with different correlation functionals, are presented in Tables 2−4. For the sake of comparison, only the deviations to the experimental data are shown in the tables. Mean absolute errors (MAE) are shown in the last line of the tables.

It can be seen from Table 2 that the equilibrium bond lengths are greatly improved in DFVB, compared to those of VBSCF. The MAE values of DFVB(LYP) and DFVB(PW) are 0.025 and 0.030 Å, respectively, close to the value of BLYP, 0.024 Å. The smallest MAE value, 0.01 Å, is obtained with B3LYP, while VBSCF gives the largest MAE value of 0.053 Å. For example, the deviation of the computed VBSCF bond length of F_2 is 0.065 Å, whereas the corresponding deviation is 0.016 Å with DFVB(LYP) and −0.011 Å with DFVB(PW). Similar results were found by the MR-DFT by Jorda et al.[31] In general, the optimized DFVB bond lengths are shorter than those of VBSCF, close to the DFT analogs.

Computational vibrational wave numbers are listed in Table 3. Roughly speaking, the accuracy of DFVB methods is better than the VBSCF method. The MAE values of DFVB(LYP) and DFVB(PW) are 54 and 68 cm^{-1}, respectively, close to 69 cm^{-1} of the BLYP method. VBSCF gives the largest MAE value of 90 cm^{-1}, and B3LYP produces the smallest one, 38 cm^{-1}. Thus, the DFVB method provides smaller deviations than VBSCF for all molecules, with exceptions of Li_2 and HF molecules.

It is shown from Table 4 that DFVB gives quite good BDE values, with MAE values of 5.9 kcal/mol by DFVB(PW) and 5.8 kcal/mol by DFVB(LYP), compared to the BLYP value of

Table 1. Singlet−Triplet Energy Gaps (ΔE_{ST}, in kcal/mol) of Diradical Systems[a]

	expt	reference	CASPT2	B3LYP	BLYP	PW91	VBSCF	DFVB LYP	DFVB PW
C	29.1[b]	1.3[c]	0.9	11.3	10.1	13.9	5.4	−4.5	−1.3
O	45.4[d]	−1.6[e]	0.9	17.0	15.5	19.8	4.9	−5.1	−1.7
O_2	22.7[f]	1.0[g]/0.7[h]	0.9	13.1	12.4	13.7	−2.4	−5.7	−5.1
NF	32.7[I]	2.6[j]	0.1	10.8	8.9	11.5	5.9	−3.0	−0.8
TMM	18.1[k]	−0.3[l]	2.0	25.7	16.6	18.4	3.4	−3.4	−0.4
CH_2	32.9[m]	1.6[c]/−1.3[e]	−6.0	−25.5	−25.6	−25.7	6.3	−7.0	−1.6
MAE			1.8	17.2	14.9	17.2	4.7	4.8	1.8

[a]Deviations from experimental values are listed. [b]From ref 28, gap of $^3P \rightarrow {}^1D$. [c]From ref 79 with SF-OD/cc-pVTZ. [d]From ref 28, gap of $^3P \rightarrow {}^1D$. [e]From ref 28 with FS-LSDA/6-311++G(2d,2p). [f]From ref 80, gap of $^3\Sigma_g^- \rightarrow {}^1\Delta_g$. [g]From ref 77 with MRBWCCSD/cc-pVTZ. [h]From ref 14 with VBCIS/cc-pVTZ. [I]From ref 76, gap of $^3\Sigma^- \rightarrow {}^1\Delta$. [j]From ref 76 with MRBWCCSDT/cc-pVTZ. [k]From ref 78, gap of $^3A_2' \rightarrow {}^1A_1$. [l]From ref 78 with MRBWCCSD/cc-pVTZ. [m]From ref 28, gap of $^3B_1 \rightarrow {}^1B_1$.
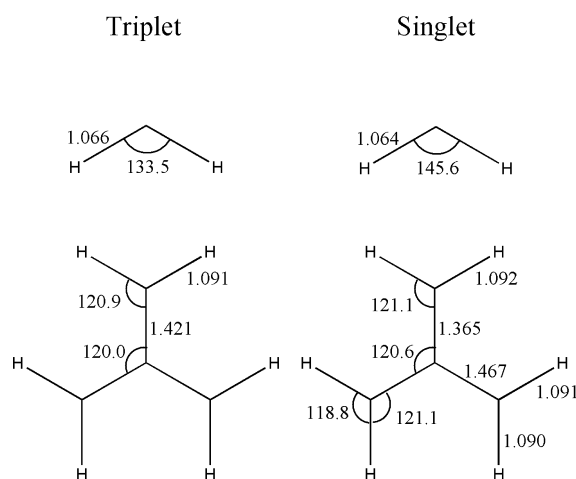

Figure 2. Optimized bond lengths (Angstroms) and angles (degrees) of singlet and triplet CH_2 (note that the states correspond to $^3B_1$ and $^1B_1$) and TMM.

Table 3. ω_e (in cm^{-1}) Calculated by DFT, VBSCF, and Different DFVB Methods[a]

mol	exp[b]	B3LYP	BLYP	PW91	VBSCF	DFVB LYP	DFVB PW
H_2	4401	18	−55	−69	−179	−92	−92
HF	4138	−13	−172	−116	15	122	177
HCl	2991	−20	−113	−69	−13	−4	63
Li_2	351	−7	−18	−18	−88	−53	−59
N_2	2359	91	−23	−1	14	73	95
O_2	1580	56	−91	−31	−76	1	60
F_2	917	139	51	90	−277	−135	−56
Cl_2	560	−18	−55	−20	57	−15	15
ClF	786	3	−56	−19	−95	−35	6
NF	1141	16	−59	−8	−86	10	52
MAE		38	69	44	90	54	68

[a]All data are listed as the deviation from experimental data. [b]Experimental values of the molecules except NF are taken from ref 81, and the value of NF is from ref 76.

8.7 kcal/mol. The smallest MAE is given by B3LYP as 3.7 kcal/mol. The largest MAE value, 32.9 kcal/mol comes from the VBSCF calculation due to the lack of dynamic correlation. DFVB produces competitively accurate BDEs for HF, O_2, F_2, Cl_2, ClF, and NF, compared to BLYP and B3LYP. The DFVB method with 11 VB structures provides deviations of −5.8 kcal/mol with DFVB(LYP) and −10.1 kcal/mol with DFVB(PW) for N_2, which is much better than the value of VBSCF, −67.3

kcal/mol. For the Au_2 molecule, the Stuttgart RSC 1997 ECP basis set takes 60 inner electrons in the ECP with relativistic correction. In the total 38 valence electrons, two electrons are taken into account for description of σ bonding. The deviations of the DFVB calculations, 18.6 kcal/mol by DFVB(LYP) and −18.2 kcal/mol by DFVB(PW), are smaller than the VBSCF deviation of −32.9 kcal/mol and close to the B3LYP deviation of −10.6 kcal/mol. These results illustrate the capacity and

Table 2. R_e (Angstroms) Calculated by DFT, VBSCF, and Different DFVB Methods[a]

mol	exp[b]	B3LYP	BLYP	PW91	VBSCF	DFVB LYP	DFVB PW
H_2	0.741	0.002	0.006	0.008	0.015	0.008	0.010
HF	0.917	0.005	0.016	0.012	−0.003	−0.010	−0.013
HCl	1.275	0.006	0.015	0.012	0.011	−0.001	−0.003
Li_2	2.673	0.028	0.038	0.054	0.272	0.157	0.197
N_2	1.098	−0.007	0.005	0.003	−0.003	−0.012	−0.014
O_2	1.208	−0.004	0.023	0.011	0.035	0.019	0.009
F_2	1.412	−0.016	0.019	0.000	0.065	0.016	−0.011
Cl_2	1.988	0.023	0.052	0.019	0.050	0.009	−0.016
ClF	1.628	0.012	0.044	0.022	0.031	−0.005	−0.023
NF	1.317	0.001	0.026	0.010	0.043	0.014	0.003
MAE		0.010	0.024	0.015	0.053	0.025	0.030

[a]All data are listed as the deviation from experimental data. [b]Experimental values of the molecules except NF are taken from ref 81, and the value of NF is from ref 76.

Table 4. Experimental D_e (in kcal/mol) Values and Relative Deviations of the Calculated D_e Values Using DFT, VBSCF, and Different DFVB Methods

						DFVB	
mol	$D_e{}^a$	B3LYP	BLYP	PW91	VBSCF	LYP	PW
H_2	109.5	3.7	0.0	−4.3	−14.6	9.4	6.0
HF	141.3	−2.6	−1.2	0.5	−30.4	−4.9	−5.0
HCl	106.4	−0.3	−1.1	1.0	−17.0	5.2	6.1
Li_2	24.4	−3.7	−3.9	−4.5	−14.6	1.7	−1.2
N_2	228.5	3.1	13.8	16.1	−67.3	−5.8	−10.1
O_2	120.3	4.3	17.7	25.4	−45.3	−11.2	−9.3
F_2	38.2	2.3	14.4	18.7	−25.7	−6.9	−7.4
Cl_2	58.0	−0.2	2.2	10.0	−21.0	−2.5	2.3
ClF	60.2	2.4	8.9	14.5	−29.0	−8.6	−6.9
NF	70.4	14.0	23.6	27.5	−32.0	−2.5	−3.3
Au_2	53.0	−10.6	−7.2	−3.0	−32.9	−18.6	−18.2
MAE		4.3	8.5	11.4	30.0	7.0	6.9

$^a D_e$ are the atomization energies at 0 K from the *Computational Chemistry Comparison and Benchmark DataBase*[82] with ZPE correction from ref 81 except that the data of NF is from ref 76 and that of Au_2 from ref 83.

improved accuracy of the DFVB method for treating transition metal systems.

Interestingly, by comparing the BDE for H_2 for various methods, it is apparent that the DCE results in the error of 9.4 kcal/mol for the DFVB(LYP) method. Thus, it is apparent that although one tends to think that DFT does not include static correlation, apparently it does. Hence, since H_2 involves only two electrons and mainly static correlation that is fully covered by VBSCF, adding the DFT correlation on top of it leads to double counting. It is interesting that while in H_2 this DCE is apparent, for other molecules it is less serious.

Table 5 shows the computed dipole moments of the NF molecule for the ground state $^3\Sigma^-$ and the first excited state $^1\Delta$

Table 5. Dipole Moments of NF (in D) for the Ground State ($^3\Sigma^-$) and First Excited State ($^1\Delta$)

	dipole	
	$^3\Sigma^-$	$^1\Delta$
VBSCF/cc-pVTZ	−0.108	0.243
DFVB(LYP)/cc-pVTZ	0.009	0.325
DFVB(PW)/cc-pVTZ	0.036	0.362
BOVB/cc-pVTZ	0.056	0.382
MCQDPT	−0.076	0.338
MRCI/aug-cc-pVQZ	0.09	0.44
expt		0.37 ± 0.06

by the VBSCF, BOVB, and DFVB methods. For $^3\Sigma^-$, VBSCF gives with a value of −0.108 D. The DFVB values, 0.009 by DFVB(LYP) and 0.036 by DFVB(PW), are different from the VBSCF datum and close to the BOVB and high-level MO

methods. For the $^1\Delta$ state, the computed VBSCF value of the dipole moment of 0.243 D compares relatively well with the experiment value, 0.37 ± 0.06 D, while DFVB(LYP) and DFVB(PW) lead to 0.325 and 0.362 D, respectively, very close to the experimental values and those of high-level VB and MO methods.

E. Barriers of Chemical Reactions. Table 6 lists the barriers for the Menshutkin reaction, $NH_3 + CH_3Cl \rightarrow [NH_3CH_3]^+ + Cl^-$, identity S_N2 reaction, $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$, and rotational barrier of $Fe(CO)_4C_2H_4$ in the gas phase. Two additional KS-DFT methods, B3LYP and BLYP, are also computed and listed in the table. It is well known that the KS-DFT method usually underestimates chemical reaction barriers.[25−27] Indeed, as expected, the B3LYP and BLYP values for the two S_N2 reaction barriers are too low. The CASSCF values of the barriers are 36.2 kcal/mol for the Menshutkin and 18.9 kcal/mol for the identity S_N2 reaction. With dynamic correlation correction, CASPT2 gives similar barrier values for the two reactions. The VBSCF barrier is 41.4 kcal/mol for the Menshutkin and 14.1 kcal/mol for the identity S_N2 reaction. Similar with high-level MO methods, the DFVB-computed barriers are close to VBSCF results. The computed CASSCF rotational barrier of $Fe(CO)_4C_2H_4$ is 13.9 kcal/mol, which is equal to the VBSCF result with all semidelocalized orbitals. With dynamic correlation correction, the CASPT2 method provides a bit higher barrier, 15.5 kcal/mol. The DFVB(LYP) and DFVB(PW) computed barrier heights are 14.9 and 16.0 kcal/mol, respectively, a bit larger than the VBSCF result and very similar with the CASPT2 value.

F. Resonance Energies of DFVB in Some Molecules. The resonance energy is an important concept for understanding the nature of chemical bonding in VB theory. The value of the resonance energy, B, depends on the level of ab initio VB methods. In most of cases, VBSCF is unable to provide B values accurately due to the lack of dynamic correlation. Currently, the most accurate VB description of resonance comes from VBCISD calculations. The total resonance energy is defined as the energy difference between the wave function with the full structure set and the lowest energy structure(s)

$$B = E_{prim} - E_{full} \tag{11}$$

where E_{prim} is the energy of the primary structure(s) that is lowest in energy and E_{full} is the energy with all structures included. Table 7 shows the total resonance energies (B, in kcal/mol) of O_2, NF, F_2, and HF molecules by various methods with the cc-pVTZ basis set. The VBSCF method provides the values of the total resonance energies with 107.5, 78.7, 39.9, and 36.0 kcal/mol for the O_2, NF, F_2, and HF molecules, respectively. If the VBCISD calculations are used as benchmarks, it is seen that BOVB tends to overestimate the values of B. The computed DFVB values are located in the range between VBCISD and VBSCF results. More specifically, the DFVB values for the HF molecule are almost the same with

Table 6. Barriers of the Menshutkin and Identity S_N2 Reactions (in kcal/mol) in the Gas Phase

	CASPT2	CASSCF	B3LYP	BLYP	VBSCF	DFVB	
						LYP	PW
Menshutkin	40.5	36.2	29.9	27.1	41.4	38.5	39.2
identity S_N2	15.5	18.9	8.8	5.4	14.1	14.2	15.2
$Fe(CO)_4C_2H_4$	15.5	13.9	10.0	8.7	13.9	14.9	16.0

Table 7. Resonance Energies (B, in kcal/mol) of O_2, NF, F_2, and HF with the cc-pVTZ Basis Set

	O_2	NF	F_2	HF
VBSCF	107.5	78.7	39.9	36.0
BOVB	128.2	123.6	60.5	48.9
VBCISD	102.1	94.2	57.7	32.3
DFVB(LYP)	104.8	82.3	51.1	35.7
DFVB(PW)	105.5	81.9	46.7	35.2

VBSCF; however, for the other three molecules, the DFVB-computed resonance energies are larger than VBSCF. In general, it shows that DFVB gives improvement to some extent over VBSCF for the resonance energies.

4. CONCLUSION

In this paper we present a density-functional-based valence bond method, DFVB. The method combines the VBSCF wave function with density correlation functionals. DFVB provides an economic route for adding the dynamic correlation effects in the framework of VB theory. The advantage of the DFVB method has two aspects. On the one hand, DFVB improves the accuracy over VBSCF by taking dynamic correlation into account from density correlation functionals. On the other hand, the DFVB method overcomes some problems with DFT that arises from the use of a single Kohn–Sham determinant. The computational cost of the DFVB method is approximately the same as that of VBSCF and much cheaper than those of the high-level VB method, such as VBCI and VBPT2.

DFVB is tested here for a variety of physical and chemical properties, including calculations of PEC, BDE, reaction barrier, singlet–triplet energy gap, and dipole moment as well as resonance energy. The dissociation curves of the H_2 molecule and the singlet–triplet energy gaps of some diradical species show that DFVB gives reasonable results for the multireference cases. Test calculations for the spectroscopic parameters of some typical diatomic molecules show that DFVB is able to match the accuracy of high-level multireference methods such as MRCC and CASPT2. In contrast to VBSCF, DFVB produces correct dipole moments for the ground and first exited states of the NF molecule. Lastly, the DFVB method improves the description for resonance energies, compared to the VBSCF method, and for the reactions tested it provides barriers at par with CASPT2.

In conclusion, the DFVB method provides a practical approach for combining ab initio VB methods with DFT functionals, which enhance the computational performance over the VBSCF method. It should be pointed out that the double-counting error still exists in the DFVB method, which should be remedied in the future. Fortunately, the double-counting error does not seem to be serious in most of the tested molecules and reactions, except for the H_2 molecule.

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Notes
The authors declare no competing financial interest.

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